

**THE FORMULATION AND CHARACTERIZATION OF
NOVEL ADSORBENTS USING METAL HYDROXIDES,
GRAPHENE, AND CLAY FOR THE EFFECTIVE REMOVAL
OF ORGANIC POLLUTANTS FROM WASTEWATER**

BY

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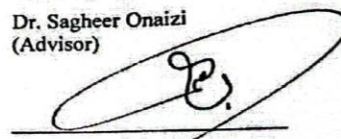
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This thesis work is dedicated to my father, mother, brothers, sisters, wife, and friends.

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LIST OF ABBREVIATIONS

LDH	Layered Double Hydroxide
LTH	Ternary Layered Double Hydroxide
RB 5	Reactive Black 5 dye
MO	Methyl Orange dye
MB	Methylene Blue dye
DR 23	Direct Red 23 dye
DB	Disperse Blue dye
IC	Indigo Carmine dye
SY	Sunset Yellow dye
MG	Malachite Green dye
BB	Basic Brown dye
AR	Acid Red dye
CR	Congo Red dye
Db	Direct black dye
DO 34	Direct Orange 34 dye
VB	Vat Blue dye
VG	Vat Green dye
RY 2	Reactive Yellow 2 dye
DY	Disperse Yellow dye
WHO	World Health Organization
ppm	Part Per Million
USEPA	U.S. Environmental Protection Agency.
BPs, BPA	Bisphenols, Bisphenol A
NPs, 2-NP	Nitrophenols, 2-Nitrophenols
CPs, 2-CP	Chlorophenols, 2-Chlorophenol
Cr	Chromium
Pb	Lead
Zn	Zinc
As	Arsenic
Ni	Nickle
Hg	Mercury
Cu	Copper
Cd	Cadmium
HSP	High Supersaturation Precipitation
LSP	Low Supersaturation Precipitation
DI	Deionized
EBT	Eriochrome Black T

RR 43	Reactive Red 43 dye
MOFs	Metal Organic Framework
(B)	Biochar
BT	Bentonite
DPA	Date palm ash
G	Graphene
CG	Calcined Graphene
GO	Graphene Oxide
rGO	Reduced Graphene Oxide
MWCNT	Multiwalled Carbon Nanotube
Ppy NF	Polypyrrole Nano Fiber
SBAC	Sludge-Based Activated Carbon
HNC	Hierarchical Nanocomposite
MV	Methylene Violet dye
AO 10	Acid Orange 10 dye
AB 14	Acid Brown 14 dye
AC	Activated Carbon
ACF	Active Carbon Fibers
BC	Bio-Carbon
SWCNTs	Single Walled Carbon Nanotubes
FPL	Fe ₃ O ₄ -PEG/LDH
MMO	Mixed Metal Oxides
ZIFs	Zeolitic Imidazole Frameworks
ARS	Alizarine Red S
CT	Chitosan
BDC	Benzene-1,4-dicarboxylate ions
RL-LDH	Rhamnolipid /LDH
NCs	Nanocrystals @ Carbon
CV	Crystal Violet
PEI@GO	Functionalized graphene oxide
PEI	Polyethyleneimine
CFA	Coal fly ash
AS	Aluminum sulphate
FS	Ferrous sulphate
GO-DEA	Functionalized graphene oxide with diethylamine
CPAB/B	cationic polyacrylamide bentonite composite
EGIS/B	Ester containing gemini imidazolium surfactant bentonite composite
PEI@GO/LTHLTH	Functionalized graphene oxide with polyethyleneimine hybrid with layered triple hydroxide
HNTs-SA-PAMAM	Halloysite nanotubes functionalized by succinic anhydride and poly(amidoamine) dendrimer
CIV	Chitosan -iso- vanillin

MMT	Magnetic montmorillonite
BP	Banana peel
OP	Orange peel
HCP-N	Hyper-crosslinked polymer-nitrogen rich
SDBS	Sodium dodecyl benzene sulfonate
PFO	pseudo first order
PSO	pseudo second order
AV	Avrami
FT-IR	Fourier-transform infrared spectroscopy
BET	Brunauer-Emmett-Teller
EDX or EDS	Energy-dispersive X-ray spectroscopy
SEM	Scanning electron microscopy
XRD	X-ray diffraction

ABSTRACT

Full Name : Salem Ahmed Bahadi
Thesis Title : The Formulation and Characterization of Novel adsorbents using Metal Hydroxide, Graphene, and Clay for Effective Removal of Organic Pollutants from Wastewater
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Date of Degree : [December 2022]

Water pollution caused by the release of harmful materials to the environment by chemical and allied industries negatively affects human health and the ecosystem. The high demand for clean water and the growing awareness of the importance of eliminating or at least minimizing pollution require the development of effective wastewater treatment approaches. Adsorption is one of the promising methods for wastewater treatment; however, the efficacy of this process requires the development of effective adsorbents. In this work, two novel adsorbents (i.e., PEI@GO/LTH and GO/BENT/LTH) were synthesized and utilized for the removal of acid red 1 (AR1), bisphenol A (BPA), methyl orange (MO), and 2 nitrophenol (2NP), respectively. The crystallinity, functional groups, and morphology of the synthesized nanocomposites were studied using different characterization techniques including XRD, FT-IR, and SEM. After the synthesis and characterization of the adsorbents, their performance in removing the above-mentioned four organic pollutants was assessed. First, the removal performance of these two adsorbents was studied by investigating the effect of pH, adsorption isotherm, kinetics, and thermodynamics. The optimum pH was attained at 6 and all other studies were carried out at pH 6. The adsorption kinetics revealed that Avrami model accurately fits the data for AR1, BPA, MO, 2NP removal with equilibrium adsorption capacities of 150.2, 348.5,

705.4, and 545 mg/g, respectively, using an initial pollutant concentration of 100 ppm. Moreover, the adsorption isotherm results revealed that Redlich-Peterson model nicely fits the experimental data for the removal of AR1, BPA, MO, and 2NP with R^2 approaching unity (i.e., 0.9952, 0.9940, 0.9986, and 0.9965), respectively. Thermodynamic analysis showed that ΔH° and ΔG° had negative values, indicating that the adsorption of AR1 and BPA on PEI@GO/LTHLTH and the adsorption of MO and 2NP on GO/BENT/LTH are exothermic process, and it is favorable toward low temperatures. The findings reported in this work demonstrate that these two novel nanocomposite adsorbents are excellent, abundant/cheap, promising, and effective for the removal of dyes and phenols from wastewater samples.

ملخص الرسالة

الاسم الكامل: سالم أحمد باهادي

عنوان الرسالة: صياغة وتوصيف مواد ماصة جديدة باستخدام هيدروكسيدات المعادن والجرافين والطين من أجل إزالة الفعالة للملوثات العضوية من المياه الملوثة.

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: ديسمبر 2022

يؤثر تلوث المياه الناجم عن إطلاق مواد ضارة بالبيئة بسبب الصناعات الكيماوية والصناعات المرتبطة بها بشكل سلبي على صحة الإنسان والنظام البيئي. يتطلب ارتفاع الطلب على المياه النظيفة والوعي المتزايد بأهمية القضاء على التلوث أو على الأقل تقليله إلى الحد الأدنى تطوير مناهج فعالة لمعالجة مياه الصرف الصحي. يعد الامتزاز هو أحد الأساليب الواعدة لمعالجة مياه الصرف الصحي ؛ ومع ذلك ، فإن فعالية هذه العملية تتطلب تطوير مواد ماصة فعالة. في هذا العمل ، تم تصنيع اثنين من الممتزات الجديدة (على سبيل المثال ، أكسيد الجرافين الوظيفي مع هيدروكسيد مزدوج الطبقات وأكسيد الجرافين المقحم مع البنتونايت وهيدروكسيد مزدوج الطبقات الثلاثية) واستخدامهما لإزالة الحمض الأحمر 1 ، بيسفينول أ ، ميثيل البرتقال ، و 2 النيتروفينول ، على التوالي. تمت دراسة التبلور والمجموعات الوظيفية ومورفولوجيا المركبات النانوية المركبة باستخدام تقنيات توصيف مختلفة بما في ذلك حيود الأشعة السينية والتحليل الطيفي للأشعة تحت الحمراء وتحويل فورييه ومجهر المسح الإلكتروني. بعد تركيب وتوصيف الممتزات ، تم تقييم أدائها في إزالة الملوثات العضوية الأربعة المذكورة أعلاه. أولاً ، تمت دراسة أداء الإزالة لهذين الماصين من خلال التحقق من تأثير الأس الهيدروجيني ، متساوي الامتزاز ، الحركية ، والديناميكا الحرارية. تم الحصول على الرقم الهيدروجيني الأمثل عند 6 وتم إجراء جميع الدراسات الأخرى عند الرقم الهيدروجيني 6. كشفت حركات الامتزاز أن نموذج افرامي يناسب بدقة بيانات الحمض الأحمر 1 و ميثيل البرتقال وبيسفينول أ و 2 نيتروفينول مع قدرات امتصاص متوازنة قدرها 150.2 و 348.5 و 705.4 و 545 مجم / جم على التوالي. باستخدام تركيز أولي للملوثات يبلغ 100 جزء في المليون. علاوة على ذلك، أوضحت نتائج الامتزاز أن نموذج ريدلر بيتيرسون يناسب بشكل جيد البيانات

التجريبية للملوثات السابقة مع اقتراب الانحدار من (0.9952, 0.9965, 0.9986, 0.9940) على التوالي. أظهرت التحاليل الدينامكية أن النتائج السلبية للطاقة الداخلية الكامنة و جيبس الطاقة الحارة تشير أن امتزاز الملوثات السابقة باستخدام ، أكسيد الجرافين الوظيفي مع هيدروكسيد مزدوج الطبقات وأكسيد الجرافين المقحم مع البنثونايت وهيدروكسيد مزدوج الطبقات الثلاثية هي عملية طاردة للحرارة وهو مناسب لدرجات الحرارة المنخفضة. توضح النتائج التي تم الإبلاغ عنها في هذا العمل أن هاتين الممتزتين النانويتين الجديتين ممتازتان ، وفيرة / رخيصة ، وواحدة وفعالة لإزالة الأصباغ والفينولات من عينات مياه الصرف الصحي.

CHAPTER 1

INTRODUCTION

1.1 Background

Over the past few decades, there have been a serious concern about the contamination of water supplies due to the discharge of several inorganic and organic materials to water bodies [1–3]. Many of the organic and inorganic substances found in contaminated waters are hazardous and carry huge risks to public health and the environment. With the growing in the world population, industrial, health, and domestic sectors, water pollution is expected to increase, hampering the sustainable development of global civilization. Augmented with the shortages in fresh water supply in many regions in the world, water pollution became a task that needs to be dealt with swiftly and properly. Moreover, hundreds of pollutants are found in the discharged water which needed to be removed to make the water good for drinking, suitable for cultivation, and other activities. Phenols, dyes and heavy metals are considered to be organic and inorganic pollutants which are discharged as a waste contamination in water from natural sources, developments of industrial activities, and from environmental problems [4].

Organic dyes are ones of the encountered pollutants in wastewater due to complexity of the aromatic structure, the high stability and thus weak to biodegrade which lead to various consequences to human health and ecosystem even at low concentrations [3,5–15]. The

annual production of dyes is 0.7×10^6 tons which are discharged from several sources [12,15–17] where hundred tons of organic dyes are discharged every year as effluent into water [18,19]. Organic dyes are classified into various categories, such as cationic, anionic, vat, direct, scattered, azo types and reactive. By evaluating these classifications, it can be summarized that, RB 5, MO, MB, DR 23, DB, IC and SY dyes have been chosen as the highest used pollutants on their categories [10,20]. Table 1-1 summarizes these types of dyes and their noxious effects.

Table 1-1: Types of dyes and their noxious effects [21–23].

Dyes	Examples	Noxious health effects
Base Dyes	(MB), (MG), (Bb).	Skin allergic, cause cancer.
Acid Dyes	(AR), (MO), (CR).	Burns and irritation for skin
Direct Dyes	(DB), (DO 34), (DB).	Cancer
Vat Dyes	(VB), (IC), (VG).	Burns, Skin irritation
Reactive Dyes	Remazol, (RB), (RY2).	Allergic problems
Disperse Dyes	(DB), (DY).	Damage DNA, Cancer

Organic dyes are usually generated from several industries including leather, plastic, paint, textile, printing, cosmetic, pulp, food, paper, fabric, and rubber [1,3,6,9,11,12,14,16,24–34]. The ubiquitous-ness of organic dyes in the water streams at high concentrations are

threatening aquatic life, posing major health risks, assimilating into human tissues, preventing the penetration of sunlight into water, and changing the color of water because they are poisonous, mutagenic, and carcinogenic [35–38]. In addition to the direct consequences of the organic dyes, they are also consuming oxygen molecules, and reducing the transparency of water [1,39]. Due to these harmful consequences of dyes to human health and the aquatic life, proper treatments to the contaminated water to meet the global limitations of WHO thus keep the life save for fauna, flora, and humanity are needed.

Phenols pollutants are ones of the most hazardous organic pollutants that are found in several local wastewater [40]. The phenolic compounds concentration in the wastewater discharged to the environment can reach up to 1000 (ppm) depending on the main source of drainage [41]. The disposal of the phenolic compounds to the environment was estimated to be greater than ten million tons annually [3,4]. Lacking of treating the discharge of phenols to environment causes several problems to human health. Table 1-2 illustrates several types of phenolic compounds with their noxious, and harmful effects to aquatic life. Moreover, phenols in environment rise the pollution of the surface water, soil, and groundwater [3,5, 6] which threatens the biological system of the environment. Accordingly, the concentration of the discharged polluted water should not exceed 5 part per million if it is discharged to the sewage system. However, if phenols are to be discharged into water bodies, the allowable concentration should not exceed 1 ppm [45,46] . According to the USEPA, the maximum allowable limit of phenolic compounds in the drinkable water is 1 ppb [47]. Therefore, before reuse the wastewater, a promising technology is needed to treat the phenolic compounds [41].

Table 1-2: Effect of phenols on human health & aquatic animals.

Phenols	Effects	Ref.
Phenols	Affect the muscle, diarrhea, and rashes of the skin	[47–51]
	Affect the human, and rats lungs	
	Cause death to the red blood cells for human	
BPs	Cause a metabolic disorder in babies	[52–55]
	Cause some kinds of cancer in the breast & glands.	
NPs	Cause some changes to the tissues of the testicular	[41,56–58]
	Decrease the number of plasma in hormones	
CPs	Cause heart diseases, and sarcoma to humanity	[59]
	Damage DNA, and cause lung cancer	
Amino phenols	Reduce the volume% and hemoglobin of fish's red blood cells	[60–62]
	Damage the respiratory and reproductive systems of human	

Heavy metals are inorganic contaminants including, (Zn), (Cd), (Cu), (Pb), (Cr),(Hg), (Ni), and (As). These metals originate from different wastewaters of industries including, steel, refinery, manufacturing of batteries, pharmaceuticals, electroplating, manufacturing of cars, and machine milling [63–68]. The existence of these pollutants in water creates hazard damages to human health and aquatic life. Heavy metals are poor biodegrade, toxic, and stored in the organisms that negatively affect the human reproductive and nervous systems, damage human organs, and cause Parkinson's and Alzheimer's [69–71]. Table 1-3 summarizes the hazard effects of heavy metals with the maximum permissible concentration in the wastewater from industries and the drinking water.

Table 1-3: Allowable Concentrations of heavy metals and their harmful effects on human health.

Heavy metal	Symbol	Permissible concentration in drinking water/wastewater (mg/L)by WHO	Noxious health effects	Ref.
Cadmium	Cd	(0.003-0.005)/0.003	Damage kidney, Burning	[72–76]
			Carcinogen, Lack of consciousness	
			Vomiting and Nausea	
Chromium	Cr	<0.05/0.05	Damage bones, Lung cancer	[77–79]
			Carcinogen, Stored in skeleton	
			Allergic and renal problems	
Mercury	Hg	<0.006/0.05 [80]	Damage kidney and gastrointestinal	[81–84]
			Liver problems	
			Appearance of some benign tumors	
Lead	Pb	<0.01/0.01 [80]	Stored in skeleton, Problems in bones	[85–87]
			Negative effects on nervous system	
Arsenic	As	<0.01/0.01	Cause cancer to liver, skin, kidney	[88–92]
			Cancer of lung and bladder	
			Cause hypopigmentation	
Zinc	Zn	<3/(2-5)	Anemia, Vomiting	[72]

The high demand for clean water and the growing awareness of the importance of eliminating or at least minimizing pollution including dyes, phenols, and heavy metals require the development of effective wastewater treatment approaches. Multiple techniques have been proposed to remediate these contaminants such as coagulation [93], biological treatment [94], ion exchange [95], filtration, and adsorption [96]. Although these

technologies are promising and effective, they are encountered with some drawbacks including generating of sludge, fouling, high cost, and producing by-products[97,98]. Among these methods, adsorption is one of the promising methods for the removal of dyes, phenols, and heavy metals from wastewater because of its low cost, and effectiveness [99,100]; however, the efficacy of this process requires the development of effective adsorbents.

1.2 Significance of this research

According to the literature, LDH is not very effective in the remediation of phenols, dyes, and heavy metals from contaminated water. On the other hand, although the application of Layered Triple Hydroxide (LTH) or ternary LDH (which contains either two divalent and one trivalent cations or one divalent and two trivalent cations) in wastewater treatment is not well documented in the literature yet, it is expected to not be much superior to LDH. Nonetheless, to the best of our knowledge, there is a huge lack of published studies on the synthesis and the application of LTH/graphene oxide, LTH/bentonite, or LTH/graphene oxide/bentonite nanocomposites for wastewater treatment. The modification/functionalization of graphene oxide prior to the inclusion in the nanocomposites is also still lacking. Therefore, this work will focus on the synthesis of nanocomposites comprising LTH, bentonite and/or (modified/functionalized) graphene oxide and their applications in treating synthetic wastewater containing different organic pollutants.

1.3 Aim of this research |

The main target of this work is to investigate the removal of different water contaminants from aqueous solutions using the most selective adsorbents. The main scope of this thesis is to:

- 1) Synthesize nanocomposites starting from LTH, bentonite, and (modified/functionalized) graphene oxide.
- 2) Characterize the synthesized nanocomposites using different techniques (e.g., XRD, FTIR, and SEM).
- 3) Screen the effectiveness of the synthesized nanocomposites in removing different water pollutants using the adsorption process.
- 4) Investigate the effects of key operational parameters (e.g., pollutants concentrations, contact time, pH, and temperature) on the adsorptive removal of water pollutants.
- 5) Investigate the efficacy of the most promising nanocomposite(s) in treating synthetic wastewater containing different organic pollutants (e.g., dyes and phenols) .

CHAPTER 2

LITERATURE REVIEW

2.1 Background

This chapter gives an overview of the different methods of the synthesis of LDH or LTH and their composites and their applications in the removal of water pollutants. Also, it gives wide comparisons of the removal of organic dyes, phenols and heavy metals using the parent LDH or their composites with carbon materials, clays, and any other adsorbents. Moreover, it sheds some light on the impact of the key operational parameters such as pH, isotherms, kinetics, and thermodynamics.

2.2 Synthesis of LDH

Several studies involving the synthesis of LDH have been published in recent years, and some of them are direct to process for a variety of industrial uses. Utilizing fundamental methods of choosing, a variety of low-cost, environmentally beneficial, and eco-friendly LDHs can be synthesized. Co-precipitation, ion exchange, reconstruction, sonochemical method, hydrothermal/solvochemical method, sol-gel method, induced hydrolysis method, and urea method are some of the frequently employed techniques [101–107].

2.2.1 Co-precipitation Method

It is the most popular technique for LDH preparation. It is divided into two categories including: high supersaturation precipitation and low supersaturation precipitation [108]. It is used for the one-pot direct synthesis of LDHs with a wide range of divalent (M^{2+}) and trivalent (M^{3+}) cations and anions which are used as precursors and precipitated at pH (8-10) by adding NaOH solution [109–111]. To improve the crystallinity and ensure the highest yield of LDH, thermal treatment is applied after the coprecipitation [108]. After preparing the sample, it is centrifuged, washed and then dried in the oven at 80 °C [16]. The chemical structure and the composition of layered double hydroxide is illustrated in Figure 2-1 and Figure 2-2.

a. High Supersaturation Precipitation (HSP)

This technique leads to less crystalline formation of the material. The procedure requires the addition of the mixed divalent and trivalent metals with a proper ratio to the basic solution which contains the interlayer anions. Keeping the addition of the salts will increase the impurities, change in pH, and form undesired ratio of metals [112].

b. Low Supersaturation Precipitation (LSP)

This method is considered to be the most preferable method in the co-precipitation. The procedure entails the gradual addition of cations into a vessel containing an excess of anions. The simultaneous addition of the alkali solution leads to the monitoring of pH and the precipitation of the cations. The formed material has high crystallinity compared to the high supersaturation precipitation [113].

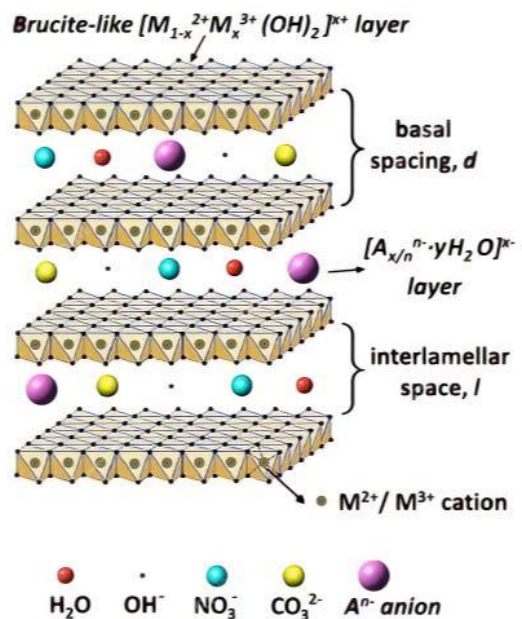


Figure 0-1: Structure of LDH [114].

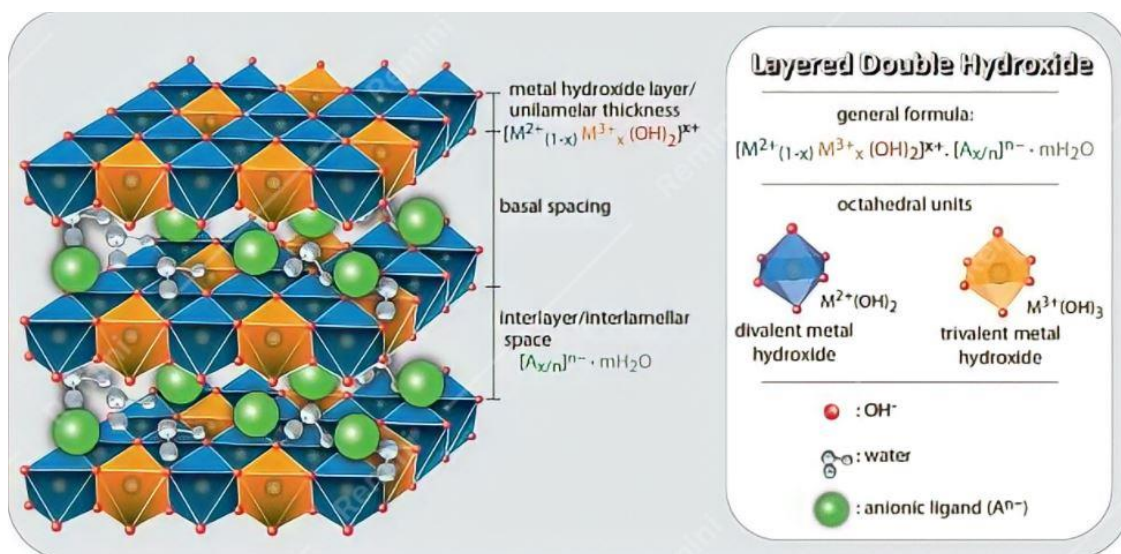


Figure 0-2: Representation of LDHs chemical composition and structure [115].

2.2.2 Sol-gel Method

Sol-gel method was first reported in 2010 by Wei and his co-workers [116]. Sol-gel is a simple and efficient wet – chemical method for the preparation of high purity metal oxide materials from LDH precursors through hydrolysis and condensation [117]. Mixture of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and basic solution of NH_4OH were added simultaneously to a beaker and heated under certain condition of the reflux as shown in Figure 2-3. Under magnetic stirring at ambient temperature, NH_4OH base is added to the suspension to maintain its pH between (8–10). The product is then filtered, washed with deionized water using centrifugation and then kept drying overnight in the oven. In order to create single layer nanosheets LDH (SLNSs), ultrasonication was used to disperse the gel in water. To have high crystallinity, the layered double hydroxide was dried in oven at temperature 80°C for 24 hours. The synthesized LDH using this method is less crystalline than coprecipitation method but it is thermally very stable [118].

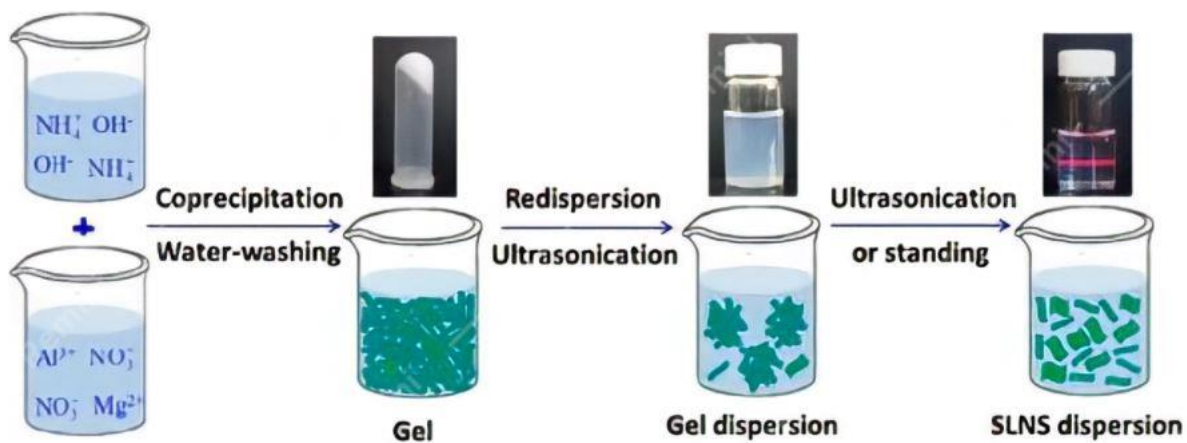


Figure 0-3: Representation of sol-gel method of LDH [119].

2.2.3 Hydrothermal Method

Under vigorous stirring at room temperature, two solutions containing cations (M^{2+} and M^{3+}) salts are introduced dropwise to another solution containing alkali solution. Thus, the mixture is placed into a Teflon-lined autoclave and heated for a longer period of time (10–48 hours) at higher temperature (100–180 °C) [120]. The acceptable pH range of the supernatant solution is within 8 to 10. The precipitated solid is washed with deionized water and ethanol and collected using centrifugation and then kept drying overnight in the oven. The synthesized LDH using the hydrothermal method has high crystallinity compared to the coprecipitation method [121] as represented in Figure 2-4.

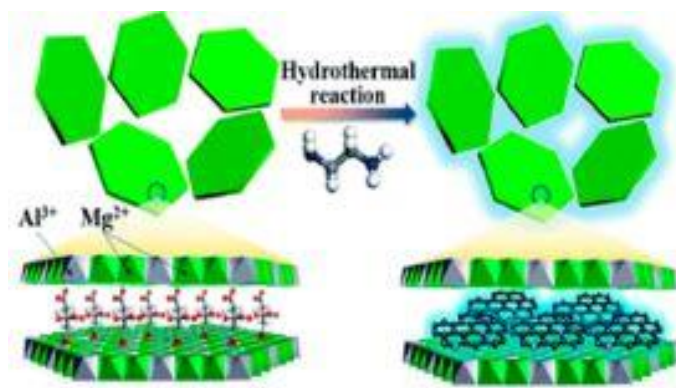


Figure 0-4: Representation of hydrothermal method [118].

2.2.4 Ion Exchange Method

This approach is considered to be suitable for the incorporation of multilayer silicates into a solution that has ionic species ready for interexchange. Figure 2-5 represents the ion exchange method where the anions exchange in the interlayer space with other anions. The suspended LDH in the solution contains anions to be interchanged. The mixture is then stirred spontaneously at ambient temperature. The precipitated solid is washed multiple

times with DI water and collected using the filtration and then kept drying overnight in the oven [105].

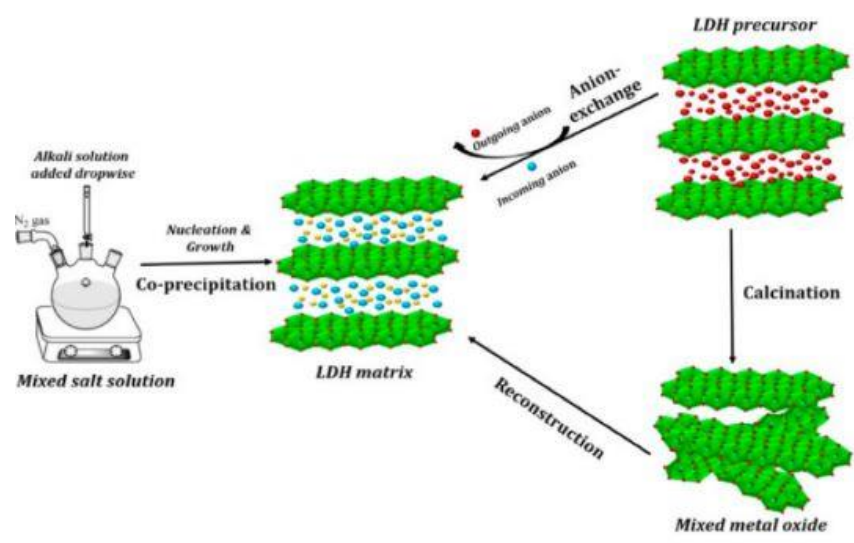


Figure 0-5: Representation of Co- precipitation method, ion exchange method , and reconstruction methods [107].

Table 2-1 illustrates some types of LDHs and their preparation methods.

Table 0-1: Types of LDH/LTH and their methods of preparation.

LDH / LTH	Pollutant	Preparation Method	Ref.
Zn-Al-LDH	2-NP	Co-precipitation	[122–125]
	-	Urea hydrolysis and ion exchange	[126]
	-	Co-precipitation and anion exchange	[127]

Mg-Al-LDH Mg-Al- CLDH Co-Al- CLDH Ni-Fe- CLDH	-	Co-precipitation	[27,129]
	-	Co-precipitation and ion exchange	[130,131]
	(EBT)	Co-precipitation	[132]
Mg-Fe-LDH	2-NP	Co-precipitation	[122–125]
Co-Al-LDH	(EBT)	Co-precipitation	[133]
Zn-Ti-LDH	-	Co-precipitation and anion exchange	[134,135]
Zn/(Al +Eu)-LTH	-	Co-precipitation	[136]
Mg/ (Al+ Fe) – LTH	Azo dye	Co-precipitation	[25,137]
Mg-Zn-Al-Fe-LDH	RR43	Co-precipitation	[138]

Ni / (Fe+ Ti) – LTH Ni / (Fe+ Ti 2) – LTH Ni / (Fe+ Ti 3) – LTH Ni / (Fe+ Ti 4) – LTH Ni / (Fe+ Ti 5) - LTH	Anionic Dyes	Hydrothermal	[139]
U Mg Al Ni -Ba Fe LTH C Mg Al Ni -Ba Fe LTH	MO	Co-precipitation	[140]
MgFeAl-Co₃ LDH	Pb II	Co-precipitation	[141,142]
Ni / (Al+ Ti)-LTH	Dyes and Antibiotic	Hydrothermal	[1]

2.3 Synthesis of LDH Composites

The LDH combination with other nanomaterials including carbon, polymers, minerals, and (MOFs) promote the adsorption capacity and the characteristics of the surface. Multiple synthetic methods are commonly used for the preparation of the LDH/LTH composites including co-precipitation, in-situ growth, solvothermal, and hydrothermal [120]. Using co-precipitation, the blending of the ultrasonicated nanomaterials in DI water with the precursor cation solutions (M^{2+} & M^{3+}) and adjusting the pH to be within (9 to 10.5). The mixture is then refluxed with spontaneous stirring for 1- 2 days. The composite is then filtered and washed, and then dried [16]. Like co-precipitation, hydrothermal method containing a Teflon reactor instead of the reflux which is operated at 100 to 180 °C. Moreover, LDH/LTH composites can be synthesized by the microwave method (Figure 2-

6) [143] under hydrothermal conditions and produce high crystalline LDH/LTH composites. Also, there are various indirect techniques for synthesizing LDH/LTH composites including exfoliation, ion exchange, and memory effect [107].

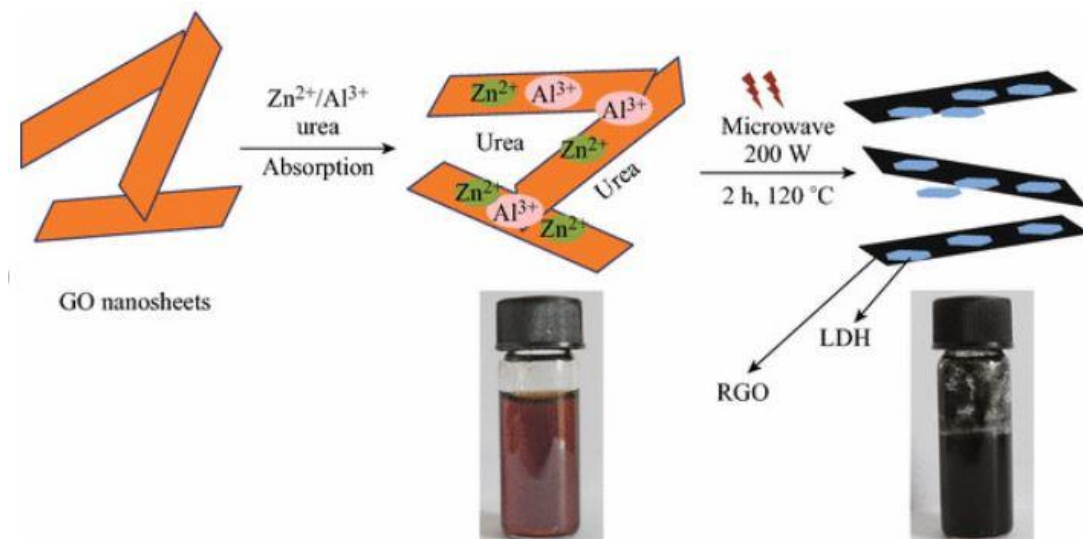


Figure 0-6: Representation of G/LDH composite using Microwave method.

Table 0-2: LDH/LTH Composites, surface area, and their method of preparation.

LDH/LTH composite	Surface Area (m^2g^{-1})	Preparation Method	Ref.
(B)- Mg-AL/LDH	443.39	Co-precipitation	[27]
DPA-Mg-Al/LDH	140.65	Co-precipitation	[144]
B-Co-Al/LDH	119.14	Co-precipitation	[133]
RGO-Zn-Al/LDH	223.4	Microwave	[143]

G-Mg-Al/ LDH Nanofiller	-	Co-precipitation	[145]
CG-Mg-Al-LDH	-	Hydrothermal	[13]
GO/LDH	-	Hydrothermal	[13]
rGO/LDH	-	In-situ growth	[13]
MWCNT-LDH	-	Co-precipitation	[146]
GO-Ni-Cr-LDH	98.2	Co-precipitation	[147]
Ppy NF/Zn-Fe-LDH	23.27	Interfacial polymerization of pyrrole	[148]
GO- Mg-Al-LDH	35.4	Hydrothermal	[149]
ZnO-LDH@C₃N₄	152.5	Co-precipitation with solvothermal	[150]
Fe₃O₄/Mg-Al-LDH	133	Co-precipitation	[151]
G/MCA-LTH	163.278	Co-precipitation	[152]
C G/MCA-LTH	268.224		
Cu-Mg-Al-(LTH) -N	-	Amine modified method	[153]
CNT/Mg-AlO-LDH	148	pyrolysis of the CoFeMgAl-TA LDH	[154]

Glycerol-modified nanocrystallined Mg/Al-LDH	71.4		
C-Glycerol-modified nanocrystallined Mg/Al-LDH	170.3	Hydrothermal	[155]
LDH/MOF HNC	1282	In-situ	[156]
Ni-CO-LDH/MOF	69	facile and “green” synthesis protocol	[157]
SBAC₁₀₀-Mg-Fe-LDH	169	Co-precipitation	[158]
SBAC₅₀₀-Mg-Fe-LDH	257		

2.4 Removal of dyes by LDH composites

2.4.1 Removal of dyes by the unmodified LDH

LDH is a two-dimensional anionic material and described as hydrotalcite. The chemical form of the layered double hydroxide is demonstrated as $[M_{(1-x)}^{2+} M_{(x)}^{3+}(\text{OH})_2]^{x+} (A^{n-})_{x/n} m\text{H}_2\text{O}$ where M^{2+} and M^{3+} represents divalent and trivalent cations (e.g., Mg^{2+} , Mn^{2+} , Cu^{2+} , Co^{2+} , Ca^{2+} , Zn^{2+} , Ni^{2+}), and (e.g., Fe^{3+} , Al^{3+} , Co^{3+} , Eu^{3+} , Ga^{3+}) respectively, and (A^{n-}) represents the interlayer anions [159]. The molar fraction is represented by x, which is in the range of (0.2 -0.33). The excellent properties of the layered double hydroxide qualifies them to be utilized as adsorbents [160] and in many applications [161]. The versatile features of the LDH including the low cost,

porosity, and the high surface area allow them to be utilized in the adsorption of organic pollutants from wastewater [162].

Several studies reported the applications of LDH or LTH for the uptake of synthetic dyes from wastewater [163]. Snehaprava Das et al. [25], reported the uptake of (MG) by Mg-Al-Fe LDHs with different ratios which have shown high adsorption capacities. Another author Nuhu Dalhat et al. [140], studied the removal of (MO) from water using uncalcined and calcined Mg-Al-Ni-BaFe/LDH. The maximum theoretical adsorption capacity of MO by (UMLDH) and (CMLDH) was 763.35 and 756.42 mg.g⁻¹ respectively. Moreover, Mukarram Zubair et al. [132], reported the sorption capacity of (EBT) from water on Co-Al, Ni-Fe, and Mg-Al - CLDH. The maximum Langmuir adsorption capacity obtained for Co-Al, Ni-Fe, and Mg-Al – CLDH was 419.87 mgg⁻¹ (60 min), 132.49 mgg⁻¹ (60 min), and 540.91 mgg⁻¹ (30 min) respectively. Table 2-3 shows several studies on the adsorption of synthetic organic dyes on LDH and LTH.

Table 0-3: Studies on the adsorption of synthetic organic dyes on LDH.

Dye	Adsorbent	Initial Conc.(mg/L)	Surface Area (m ² g ⁻¹)	Adsorption Capacity(mg/g) or Removal %	Adsorption Conditions			Ref.
					T°C	pH	t(min)	
(MO)	CoFe-LDH	300	168.82	1290	25	7.3	5	[164]
	CuMgAl-LDH	100	131	79.2/98	25	7	180	[165]
	ZnAl-LDH	0.05mMol/L	-	1273/100	25	8	30	[166]
	CMgNiAl-LDH	20	-	375	25	8	30	[167]
	ZnAl-LDH	100	104	1153/100	25	-	360	[168]
(EBT)	CoAl-LDH	20	44.2	361.06/86.46	25	2	120	[133]
	MgAl-CLDH		69.5	419.87/93.13				

(RR)	CoAl-CLDH	20	41.4	540.91/96.54	25	2	60	[132]
	NiFe-CLDH		17.1	132.49/91.5				
	NiAl-LDH	20	-	37.71	25	5.8	120	[169]
	ZnAl-LDH	100	104	390/22	25	-	360	[168]
	MgFe-LDH		125.799	150.03/55				
	MgAlFe-LDH	100	207.792	210.4/70	25	6.5	90	[138]
	MgZnAlFe-LDH		317.214	279.23/85				
(MV)	CuFe-LDH	20	-	-/100	25	5.6	18	[170]
(MB)	Mg ₃ Al-LDH	50	-	45.93/99	25	7	60	[171]
(CR)	MgAl-LDH	100	-	520.83	25	-	4320	[162]
	NiAl-LDH	10	-	120.5/96.1	25	6	30	[172]
	ZnCr-LDH	-	-	15.25/60	25	4	60	[173]
	MgAl-LDH	160	-	65/92.5	25	9.17	140	[174]
(AR)	ZnAl-LDH	100	104	1540/90	25	-	360	[168]
	MgAl-LDH	100	104	-/93.1	25	10	150	[175]
(DR 23)	CoFe-LDHs	20	108.9	-/95.6	25	6	30	[176]
(AO10)	MgFe-LDH	200	-	50	25	3-13	12	[177]
	MgFe-CLDH			205			9	
RR-120	MgAl-LDH	500	159	800/80	25	5	120	[178]
(AB 14)	MgFe-LDH	10	35.4	41.7/65	25	4	3	[179]
	CMgFe-LDH	40	131	370/100				

2.4.2 Removal of dyes by LDH composites with carbon materials

Due to their special qualities, which include a greater anion exchange capacity, a structural memory effect, low prices, and remarkable recyclability, LDH materials have shown considerable potential applications in various fields. Combining LDH with other

nanomaterials might improve the properties of the surface (area and pores) and enhance the adsorption capacity of the composite. Various nanomaterials can be combined with LDH/LTH to provide great efficacy. Among these nanomaterials, carbon materials can be utilized to enhance the performance of the adsorption due to their excellent features including large active sites, good porosity, surface charges stability, and huge sources. The commons sources of carbon materials are AC, CNT, graphene-based, polymers, organic amines, ACFs, B-C, fullerene C₆₀, etc. [180]. LDH/LTH-carbon composites can be synthesized using several methods such as co-precipitation, in-situ growth, solvothermal, and hydrothermal [120]. Carbon nano structures with LDH/LTH (CNS-LDH/LTH) are one of the promising adsorbents which treat water from toxic pollutants including organic dyes [181]. Several studies reported the applications of (LDH/LTH)- carbon composites for the uptake of synthetic dyes from wastewater. Amin et al. [182], reported 90% uptake of (RB5) after 60 minutes from aqueous solution by (NiZnFe LDH/BC). Moreover, the GO/NiAl-LDH and GO/NiCr-LDH have shown good uptake in the removal of (MO) from aqueous solution as mentioned in these two studies [120,147] respectively. Furthermore, Mallakpour and Hatami studied the LDH @ Fe₃O₄/PVA and its removal of MO. They have reported that, the maximum efficacy achieved was 97% at 0.05 g dosage of the adsorbent and 100 mg/L initial concentration. The adsorption capacity of the proposed adsorbent was superior even after four regeneration cycles. In this study [183], the removal of (MB) was tested using the positive charge carbon – dot/MgAl-LDH adsorbent. This composite has shown 96% efficient removal of MB after 60 minutes. Also, GO/LDH-aerogel has shown better sorption affinity of MB due to its stability, and hydrophilicity [184]. Table 2-4 represents several carbon materials containing LDH.

Table 0-4: Studies on the adsorption of synthetic organic dyes on LDH/carbon composites.

Dye	(LDH/LTH)/carbon composite	Initial Conc.(mg/L)	Surface Area (m ² g ⁻¹)	Adsorption Capacity or Removal %	Adsorption Conditions			Ref.
					T°C	pH	t(min)	
(CR)	CNT/MMO	100	148	1250	25	6	120	[185]
	MWCNTs-LDHs	150	124.974	595.8	25	4	300	[186]
(MO)	GO/NiCr-LDH	100	98.2	312.25/99.4	25	6.7	120	[147]
	Calcined Glycerol-modified/MgAl-LDH	600	170.3	1062	25	4.5	20	[155]
	Uncalcined Glycerol-modified/MgAl-LDH		71.4	443.5			30	
	G/MCA-LDH	30	163.278	384.62	25	3	240	[152]
	C G/MCA-LDH		268.224	434.78	25	3	180	
	rGO/NiCr-CO ₃ - LDH	-	98.2	312.5	33	-	240	[187]
	rGO/Ni/MMO	-	-	210.8	25	7	960	[147]
	C _{4x} -LDH	32.7	758	328.95	30	7	180	[188]
	2FPL	1000	-	775.19	30	6.8	24	[189]
	4FPL			826.44				
	6FPL			833.33				
(MB)	Carbon dot/MgAl-LDH	80	-	185/96	25	5	60	[183]
	GO aerogels/MgAl-LDH	-	-	125	-	7.2	1440	[190]
(EBT)	G/NMA-LDH	-	272.79	263.16	25	4	180	[191]
	C G/NMA-LDH	-	294.31	384.62	25	4	180	
(IC)	SWCNTs/CuAl-LDH	100	-	196.78	20	3	6	[192]
Safranin-T dye	Ppy NF/Zn-Fe-LDH	5	23.27	-/99.99	25	5	360	[148]

2.4.3 Removal of dyes by LDH composites with minerals

Recent studies put their attention to the LDH/LTH based nanocomposites including the combination with polymers, carbon, minerals, and other nanomaterials for the uptake of several hazard pollutants such as dyes from aqueous solutions. Furthermore, these nanocomposites exhibited superior affinity of the removal of toxic pollutants due to their great properties added to the parental materials including higher sorption capacity, large active sites, and surface area improvement [193]. One of the promising composites is the hybrid of LDH/LTH with minerals such as bentonite, clay, metals, etc.

Many studies reported the adsorption of organic dyes using (LDH/LTH)/ minerals composite. Lu et al. [162] studied the removal of (CR) using the LDH/ iron oxide composite ($\text{Fe}_3\text{O}_4/\text{MgAl-LDH}$). This hybrid has shown maximum uptake capacity of (813 mgg^{-1}) in the removal of CR from aqueous solution compared to the parental LDH and Fe_3O_4 which have shown low sorption capacity (520 and 133.7 mg.g^{-1}) respectively. Therefore, LDH hybrids improve the adsorption capacity by eliminating the toxicity of dyes. Recently, Ma et al. [194] reported 98% removal of CR after 40 min using a superior (MgZnCr-LDH/TiO_2) composite. Another ($\text{Fe}_3\text{O}_4/\text{ZnCr-LDH}$) composite was synthesized using hydrothermal method by Chen et al. [195] and it has shown 81.23 % removal of (MO). Table 2-5 shows many studies of LDH/ mineral composites in the removal of dyes.

Table 0-5: Studies on the adsorption of synthetic organic dyes on LDH /mineral composites.

Dye	Adsorbent	Initial Conc.(mg/L)	Surface Area (m ² g ⁻¹)	Adsorption Capacity or Removal %	Adsorption Conditions			Ref.
					T°C	pH	t(min)	
(MO)	Fe ₃ O ₄ / ZnCr-LDH	50	185.2	240.16/81.23	112-142	6.4-7.3	35-59	[195]
	Hierarchical SiO ₂ /LDH	0.092mol/L	-	166.1/92	25	4.5	10	[196]
(CR)	Fe ₃ O ₄ /MgAl-LDH	200	133	253	25	2	30	[151]
	Fe ₃ O ₄ @MgAl-LDH	100	57.2	404.6/99.8	25	-	30	[197]
	MgZnCr-TiO ₂ -LDH	100	170.336	526.32/98	40	5.5	40	[194]
	Fe ₃ O ₄ @MgAl-LDH	100	-	813	25	-	4320	[162]
(MB)	TiO ₂ /ZnAl-LDH	3*10 ⁻⁵ M	153.6	6.5*10 ⁻⁶ mol/g	25	9	-	[198]
(EBT)	Bentonite-CoAl-LDH	20	119.14	675.67/92.03	25	2	120	[12]
(AR)	Fe ₃ O ₄ /MgAl-LDH	40	133	92	25	2	30	[151]
(RR)	Fe ₃ O ₄ /MgAl-LDH	100	133	97	25	2	30	[151]

2.4.4 Removal of dyes by different LDH composites

As mentioned above, LDH/LTH with carbon materials, and minerals have shown great removal of synthetic dyes from aqueous solution due to their superior properties. In this section, other composites such as (MOFs), ZIFs, etc. Containing LDH/LTH will be discussed. Removal of some cationic and anionic dyes by (LDH/LTH) composites has

been reported in the literature. Lesbani et al. and Bi et al. [199,200] studied the removal of (MB) using the based Ca/Al-LDH-(B) and Heteropoly blue/ZnAl-LDH respectively . These composites have shown better sorption capacity (32.535 mgg^{-1}) and (30.87 mgg^{-1}) than the pristine LDH. Table 2-6 summarizes different LDH composites with their adsorption conditions on the removal of different dyes.

Table 0-6: Studies on the adsorption of synthetic organic dyes on different LDH composites.

Pollutant	Adsorbent	Initial Conc.(mg/L)	Surface Area (m^2g^{-1})	Adsorption Capacity or Removal %	Adsorption Conditions			Ref.
					T°C	pH	t(min)	
(MB)	Ca/Al-LDH-biochar	35	158.291	32.535	60	5	-	[199]
	Heteropoly blue/ZnAl-LDH	40	-	30.87/75	25	6.3	300	[200]
	ZIF-67@CoAl-LDH	-	374.3	57.14/79.9	30	-	100	[201]
(MO)	ZIF-67@CoAl-LDH	-	374.3	180.5/72.3	30	-	90	[201]
	ZIF-67@LDH	200	172.3051	1029.59	30	-	15-20	[202]
	DI-LDH Ns	200	126.3	846.6	25	9	5	[203]
	DM-LDH Ns	200	96.6	327.4	25	9	120	[204]
	Flower-like-NiAl-LDH	100	133	500.6	25	3	100	
	FH-CpAl-LDH	100	318.13	2189.23	25	4	1440	[205]
	Starch/NiFe-LDH (2:1)	20	-	387.59/90	25	3	180	[206]
	LDH- Cu-(BDC) MOF	5	-	600/99	25	-	20	[207]

(ARS)	ZIF-67@LDH	200	172.3051	1171.1	30	-	15-20	[202]
(CR)	Mg-Al-LDH /CT	200	24.556	344.828	60	-	120	[208]
	Flower-like microspheres Ni/Al-LDH	100	153.3	242.4/94.67	25	6	48	[209]
(AR)	2-Hydroxyethyl ammonium acetate/MgAl-LDH	180	96.7	313.6/95.8	25	6	500	[210]

2.5 Removal of phenols by LDH composites

2.5.1 Removal of phenols by the unmodified LDH

The discharge of phenolic compounds into water bodies results in hazards to human health and environment because of their persistence and toxicity. Distinct types of phenolic compounds are categorized as toxic organic pollutants including BPA, 2-NP, 2-CP, etc. The WHO recommends that the maximum limit of phenolic compounds in the drinking water is 1×10^{-6} g/L. In the natural waters, the maximum limit for 2-Nitrophenol is 2×10^{-6} g/L [211]. Different technologies as adsorption (as mentioned in the previous sections) are required to remove these toxic phenolic compounds from aqueous media [212]. Layered double hydroxides (LDHs) and their composites are considered as green adsorbents to adsorb pollutants from water due to their superior properties including large surface area, huge active sites as aforementioned. Many studies reported the adsorption of phenolic compounds from aqueous solutions by LDH/LTH.

Dalla Nora et al.[122], studied the removal of 2-NP from aqueous media using Mg-Fe/LDH and Zn-Al/LDH. These two LDHs were synthesized using coprecipitation method

with different divalent and trivalent components. The maximum sorption capacity of 2-NP from water using Mg-Fe/LDH and Zn-Al/LDH were 165 and 290 mgg^{-1} respectively. Furthermore, He et al. [213] reported the removal of 4- NP (also called p-Nitrophenol) and phenol from water using Mg-Al/LDH. The maximum Langmuir adsorption capacity were 196.7 mgg^{-1} and 42.9 mgg^{-1} of 4- Nitrophenol and phenol, respectively. Other studies of the uptake of phenolic compounds on LDH/LTH are shown in Table 2-7.

Table 0-7: Studies on the adsorption of phenolic compounds on LDH.

Phenolic compounds	Adsorbent	Initial Conc.(mg/L)	Surface Area (m^2g^{-1})	Adsorption Capacity or Removal %	Adsorption Conditions			Ref.
					T°C	pH	t(min)	
Phenol	CLDH	40	29.74	59.09/80	25	-	1440	[214]
	Mg-Al/LDH	50	-	42.9/48.8	25	-	300	[213]
	C MgZnAl-LDH (500 °C)	-	84.6	11.9	25	7	-	[215]
				14.7	65			
(2-NP)	Mg-Fe/LDH	500	34.2	165		3	55	[122]
	Zn-Al/LDH		104.1	290				
(4-NP)	Mg-Al/LDH	50	-	196.7/82.8	25	-	300	[213]

2.5.2 Removal of phenols by LDH composites with carbon materials

The penetration of phenolic compounds into water causes severe problems to the environment and humans. The hybrid of LDHs with other material will show better adsorption due to the improvement of surface area and active sites. The synthesis of these hybrids of LDH is similar to the pristine using one of methods mentioned above. Among

these materials which can be combined with LDH/LTH is carbon. Few sources reported the uptake of phenolic compounds from aqueous media using (LDH/LTH)/carbon materials.

Dalhat Mu'azu et al. [216], investigated the removal of phenol from water using the Sewage sludge ZnCl₂/AC- MgFe-LDH. This composite has shown high surface area (233.75 m²g⁻¹) which resulted in a maximum sorption capacity of 138.69 mgg⁻¹ at 298K. Furthermore, Dalhat Mu'azu et al. [217] studied the (SBAC-LTH) on the removal of phenol. This adsorbent has achieved better adsorption capacity (216.76 mgg⁻¹) of phenol at these conditions (T= 535 °C, pH= 6, & C_i= 125 mg/L).

2.5.3 Removal of phenols by LDH composites with minerals

It was found that phenolic compounds might be well separated using various materials such as LDHs due to their efficacies to adsorb phenols. In this section, combination of minerals including (metals, clay, bentonite, etc.) with LDH/LTH on the removal of phenols will be discussed. Properties of minerals will add superior features to LDH such as ionic exchange and surface area improvement. Countable studies put their focus on the removal of phenolic compounds using (LDH/LTH)/ minerals composite. Lupa et al. [218] synthesized Aliquat 336 functionalized Zn₄-Al-LDH. In this study three different materials have been synthesized using coprecipitation method. Ionic Liquid (IL)- Zn₄-Al-LDH, Zn₄-Al-LDH-IL, and Zn₄-Al-LDH have shown better sorption capacity of 68.02, 34.5, and 23.4 mgg⁻¹ respectively.

2.5.4 Removal of phenols by different LDH composites

As discussed above, the toxicity of phenols into the environment motivates researchers to find green and promising adsorbents to separate these organics from aqueous solutions. Modified and un-modified layered double hydroxides were synthesized to remove phenols and other pollutants from water. Some researchers put their focus on the adsorption of phenols by various composite with LDH/LTH. Yu Bi et al. [219] reported the removal of p-cresol (also called 4-methylphenol) using (RL-LDH). Moreover, this study presented the comparison of RL-LDH (different composition of Mg^{2+}/Mg^{3+}) with its pristine LDH. Even if the surface area of composites is smaller (RL-LDH1 = 8.75 m²/g, RL-LDH2 = 11.71 m²/g) than LDH (39.39 m²/g), the sorption capacity of the composites is higher, and this might be explained by adsorption mechanisms. At 293 K, the removal of p-cresol by RL-LDH2 (36.55 mgg⁻¹) is higher than RL-LDH1 (28.65 mgg⁻¹) and LDH (1.4 mg.g⁻¹).

2.6 Removal of heavy metals by LDH composites

2.6.1 Removal of heavy metals by the unmodified LDH

The discharge of heavy metals into the environment causes harmful effects to human bodies. Before the discharge of these harmful metals into the environment, treatment is required. Among all technologies for heavy metals removal, adsorption is considered as an efficient method due to its low cost of operation, friendly to environment, small fouling, and adsorbents could be easily regenerated via adsorption. Among all adsorbents, LDHs are considered as promising adsorbents for removal of several hazardous pollutants from water due to their versatilities in the structure and composition [220]. The sorption of contaminants on LDH is economical, non-toxic, and efficient [221]. Many studies reported

the uptake of heavy metals from aqueous media using layered double hydroxide (LDH) as illustrated in Figure 2-7.

Guo et al. [222] studied the removal of (Cr^{6+}) and (Cd^{2+}) from water using the synthesized ZnNiCr-LDH. This adsorbent was synthesized by hydrothermal method, and it has shown maximum sorption capacity of 28.2 mgg^{-1} and 60 mgg^{-1} for (Cr^{6+}) and (Cd^{2+}) respectively. Furthermore, Amin et al. [223] reported the synthesis of Zn/Fe-LDH and its composites for the removal of (Cu^{2+}). This study investigated that the Zn/Fe-LDH has presented a better sorption capacity of 25.38 mgg^{-1} using Langmuir model. Other studies for the removal of heavy metals on LDH are summarized below in Table 2-8.

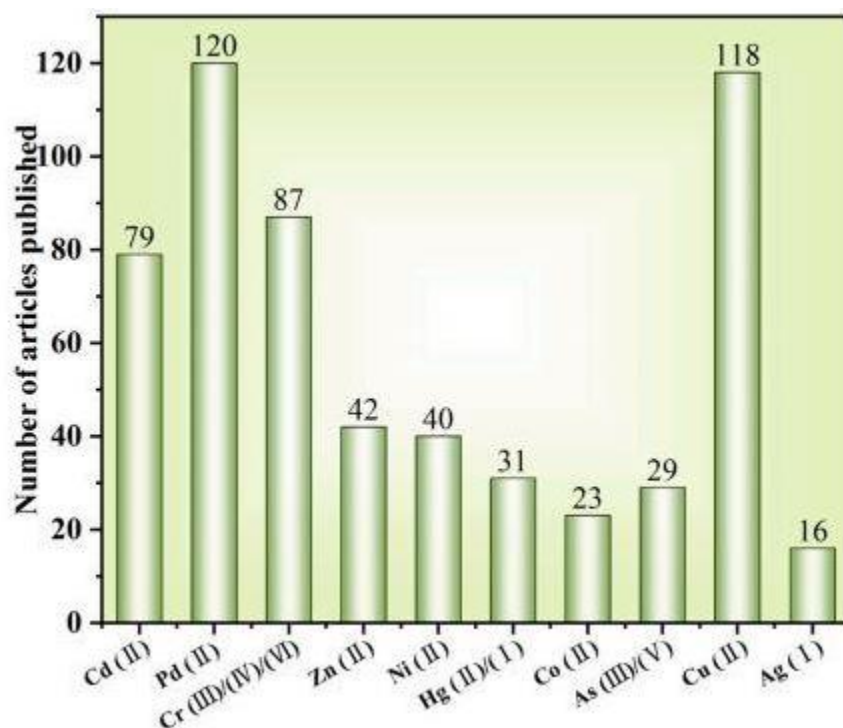


Figure 0-7: Number of published papers on the removal of heavy metals by LDH-based [224].

Table 0-8: Studies on the adsorption of heavy metals on LDH.

Heavy Metal	Adsorbent	Initial Conc.(mg/L)	Surface Area (m ² g ⁻¹)	Adsorption Capacity or Removal %	Adsorption Conditions			Ref.
					T°C	pH	t(min)	
Pb(II)	MgAl-LDH	300	78.07	192.3	25	-	240	[225]
	MgFeAl-CO ₃ -LDH	100	80.77	117.86	25	5.45	180	[141]
Cu(II)	MgCuAl-LDH	150	63.45	639	25	9	240	[226]
	MgAl-LDH	300	78.07	45.05	25	-	240	[225]
	Zn/Fe-LDH	60	69	25.38	-	6	60	[223]
Cd(II)	MgCuAl-LDH	150	63.45	457	25	9	240	[226]
	MgAl-LDH	300	78.07	192.3	25	-	240	[225]
	ZnNiCr-LDH	-	354.36	60	25	2	-	[222]
Cr(VI)	ZnNiCr-LDH	-	354.36	28.2	25	2	-	[222]
	Ni ₄ Fe-LDHs	4	17.847	26.78/97	25	-	60	[227]
	MgAl-LDH	10	83.95	17	30	6	240	[228]
	ZnAl-LDH	40	56.1	68.07	25	6-7	-	[229]

2.6.2 Removal of heavy metals by LDH composites with carbon materials

As known, LDHs materials are effective for water remediation. However, carbon-based materials including graphene (G), polymers, (AC), etc. could effectively improve the activity surface of LDH. Therefore, the combination of LDH and carbon materials enhance the surface area, provide a microporous domain which allow the diffusion and hence exhibit significant promotion in the adsorption potential for water separation compared to their parental LDH [230]. Many reviews demonstrated the synthesis of LDH composites

(such as LDH/carbon materials) with their applications in the remediation of pollutants specifically heavy metals.

The adsorption of Cr^{6+} was studied by Yuan et al. [230] on the calcined graphene/MgAl-LDH (G/LDH). The G/LDH was first prepared by urea-hydrolyzed hydrothermal method and then by heating it at high temperature to obtain the calcined composite to remove the hexavalent chromium from water with adsorption capacity of 172.55 mgg^{-1} . Moreover, the adsorption of (Cd^{2+}) and (Pb^{2+}) was reported by Baruah et al. [231] on NiFe CO_3 -LDH/NGO which is considered as carbon material (GO) containing LDH. This composite has shown excellent sorption capacity of 971 and 986 mgg^{-1} for Cd^{2+} and Pb^{2+} respectively. In addition, Wang et al. [232] studied the removal of (Cu^{2+}) using the (B) /MnAl-LDH. It was synthesized using hydrothermal method and then used to remove Cu^{2+} with sorption capacity of 74.07 mgg^{-1} . Carbon nanotubes hybrid with LDH (LDH/CNTs) were synthesized by Amin et al. and used to adsorb Cu^{2+} from aqueous media. After 60 min, LDH/CNTs have shown superior affinity of 39.53 mgg^{-1} . Table 2-9 represents some studies on the removal of heavy metals using LDH/carbon materials.

Table 0-9: Studies on the adsorption of heavy metals on LDH/carbon composites

Heavy Metal	Adsorbent	Initial Conc.(mg/L)	Surface Area (m ² g ⁻¹)	Adsorption Capacity or Removal %	Adsorption Conditions			Ref.
					T°C	pH	t(min)	
Cu ²⁺	CNF/LDH	-	43.7	219.6	RT	5	120	[233]
	Polysulfide/LDH	-	-	127	-	3	-	[234]
	NCs/MgAl-LDH	-	5.61	19.93	-	6	60	[235]
Cr ⁶⁺	CNF/LDH	-	43.7	341.2	RT	5	120	[233]
	LDH/CNs	-	-	35.6	25	-	720	[236]
	Carbon/MgAlO-LDH	-	285	172.94	50	5.5	120	[237]
Cd ²⁺	LDH/CNs	-	-	48.5	25	-	720	[236]
	Polysulfide/LDH	-	-	57	-	3	-	[234]
U ⁶⁺	rGO/LDH	130	256.8	277.8	25	4	180	[238]
	GO./LDH	10	28.73	129.9	25	4.5	720	[239]
	Fe ₃ O ₄ /C/NiAl-LDH	-	77	174.2	25	6	180	[240]
Pb ²⁺	Polysulfide/LDH	-	-	483	-	3	-	[234]
	Fe ₃ O ₄ /GO/MgAl-LDH	-	-	173	25	5	600	[241]
As ⁵⁺	Fe ₃ O ₄ /G/MgAl-LDH	-	123.3	73.14	-	6	480	[242]
	GO/MgAl-LDH	-	35.4	180.26	-	5	240	[149]

2.6.3 Removal of heavy metals by LDH composites with minerals

70 percent of adsorption processes is linked to adsorbents [243], hence researchers put their concern in the development of novel adsorbents. LDH nanocomposites provide a new

window for researchers to figure out the adsorption tendency into toxic pollutant. In this section, the relative studied on the removal of heavy metals on (LDH/LTH)/ mineral composites are highlighted.

Kim et al. [244] studied the adsorption of chromate ions (CrO_4^{2-}) using Bentonite (BT) /LDH nanocomposite. In this study, the adsorbent was prepared by different methods such as coprecipitation simple solid-phase hybridization (SP), exfoliation-reassembly (ER). According to this study, it was found that BT/LDH synthesized by (SP) has achieved a maximum at 67% removal of chromate. Further studies of the removal of heavy metals by LDH/mineral composites are summarized in Table 2-10.

Table 0-10: Studies on the adsorption of heavy metals on LDH /mineral composites.

Heavy Metal	Adsorbent	Initial Conc.(mg/L)	Surface Area (m^2/g)	Adsorption Capacity or Removal %	Adsorption Conditions			Ref.
					T°C	pH	t(min)	
Pb²⁺	PAAS/LDH	50	20.1	345.4	40	-	150	[245]
	MnO ₂ /MgAl-LDH	100	-	49.87/96.73	25	4	192	[246]
	MoS ₄ ²⁻ /MgAl-LDH	-	-	290	25	2-10	60	[247]
	Cl/MgAl-LDH	20	-	143.85/81.05	30	4-6	120	[248]
Cr⁶⁺	Cl/MgAl-LDH	40	-	112.7/49.56	30	4-6	30	[248]
	LDH@ MoS ₂	-	-	76.3	25	5	120	[249]
	MoS ₄ ²⁻ /MgAl-LDH	-	-	130	RT	-	720	[250]
	Fe ²⁺ /MgAl/LDH	-	-	649.87	30	-	1440	[251]
	CoFe ₂ O ₄ /MgAl-LDH	-	121	72.4	-	2	-	[252]
As⁵⁺	MoS ₄ ²⁻ /MgAl-LDH	-	-	56	RT	-	720	[250]
	TiO ₂ /LDH	-	194.8	101.32	30	10	1440	[253]

	AsO ₄ /ZnAl -LDH	-	-	41.58	25	12	150	[254]
Cu²⁺	MoS ₄ ²⁻ /MgAl-LDH	-	-	181	25	2-10	60	[247]
	Cl/MgAl-LDH	40	-	143.85	30	4-6	30	[248]
As³⁺	TiO ₂ /LDH	-	194.8	29.8	30	10	1440	[253]
	MoS ₄ ²⁻ /MgAl-LDH	-	-	99	RT	-	720	[250]

2.6.4 Removal of heavy metals by different LDH composites

Although the discharge of heavy metals has always been a major concern, scientists have intensified because of the toxicity of heavy metals penetration. Among adsorbents that have been used to date, LDHs and their composites are considered as green adsorbents due to the low cost and their high surface area. Recently, LDH/LTH composites have shown great attention and attraction for water remediation [221]. Literature is full of studies containing LDH composites which are effective for the removal of heavy metals including LDH/ acids, LDH/enzymes, etc.

Li et al.[255] reported the removal of copper from aqueous media using Rhamnolipid/MgAl-LDH. At 20 °C Rhamnolipid/MgAl-LDH has removed copper with sorption capacity of 116.14 mg/g, and it has surface area of 11.71 m²/g. Furthermore, The adsorption of (Cr) from water was studied by Guo et al. [256] using Egg shell/MgAl membrane-LDH and it has shown sorption capacity of 27.9 mg/g after 30 minutes. Summarized studies on the removal of heavy metals using various LDH composites are listed in Table 2-11.

Table 0-11: Studies on the adsorption of heavy metals on different LDH composites.

Pollutant	Adsorbent	Initial Conc.(mg/L)	Surface Area (m ² g ⁻¹)	Adsorption Capacity or Removal %	Adsorption Conditions			Ref.
					T°C	pH	t(min)	
Pb ²⁺	Sulfonated-lignin/MgAl-LDH	-	0.7	123	25	5.7	360	[257]
	Humate/MgAl-LDH	-	-	0.48mmol/g	25	5	2880	[258]
	Tartrate/MgAl-LDH	-	74.7	123.3	25	5-6	-	[259]
				143.6	50			
	Glutamate/MgAl-LDH	120	-	68.49	25	5	-	[260]
	MgAl-Cys-LDH	300	-	186.2	25	-	240	[261]
Cu ²⁺	Sulfonated-lignin/MgAl-LDH	-	0.7	64	25	5.7	360	[257]
	Humate/MgAl-LDH	-	-	1.326mmol/g	25	5	1440	[258]
	MgAl-Cys-LDH	100	-	58.07	25	-	240	[261]
	Tartrate/MgAl-LDH	-	74.7	30.76	25	5-6	180	[259]
				36.67	35			
				51.27	45			
	Rhamnolipid/MgAl-LDH	-	11.71	116.14	20	5.5	120	[255]
	EDTA/MgAl-LDH	-	-	-	-	5	15	[262]
Cr ⁶⁺	Egg shell/MgAl membrane-LDH	-	-	27.9	25	5.1	30	[256]
	EDTA/NiFe ₂ O ₄ /ZnAl-LDH	-	1.5	64.28	25	6	120	[263]
	PANI@Nd-LDH	-	-	219	RT	-	210	[264]
	MF-LDO	-	205.82	148.7	25	-	10	[265]

	Co-Al-LDH@Fe ₂ O ₃ /3DPCNF	50	-	400.4	RT	2	60	[266]
Cd²⁺	Humate/MgAl-LDH	-	-	0.18mmol/g	25	5	2880	[258]
				0.177	15			
				0.177	35			
	MgAl-Cys-LDH	100	-	93.11	25	-	240	[261]
	EDTA/MgAl-LDH	-	-	-	-	5	9.6	[262]

2.7 Effects of operational parameters in adsorption

2.7.1 Effect of pH

The chemistry and surface morphology of the adsorbents are substantially impacted by pH, which has a considerable impact on the performance of LDHs and their composites [267]. This phenomenon can be explained by the adsorbent's surface charge and the ionic chemistry of the solution. At pH 3 or lower, it was asserted, the surface of the adsorbent carries the positive charge and offers significant electrostatic interaction with anionic dyes, resulting in better adsorption efficiency. Opposite to that, a negative charge on the adsorbent surface causes a poor contact between the LDH surface and an anionic dye at pH > 4 [155,204]. For example, Shan et al. [268] investigated the sorption of three red dyes (CR, RR, AR1) on CoFe-LDH. Figure 2-8 represents the pH effect on sorption of the three dyes using CoFe-LDH. It can be noticed that at lower pH, CoFe-LDH shows high adsorption compared to higher pH.

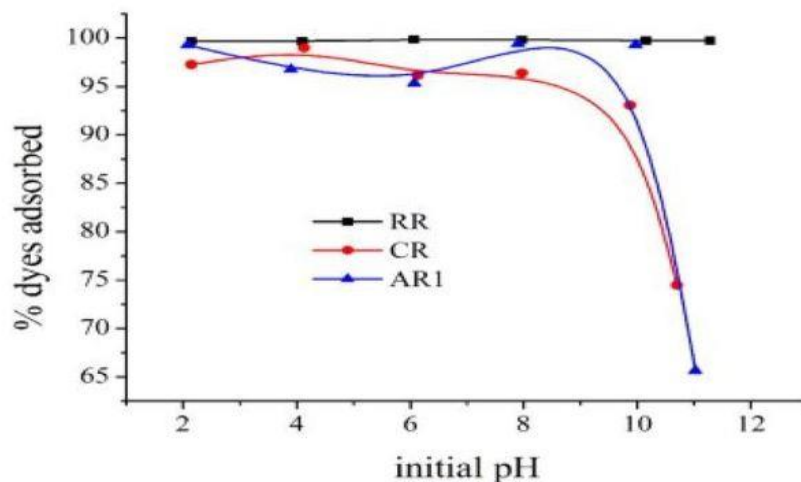


Figure 0-8: The influence of pH on the adsorption of RR, CR, and AR1.

The pH effect on the maximum sorption capacities of heavy metals on various LDH composites have been shown above in (Table 2-8 - Table 2-11). It can be observed that, the maximum adsorption capacity of Cd^{2+} , Pb^{2+} , Cu^{2+} , Cr^{2+} , Hg^{2+} and U^{6+} are at pH (3-5), (5-6), (5-6), (2-6), 6 respectively. Some studies reported that, at low pH the adsorption ability of divalent metal ions will be lower due to the dissolution of the LDH composites and the acidic hydrolysis [235,269] and similarly for pH greater than 7, it may cause hydrolysis for divalent metal ions, hence the sorption capacity will be decreased [260]. Furthermore, the maximum adsorption capacity of cationic and anionic dyes on LDH hybrids are reported at ~ 6 and $\sim(2-6)$ respectively as represented in (Table 2-3 – Table 2-6). Also, the maximum adsorption capacity of phenol on SBAC/LTH was investigated at pH 6 as reported in [217].

2.7.2 Effect of temperature

Temperature is another factor that has a significant effect on the adsorption efficacy [270]. For the case of endothermic processes, the relation is linear, hence as the adsorption temperature increases, the sorption capacity increases [238]. This occurs because the pollutants (dyes, heavy metals, and phenols) mobility increases in the aqueous media which then improves the adsorption sites accessibility.

Ahmed et al. [271] claimed that, the adsorption capacity of (CR) on Mg-Fe-CO₃/LDH increases by increasing the adsorption. Furthermore, Yuan et al. [230] reported that, the removal of Cr(VI) on calcined G/LDH increases by increasing the operating temperature. All these are indicated by the positive value of (ΔH) and (ΔS), where the increases in the negativity of Gibbs free energy (ΔG) indicates the spontaneity of the adsorption process as shown in Table 2-12. Other studies are summarized in Table 2-12 which support the linearity between the operating temperature and the adsorption capacity.

In contrast, for the exothermic processes, the uptake of pollutants from wastewater is inversely proportional to the adsorption temperature. This happens due to the fact that by increasing the adsorption temperature, the forces between the active sites on the surfaces of LDH composites and the pollutants minimize, hence the sorption capacity decreases [272]. Zang et al. [183] reported the removal of methylene blue on carbon dot/LDH and he investigated that, by increasing the operating temperature, the adsorption capacity decreases which also indicated by the negative value of the enthalpy (ΔH) = -12.2 KJ/mol.

Table 0-12: Thermodynamic parameters for the removal of pollutant on LDH and LDH composites (Endothermic Process).

Pollutant	Temperature °C	ΔG (KJ/mol)	ΔH (KJ/mol)	Ref.
(CR)&	20	-7.74		
[Mg-Fe-CO ₃ /LDH]	25	-8.61	37.214	[271]
	23	-10.1		
	50	-12.34		
Cr (VI) &	20	-4.17		
[CG/LDH]	30	-4.51	16.94	[230]
	40	-5.64		
Pb(II) &	25	-29.1		
[tartrate-LDH]	30	-30.1	30.7	[259]
	40	-32.1		
	50	-34.1		
(2-NP) &	25	-5.72		
[LDH]	35	-9.45	63.45	[122]
	45	-11.02		
	55	-12.91		
Cu(II) &	15	~13		
[LDH-H100]	25	-13.8	33.7	[258]
	35	-16.25		
Cd(II) &	15	-10.2	20.7	
[LDH-H100]	25	-11.9		[258]
	35	-12.3		

2.7.3 Effect of the variation of the initial concentration and contact time

At equilibrium, the amount of solute adsorbed (removed) and the concentration of pollutant in the solution are related by the adsorption isotherm. The adsorption uptake capacity is predicted using isotherms. The performance of adsorption is influenced by the solution phases (solid-liquid or solid-gas) as well as process variables like pH effect, initial concentration and contact time [16]. The effective of adsorption process can be examined by various isotherms models which are applied to the experimental data to investigate the real mechanism of the interaction between the adsorbent and the pollutant [15]. Various empirical isotherm models have been used to analyze data. The most commonly used models are Freundlich and Langmuir. The Langmuir model assumes that the surface is homogenous, with no interactions between adsorbed molecules, and that adsorption sites are identified [273]. This model assumes that adsorption occurs via the development of an adsorbate monolayer, which results in the equation:

$$q_e = q_{\max} \times \frac{K_L \times C_e}{1 + K_L \times C_e} \quad (2-1)$$

where $q_{\max}$ is the maximum capacity adsorbed (mg/g), K_L represents the adsorbent equilibrium constant (L/mg) which depends on the experimental conditions and C_e expresses the concentration of the adsorbate at equilibrium (mg/L).

The Freundlich isotherm is an empirical equation that assumes that during the adsorption process, the adsorption surface becomes heterogeneous. The Freundlich isotherm can be expressed using the equation below.

$$q_e = K_F C_e^{1/n} \quad (2-2)$$

Where K_F is the coefficient of the adsorption which defined as the amount of the adsorbate adsorbed on the adsorbent at equilibrium, $(\frac{1}{n})$ is the intensity of the adsorbate on the adsorbent that behave as heterogenous as the value of $(\frac{1}{n})$ goes to zero, while it follows Langmuir isotherm as the value of $(\frac{1}{n})$ reaches 1 [274]. Table 2-13 summarized Langmuir, Freundlich, Tempkin, Redlich-Peterson, and Liu isotherm models with their parameters. Various studies reported the adsorption of toxic pollutants including dyes, phenols, heavy metals, etc. on LDH/LTH composites. Most of these studies are correlated with Langmuir model, while some cases are correlated to Freundlich.

Deng et al. [252], Huang et al. [275], Ruan et al. [147], and Yang et al. [187] investigated that, the adsorption of Cd(II), Pb(II), Cu(II), Cr(VI), Methylene blue (MB), Methyl orange (MO), and Red dyes on LDH composites has been described by Langmuir model. Other studies reported that, Freundlich is well fitting with the experimental data compared to Langmuir [230,235].

Table 0-13: Mathematical Representation of nonlinear isotherm models [276].

Model	Mathematical Representation	Parameters
Freundlich	$q_e = k_F C_e^{1/n}$	k_F
		n
Langmuir	$q_e = q_{\max} \times \frac{k_L \times C_e}{1 + k_L \times C_e}$	$q_{\max}$
		k_L
Liu	$q_e = \frac{q_{\max} \cdot (k_g \times C_e)^{n_L}}{1 + (k_g \times C_e)^{n_L}}$	$q_{\max}$
		k_g
Temkin	$q_e = \beta \times \ln(A \times C_e)$	β

Redlich-Peterson	$q_e = \frac{K_R \times C_e}{1 + a_R \times C_e^G}$	K_R
		a_R
		G

For the adsorption kinetics, contact time is a crucial consideration when evaluating how favorable the adsorption process is. The elimination of pollutants from aqueous solutions generally increases as the contact time of adsorption increases until equilibrium is reached. Figure 2-9 represents the kinetic effect for the adsorption of Ni^{2+} , Cu^{2+} , and Pb^{2+} on unmodified and modified palygorskite-LDH. Yang et al. [277] reported the removal of Ni^{2+} , Cu^{2+} , and Pb^{2+} on unmodified and modified palygorskite-LDH and it showed that the adsorption was very fast (1 min) for the unmodified palygorskite-LDH and 10 min for the modified palygorskite-LDH and it reached equilibrium after 4 min and 20 min respectively. As reported in some studies, the fast adsorption rate of the aforementioned heavy metals on palygorskite-LDH is referred to the removal on LDH layers by metal complexation or hydroxide precipitation and then the slow removal rate is referred to the physical removal of the support composite materials on LDH. Furthermore, the adsorption rate of Lead (II) is faster than Nickle and Copper which is due to the high affinity and interaction of Lead with the LDH composites surface to compose $\text{Pb}(\text{OH})_2$. The shorter time to reach equilibrium is considered as a main factor for the application of layered double hydroxide (LDH) composites in the industrial scale design of water treatment [15]. In order to demonstrate the good interaction mechanisms between the adsorbent and the pollutant, different kinetic models are proposed such as pseudo-1st order and pseudo 2nd order to best describe and fit the experimental data [278,279]. In some studies, other kinetic models are used as summarized in Table 2-14. In addition, the removal of dyes, phenols, and heavy

metals by LDH composites with their adsorption kinetics and isotherms are shown in Table 2-15.

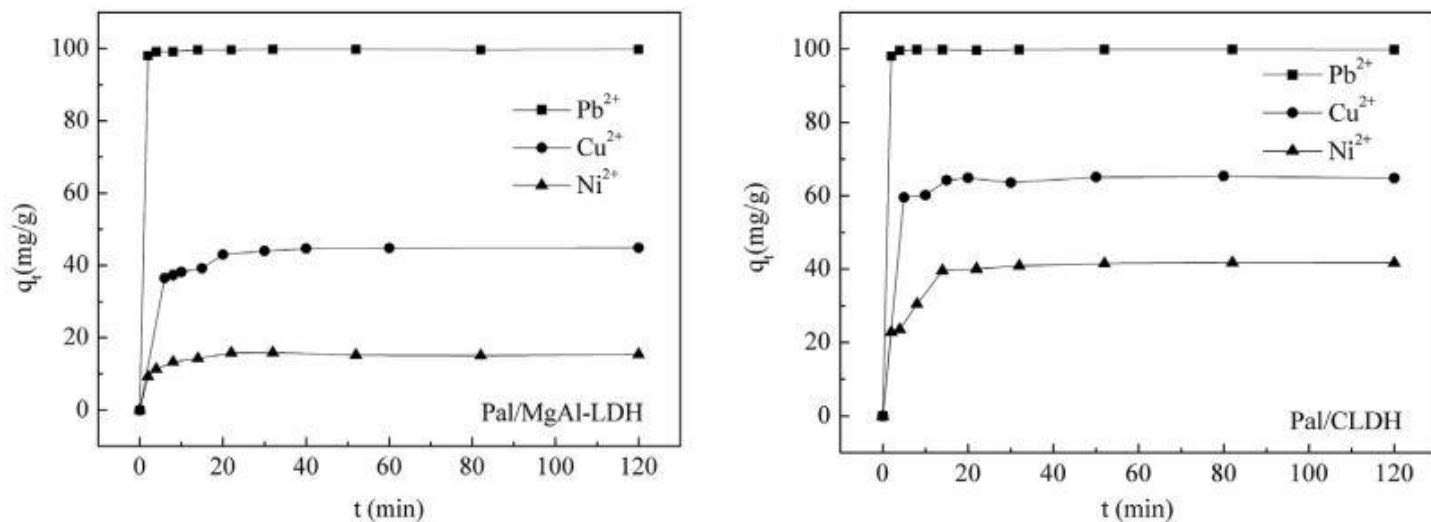


Figure 0-9: Representation of the adsorption kinetic on the removal of Ni^{2+} , Cu^{2+} , and Pb^{2+} by calcined Pal/LDH & uncalcined Pal/LDH [277].

Table 0-14: Mathematical Representation of nonlinear kinetic models [276].

Model	Mathematical Representation	Parameters
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta t)$	α
		β
Pseudo-1 st Order	$q_t = (1 + e^{-k_1 t})$	K_1
Pseudo-2 nd Order	$q_t = \frac{q_e^2 \cdot k_2 t}{1 + q_e k_2 t}$	q_e
		K_2
Intra-Particle Diffusion	$q_t = k_d t^{1/2} + C$	K_d
		C
Avrami Fractional	$q_t = q_{\max} [(1 - \exp(k_{av} t))]^n$	$q_{\max}$
		k_{av}
		n

Table 0-15: Adsorption isotherm and kinetic models for removal using LDH and its composites.

Adsorbent	Adsorbate	Isotherm Model	Kinetic Model	pH	Ref.
Mg-Al/LDH	MO	Freundlich	2 nd Order	4	[280]
C G/LDH	Cr (VI)	Freundlich	2 nd Order	2	[230]
Mg-Fe/LDH	2-Np	Freundlich	2 nd Order	3	[122]
Zn-Al/LDH	2-Np	Freundlich	Elovich	3	
C-dot- LDH	MB	Langmuir	2 nd Order	6	[183]
Tartrate/LDH	Pb(II)	Sip	2 nd Order	5-6	[259]
GO/zero-valent Ni/LDH	MO	Langmuir	2 nd Order	7	[187]
Bio-ceramic/LDH	P	Freundlich	2 nd Order	7	[281]
Bentonite/LDH	EBT	Langmuir	2 nd Order	~2	[12]
Methionine/LDH	As(III)	Langmuir	2 nd Order	6	[282]
CNT/MgAlO/LDH	CR	Langmuir	2 nd Order	5	[185]
Citrate/magnetic/LDH	U(VI)	Freundlich	2 nd Order	6	[283]
Surfactant/LDH	AR	Langmuir	2 nd Order	6-7	[284]
Ni-Zn-Cr LDH	Acid scarlet GR	Langmuir	Intra-Particle	5	[285]
Calcined-Mg-AL LDH	Acid blue 113	Langmuir	Avrami	-	
Pal/LDH	Cu(II) Pb(II) Ni(II)	Langmuir	2 nd Order	3	[277]

2.8 Adsorption mechanisms

Adsorption is considered as the accumulation of materials (contaminates) at the interface between two phases solid-gas or solid -liquid [286]. Intermolecular forces of attraction between the adsorbent and the adsorbate are often what cause adsorption to happen. Moreover, surface forces at the interface intensify the solutes on the surface of the adsorbent when a solution media containing adsorbate encounters the adsorbent. Adsorption is thought to be a suitable for water treatment [287]. Adsorption mechanism of various harmful pollutants on LDH-composites are primarily influenced by the type of adsorbent (composite materials) and adsorbate (contaminants). The most common mechanisms contributed to the adsorption of heavy metals, dyes, phenols, etc. on LDH composites are hydroxide precipitation, physical adsorption, chelation (surface complexation), electrostatic attraction, pi-pi interactions, and chemical bonding [235,238,242] as summarized in Figure 2-10 and Figure 2-11. FT-IR is used to best describe the interaction of adsorption mechanisms and initiate the involved groups in the pollutant removal [288].

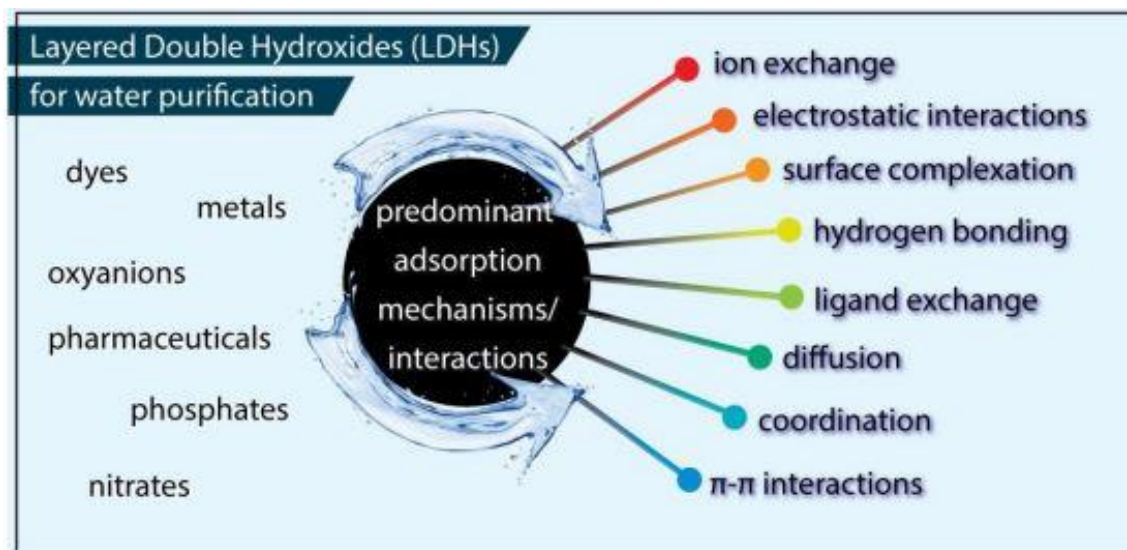


Figure 0-10: Predominant adsorption mechanisms for water purification [276].

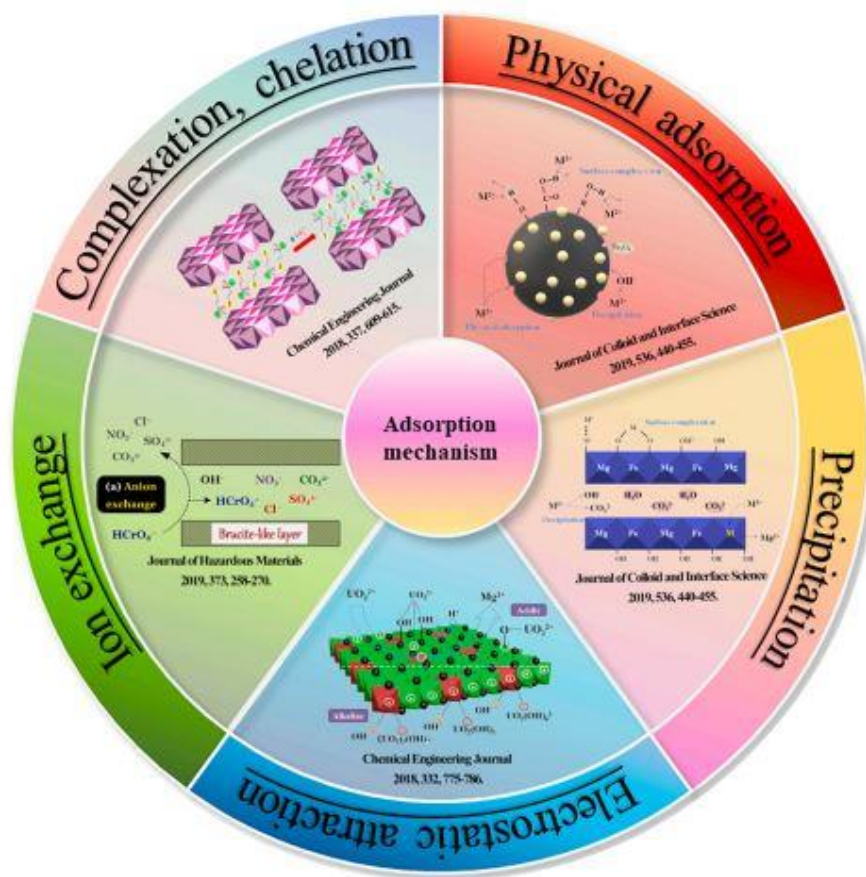


Figure 0-11: Adsorption mechanisms of heavy metals by LDH composites [224].

Chebli et al. [289] and Guzman-Vargas et al. [290] investigated that, unlike heavy metals, the adsorption of organic dyes (cationic and anionic) is not controlled primarily by an ion exchange mechanism , but it is explained by an electrostatic attraction between the negatively or positively charged surfaces of LDH-composites with cationic and anionic dyes, respectively. Additionally, dye molecules can be bonded with the hydroxyl groups on the surface of LDH and its composites by H-bonding [291]. Moreover, Zang et al.[183] reported that, the existence of oxygen functional groups on the carbon materials surfaces is considered as active sites for synthetic dyes and they show that, the removal of Methyl blue by LDH/C-dot composite depends on pH and proper in acidic medium as shown in Figure 2-12. This proves that the adsorption mechanism between the anionic MB and the

positive charge on LDH/C-dot composite is electrostatic attraction. Similar behavior of the adsorption of dyes, phenol, heavy metals, etc. on LDH composites was summarized in Table 2-16.



Figure 0-12: Representation of the adsorption of Methyl blue on LDH/C-dot [183].

Table 0-16: Adsorption Mechanisms for different pollutants on LDH composites.

Adsorbate	Adsorbent	Adsorption Capacity (mg/g)/%Removal	Adsorption Mechanism	Ref.
Cr(VI)	BC@ EDTA/LDH	55.19	Surface adsorption and Memory effect	[292]
(CV)	Biomass/LDH	354.05	Electrostatic attraction Complexation, chelation	[293]
Cu(II)		158.57		
Zn(II)		175.25		[294]

Pb(II)	LDH/VMT	142.65	Isomorphous replacement, precipitation	
Ni(II)		222.8		
Pb(II)		99.8	Complexation, chelation	[277]
Cu(II)	Pal/MgAl-LDH	44.9		
Ni(II)		15.4		
As	MgAl-LDH		Isomorphous replacement, Ion exchange	[295]
Co		-		
2NP	ZnAl-LDH	290	Electrostatic repulsion	[122]
	FeAl-LDH	165		
EBT	Bentonite/LDH	675.67	Electrostatic, surface adsorption and chemical interaction	[133]
CR	CNT/LDH	1250	Electrostatic interaction, H-bonding and chemical bonding	[185]
MO	GO/LDH	312.5/99.4	External adsorption	[147]
Phenol	SBAC/LTH	216.76	Surface adsorption and π - π interactions	[217]

2.9 Reusability of LDH and its composites

From economics and the environment point of view, regeneration of spent LDH and LDH composites for repeated adsorption processes is of a major significance. Despite the fact that many studies have been investigated for the adsorption of hazardous adsorbates on LDH composites, few research studies have examined the regeneration of the used LDH composites and examine their propensity to remove toxic pollutants after a particular

number of cycles [230,259]. The type of desorption reagent and the contact time of the desorption are often key factors in the regeneration of the spent LDH composites [252,296]. For the regeneration of adsorbents, two commonly techniques are used; thermal and chemical treatments. For thermal treatment, the adsorbents are first washed with deionized water before calcination at various temperatures. For regeneration using chemical treatment, many reagents and chemicals are used. The spent material (adsorbent) is initially mixed. Then, the adsorbent is reused again after centrifuging the solution.

Yuan et al. [230] reported the regeneration of LDH composites on the removal of Cr (VI) by Na₂CO and NaOH mixture. After 6 cycles of regeneration (twelve hours desorption time), they reported the adsorption propensity had decreased by 7.4%. Furthermore, Ruan et al. used ethanol as a reagent for the regeneration of LDH composite on the removal of (MO) [147]. Table 2-17 summarizes the regeneration process and conditions (method/solvent used, duration, temperature, etc.) of the spent (i.e., used) LDH composites for several studies.

Table 0-17: Regeneration processes and conditions (method/solvent used, duration, temperature, etc.) of the spent (i.e., used) LDH composites

Adsorbate	Adsorbent	Regeneration					Ref.
		Reagent	Cycle	Remarks	Time (h)	T°C	
MG	Mg/(Al+Fe)/LDH	Ethanol + DI	3	> 90% after cycle 3	0.5	100	[25]
MO	MgAlNi(LTH)-BaFe	0.1M NaOH	4	Fresh: 98.12% 81.1% after cycle 4	3	80	[14]
Cr(VI)	CNF/LDH	1 M Na ₂ CO ₃	5	Fresh: 341.2mg/g 323.1mg/g after cycle 5	12	80	[297]

2-NP	ZnAl/LDH	Thermal process	5	qe increased along the cycles	-	600 °C	[122]
	MgFe/LDH		5				
U(VI)	rGO/LTH	0.1 M NaHCO ₃	3	Fresh: 252.81.2 mg/g decreased to 245.62 mg/g after cycle 3	-	-	[238]
Pb(II)	Tartrate/LDH	0.1M NH ₄ ⁺	2	Fresh: 96.79% decreased to 82.28% after cycle 2	-	-	[259]
Cr(VI)	C G/LDH	0.1 M (NaOH+ Na ₂ CO ₃)	6	Exhibited 87.65 % after 6 cycles (decreased 7.4% compared to original)	12	500 °C	[230]
Cr(VI)	Vermiculite/LDH	0.01 M Na ₂ CO ₃	10	Exhibited 80 % after 10 cycles (decreased 10 % compared to original)	-	-	[298]
Cr(VI)	Polyacrylonitrile/LDH	0.01M NaOH	10	Fresh: 95 % decreased to 90 % after cycle 10	24	-	[299]
MO	GO-ZVN/LDH	0.01M Co(NO ₃) ₂ +10mg Oxone	5	Exhibited 73 % after 5 cycles (decreased 26 % compared to original)	-	-	[187]
MO	RGO-NiCr CO ₃ /LDH	Ethanol	3	(S1): Decreased from 99.4% to 83%. (S2): extremely low from 1-3 cycles. (S3): Decreased from 97.5% to 85%. (S4): Decreased from 86 % to 70 % after third cycle	-	-	[147]
	NiCr -DBS /LDH						
	NiCr Laurate /LDH						
	NiCr CO ₃ /LDH						

CHAPTER 3

Novel Functionalized Graphene Oxide/Ternary Layered

Double Hydroxide for Acid Red 1 and Bisphenol A

Adsorption from Aqueous Media

This study reports on LTH intercalated with functionalized graphene oxide (PEI@GO) synthesized via co-precipitation method. The prepared PEI@GO supported LTH was employed as a nanomaterial for the adsorption of Acid Red 1 (AR1) and Bisphenol A (BPA) from aqueous solution. Furthermore, the effect of pH of the synthetic wastewater samples, initial concentration, contact period, and temperature were investigated. Remarkable improvements in the removal of AR1 and BPA were noticed using PEI@GO/LTH compared to the parent materials. PEI@GO/LTH exhibited maximum sorption capacities of 155.51, and 352.03 mg/g for AR1 and BPA, respectively. The isotherms data were best fitted by Redlich-Peterson model for the two adsorbates, indicating the monolayer adsorption process. The Avrami model nicely fitted the AR1 and BPA kinetics data with R^2 (0.995 and 0.9952), respectively, where the electrostatic attraction and π - π interactions are the most dominant adsorption mechanisms for AR1 and BPA, respectively. Adsorption thermodynamic analysis demonstrated that the AR1 and BPA adsorption into PEI@GO/LTH is an exothermic and physical process. Therefore, this

work ensures the effectiveness and the superiority of the synthesized PEI@GO/LTH nanocomposite for the uptake of toxic organic pollutants from aqueous media.

3.1 Introduction

Since the industrial revolution, there has been an exponential growth in industrial and anthropogenic activities, resulting in the daily discharge of significant volumes of water contaminated with several organic and inorganic pollutants into water bodies. Many of the pollutants in the discharged wastewaters from several industries (e.g., textile, paint, food, printing, pulp and paper, cosmetics, fabric, oil refining, and rubber [1,3,34,282,300]) are hazardous to human and aquatic creatures, potentially carcinogenic, nonbiodegradable, thermally-stable [301,302], taint of groundwater and surface water [41,43,44], can prevent sunlight from penetrating water bodies, and endanger the ecosystem balance. As a result, the discharge of untreated wastewaters can seriously harm both human health and the environment. To comply with the relevant environmental regulations and to protect fauna and flora, it is therefore of the utmost importance to eliminate or at least significantly reduce (to acceptable discharge levels) the concentrations of organic and inorganic pollutants prior to water discharge or reuse. Accordingly, the development of effective wastewater treatment approaches is of a pressing need.

There are several techniques that have been applied for remediating wastewaters such as coagulation [93], biological treatment [94], ion exchange [95], filtration, distillation [303,304], and adsorption [96,305,306]. Among these processes, adsorption is one of the most effective and promising methods due to its low cost, simplicity, and effectiveness in

removing contaminants to a very low concentration [99,100]. However, the efficacy of this process requires the development of effective adsorbents.

One class of the widely utilized adsorbents is layered double hydroxides (LDHs). LDHs are two-dimensional ionic materials having hydrotalcite-like structure. The proposed chemical formula of LDHs is $[M_{(1-x)}^{2+} M_{(x)}^{3+}(\text{OH})_2]^{x+} (\text{A}^{n-})_{x/n} m\text{H}_2\text{O}$ where M^{2+} and M^{3+} represent divalent (e.g., Mg^{2+} , Mn^{2+} , Cu^{2+} , Co^{2+} , Ca^{2+} , Zn^{2+} , Ni^{2+}) and trivalent (e.g., Fe^{3+} , Al^{3+} , Co^{3+} , Eu^{3+} , Ga^{3+}) cations, respectively, and (A^{n-}) represents the interlayer anions [159]. The molar fraction of the trivalent cations is represented by x , which is typically in the range of 0.2–0.33. The excellent properties of LDHs qualify them to be utilized in many applications [161], including as adsorbents [160]. The versatile features of LDHs including their low cost, porosity, the excellent ion exchange ability, and the high surface area make them good candidates for the adsorption of various water pollutants. For instance, Tong et al. [175] reported 93.1% removal of acid red G (ARG) using MgAl-LDH. Moreover, Chen et al. [176] reported 95.6 % removal of direct red 23 (DR23) using CoFe-LDH. Despite the promising results reported in some studies, the LDH performance is not always satisfactory. For example, Boubakri et al. [178] studied the adsorption of acid brown 14 (AB14) on MgFe-LDH and reported an adsorption capacity of 41.7 mg/g. Furthermore, He et al. [213] reported 48.8 % removal of phenol (corresponding to an adsorption capacity of 42.9 mg/g) using MgAl-LDH.

Another class of adsorbents that has attracted great research attention in the past couple of decades is graphene-based materials. For instance, Linyan et al. [307] studied the adsorption of p-nitrophenol, o-nitrophenol, m-nitrophenol, and 1-naphtol on graphene oxide (GO) and reported an adsorption capacity of 1020.8, 947.3, 1049.6, and 1036.7 mg/g.

Despite the satisfactory performance of GO in some studies, GO is not always satisfactory. For example, Robati et al. [308] studied the adsorption of methyl orange (MO) on GO and reported an adsorption capacity of 16.8 mg/g respectively. Furthermore, Li et al. [309] and Mukherjee et al. [310] reported 63.1 % and 74 % removal of phenol using GO.

Recently composites of LDHs with carbon materials such as graphene opened a new window for research, aiming for fast and high removal of pollutants. However, only a couple of studies have reported the removal of water pollutants using graphene/LDH composite. For instance, Dhar et al. [129] studied the adsorption of Methylene blue (MB) on GO/MgAl-LDH and reported an adsorption capacity of 271.8 mg/g. In another study, Ruan et al. [147] utilized the reduced graphene oxide/Ni-Cr-LDH composite for Methyl orange (an azo dye) removal and reported 312.3 mg/g uptake capacity. The aforementioned studies demonstrated that LDHs hybridized with graphene materials are potentially effective materials to remove various contaminants from aqueous media due to their high sorption performance, high surface area, and excellent ion exchange ability.

Another approach to improve the adsorption performance of LDH, GO, and their composites might be achieved via the functionalization of GO with amines and/or the inclusion of a third metal in the LDH framework. Indeed, Al-Qadri et al. [311] have demonstrated a significant improvement in the adsorption performance of GO upon modifying it with amines. However, the adsorption performance of amine-modified GO/LTH composites is still not reported in the published literature to the best of our knowledge. More interestingly, the introduction of a third metal to the LDH framework and its intercalation with amine-functionalized GO is yet to be tackled for any application. Therefore, the main aim of this work is to synthesize PEI@GO/LTH nanocomposite and

to utilize it for the adsorptive removal of two toxic water pollutants (BPA and AR1) from synthetic wastewater samples. The performance of this novel nanocomposite has been benchmarked to those of its parental materials (i.e., GO, PEI@GO, LTH, and GO/LTH). The crystallinity, functional groups, and morphology of the synthesized PEI@GO/LTH nanocomposite were studied using different characterization techniques. Furthermore, the effects of key operational factors (i.e., pH of the synthetic wastewater samples, initial pollutant concentration, adsorption time, and temperature) on the adsorption of AR1 and BPA have been investigated. Moreover, zeta potential measurements have been carried out to shed some light on the potential adsorption mechanism(s).

3.2 Materials and Methods

3.2.1 Materials

Polyethyleneimine (PEI), acid red 1 (AR1), bisphenol A (BPA), magnesium nitrate hexahydrate [$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], ferric nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], aluminum nitrate nonahydrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], graphite powder, potassium permanganate, sulfuric acid (98%), phosphoric acid (85%), hydrogen peroxide (30%), hydrochloric acid (37%), sodium hydroxide, sodium carbonate, and potassium hydroxide were purchased from Sigma Aldrich and used without further purification.

3.2.2 GO Synthesis

The typical GO synthesis procedure is briefly as follows. Sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4), with 9:1 volumetric ratio, were mixed in a 1000 mL beaker and the solution was kept and stirred at room temperature in an ice bath (to keep the temperature

under control) for a couple of minutes. Then, 6 g graphite powder was added to the above solution and kept stirring for ~ 15 min. After that, 36 g potassium permanganate (KMnO_4) were added slowly and in small quantities in order to prevent sudden increases in the temperature and potentially outbursts. The mixture was then kept and stirred for 12 h at 50°C . To quench the reaction, 400 g of ice was added to the suspended mixture followed by couple of minutes stirring. Then $\sim 3\text{-}4$ ml of hydrogen peroxide (H_2O_2) were added to the above mixture to ensure the complete halt of the reaction and turned the mixture to yellow brownish color and the mixture was kept stirring at room temperature for 12 h. The formed GO was then purified and recovered by washing and centrifuging it 4 times with distilled water and 3 times with 10% HCl [312] to ensure the removal of impurities. After that, it was kept drying in the oven at 50°C and finally the powder GO was obtained after grinding.

3.2.3 Functionalization of GO with PEI (PEI@GO)

PEI@GO was prepared by first dispersing 1 g of GO in 1000 mL distilled water, followed by 1 h sonication at 50% amplitude with 30/3 sec pulse on/off. Then, 100 mg PEI was added to the GO suspension and the mixture was stirred vigorously at room temperature for 2 h. After that, 2 g KOH was added to the above mixture, and it was stirred for 10 min at room temperature. Following this step, the suspension was stirred and refluxed at 90°C for 24 h. With time, the color of the dispersion turned from yellow brown to black, suggesting the successful functionalization of GO with PEI. To purify and recover the formed PEI@GO, the suspension was centrifuged at 8000 rpm for 15 min and washed at least 7 times with distilled water. Finally, the obtained PEI@GO was dried in oven at 50°C and ground to obtain fine PEI@GO powder.

3.2.4 Synthesis of LTH, GO/LTH and PEI@GO/LTH Nanocomposites

The co-precipitation method was used to synthesize LTH. Two solutions referred to as solution A, which contained 27.9 mM Na_2CO_3 and 334.8 mM NaOH , and solution B containing 111.6 mM $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 11.16 mM $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 44.64 mM $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were prepared. Then, solutions A and B were drop-wise added simultaneous to 100 mL distilled water, previously adjusted to pH 10 using solution A. During the addition of solutions A and B, the mixture was continuously stirred at room temperature; the pH of the mixture was kept at 10-12 by controlling the addition rate of solutions A and B. After that, the obtained suspension was further stirred for 17 h at room temperature. To remove excess salts, the obtained suspension was centrifuged at 8000 rpm and washed with distilled water at least seven times. Finally, the formed LTH was dried in oven at 80 °C and then, it was ground to obtain fine LTH powder.

To prepare GO/LTH nanocomposite, a certain amount of GO (the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ /GO mass ratio was fixed at 6) was added to 150 mL distilled water and stirred for 30 min at room temperature to disperse GO. Then, the pH of the GO suspension was adjusted to be within [10 and 11] using solution A while keeping the solution under stirring. Then, GO suspension was sonicated at 50% amplitude for 1 h. Finally, to obtain GO/LTH composite, a similar procedure as in the case of the pristine LTH preparation described above was utilized.

For the preparation of PEI@GO/LTH, same procedure as in the case of GO/LTH synthesis was performed with the replacement of GO with PEI@GO.

3.2.5 Adsorption Experiments

Several adsorption tests were carried out in order to evaluate the adsorption performance of PEI@GO/LTH under various conditions. Initially, the performance of PEI@GO/LTH was contrasted to those of GO, PEI@GO, LTH and GO/LTH using AR1, and BPA as dye and phenolic pollutant models. The conditions of these adsorbent screening tests were: pollutant (AR1 or BPA) concentration = 100 mg/L, adsorbent dose = 50 mg/L, initial pH = 6, temperature = 25 °C, contact time = 20 h, and shaking speed = 250 rpm. After every experiment, about 5 mL of each sample was filtered and subjected to analysis using UV-Vis spectroscopy in order to measure the residual pollutant concentration. These screening tests revealed the superiority of the PEI@GO/LTH nanocomposite and, thus, it was used for further studies (i.e., effects of pollutant concentration, contact time, initial pH of the synthetic wastewater samples, and temperature).

The variation of the initial concentrations of AR1 (in the range 0-500 mg/L) and BPA (in the range 0-100 mg/L), separately, while keeping all other variables fixed enabled the establishment of the experimental adsorption isotherms, which were regressed using four adsorption isotherm models listed in Table 2-13. Similarly, varying the contact time between PEI@GO/LTH nanocomposite and the two adsorbates enabled the prediction of the adsorption kinetics parameters using the models displayed in Table 2-14. In these isotherm and kinetics tests, the initial pH of the aqueous solutions and process temperature were fixed at 6 and 25 °C, respectively. To reveal the pH and temperature effects on the adsorptive removal of AR1 and BPA, pH was varied from 2 to 12 at a fixed temperature of 25 °C while the temperature was varied from 10 to 55 °C, during which the initial pH was kept at 6.

3.2.6 Zeta Potential Measurements

Zeta potential measurements were conducted in order to evaluate the adsorption mechanisms of AR1 and BPA on the PEI@GO/LTH nanocomposite and other utilized adsorbents (i.e., GO, PEI@GO, LTH, and GO/LTH). In these measurements, aqueous solutions containing 1 mM NaCl as the background electrolyte were first purged with N₂ for 3 min in order to remove dissolved gases (e.g., CO₂ and O₂). Then, the initial pH of these aqueous solutions was adjusted to the desired value (2, 4, 5, 6, 8, 9, 10, and 12) using either 100 mM HCl or NaOH. The prepared pH solutions were purged with N₂ again after adding the PEI@GO/LTH at a dosage of 50 mg/L to each of the above samples. Following the PEI@GO/LTH addition and purging, the samples were placed on a shaker and they were shaken at 250 rpm for 24 h. Then, each sample was sonicated at 25% amplitude for 7 min immediately before subjecting them to zeta potential measurements. The above procedure was repeated for all other adsorbents examined in this study.

3.3 Results and Discussion

3.3.1 PEI@GO/LTH Nanocomposite Characterization

a. FT-IR Analysis

The FTIR spectra of GO, PEI@GO, LTH, GO/LTH, and PEI@GO/LTH, ranging between 500 and 4000 cm⁻¹ are displayed in Figure 3-1. In GO sample, an adsorption band centered at 3392 cm⁻¹ can be attributed to the stretching mode of OH group. The peak observed at 1714 cm⁻¹ belongs to the stretching modes of C=O while the other two bands centered at 1649, and 1193 cm⁻¹ are due to C=C, and C–OH stretching modes, respectively [313]. After adding PEI, sharp decrease in transmittance intensities of OH, C=O, and C=C,

indicating intercalation of PEI on the GO layers. new peaks appeared at 1570 and 1115 cm^{-1} which corresponded to N-H and CONH bending vibrations indicating that GO was functionalized by PEI. For the LTH sample, the absorption band centered at 3392 cm^{-1} can be ascribed to the stretching mode of OH group while the sharp band observed at 1356 cm^{-1} is either due to interaction of NO_3 anions within the layer or the translational mode of both Mg-OH and Fe-OH [314,315]. Similar to the XRD results, the FTIR bands of the GO/LTH, and PEI@GO/LTH are similar to the LTH, except the appearance of the peak at 1570 cm^{-1} in PEI@GO/LTH which attributed to the amino group resulted by PEI addition.

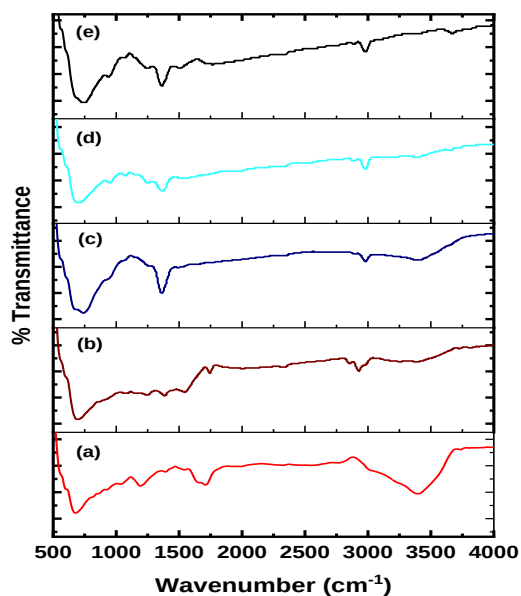


Figure 3-1: FTIR Spectra of (a) GO, (b) PEI@GO, (c) LTH, (d) GO/LTH, and (e) PEI@GO/ LTH.

b. SEM and EDX Analysis

The morphologies of GO, PEI@GO, LTH, GO/LTH, and PEI@GO/LTH, were characterized via SEM technique. As can be seen, the morphology of GO (Figure 3-2a) shows a dense flake-like morphology with different sizes. The numbers of layers PEI@GO sample displayed in Figure 3-2b are less than that in GO and the surface of the sample becoming an unevenly sized flakes stacked one to one with different sizes and shapes at micron scale. The SEM of the LTH (Figure 3-2c) shows that the surface of the sample consists of nanosheets assembled by numerous tightly of uniformly-sized nanoparticles with of 20–40 nm diameters. Interestingly, upon intercalating GO with LTH sample, the surface morphology sequentially turned into tiny nanosheets and the size distribution of the sheets as well as the thickness are almost uniform as shown in Figure 3-2d, while Figure 3-2e shows the morphology of PEI@GO/LTH sample where the nanoparticles of LTH anchoring the PEI@GO sheets. Such high surface area can provide the active sites for the uptake of toxic organic pollutants from aqueous media.

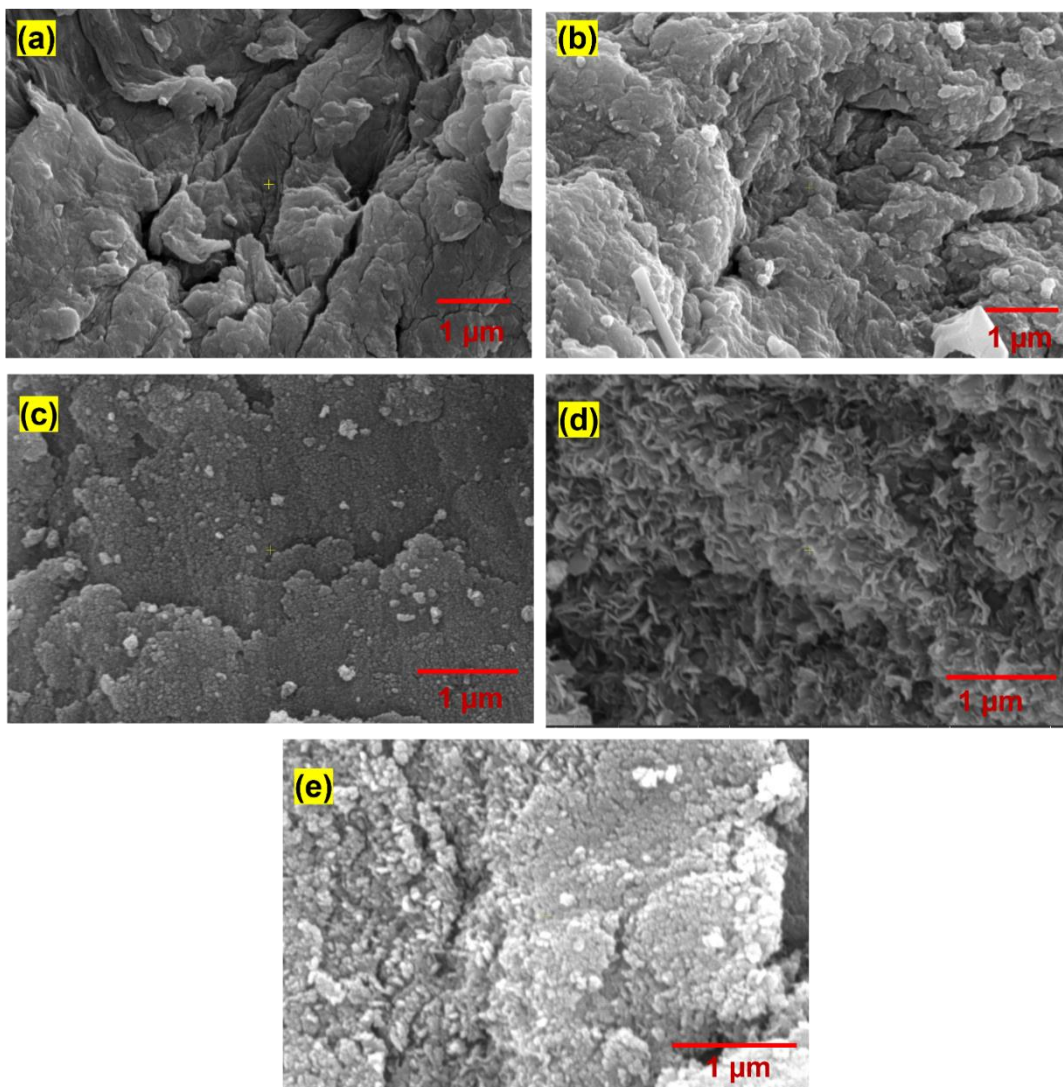


Figure 3-2: SEM images of (a) GO, (b) PEI@GO, (c) LTH, (d) GO/LTH, and (e) PEI@GO/LTH.

Figure 3-3 shows the EDX analysis for PEI@GO/LTH. EDX mapping of PEI@GO/LTH illustrated extensive dispersion of Mg, Al, Fe, O, C, and N elements confirming that PEI and GO were uniformly distributed on the surface of LTH. Table 3-1 displays the atomic percentages for the elements in GO, PEI@GO, LTH, GO/LTH, and PEI@GO/LTH.

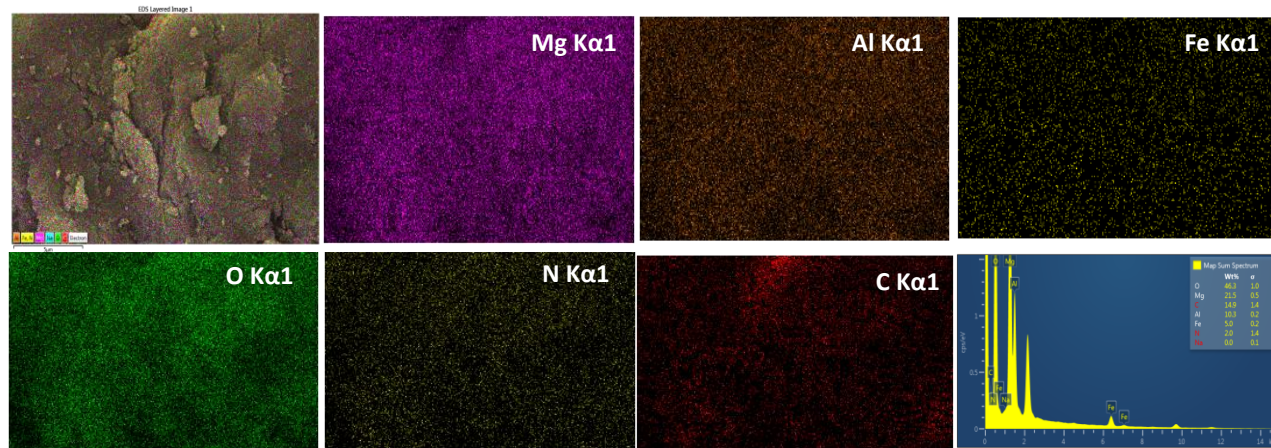


Figure 3-3: EDX mapping and EDX spectrum of PEI@GO/MgFeAl-LTH.

Table 3-1: Elemental analysis of GO, PEI@GO, LTH, GO/LTH, and PEI@GO/LTH.

Adsorbent/Atomic %	C	O	N	Mg	Fe	Al	C/O	C/N	Al/Fe	Mg/(Fe+Al)
GO	64.3	35.7	-	-	-	-	1.8	-	-	-
PEI@GO	66.2	19.9	13.9	-	-	-	3.3	4.8	-	-
LTH	22.9	52.2	5.3	13.0	1.4	5.2	0.4	4.32	3.71	1.9
GO/LTH	39.2	43.4	2.8	9.9	0.8	3.9	0.9	14.0	4.9	2.1
PEI@GO/LTH	22.0	51.4	2.5	15.7	1.6	6.8	0.4	8.8	4.3	1.9

c. XRD Analysis

Figure 3-4 displays the diffraction patterns for GO, PEI@GO, LTH, GO/LTH, and PEI@GO/LTH. As can be observed, the XRD pattern of the GO sample shows two main peaks centered at 9.65° , and 42.60° , corresponding to the reflections of (002) and (101) planes, respectively. The interlayer distance “ d ” of the GO calculated using Bragg’s Law was found to be at around 0.901 nm, which is in a good agreement with that reported in the

literature [316,317]. After adding PEI to the GO suspension, the two peaks of GO disappeared and a wide peak at around $2\theta = 23.5^\circ$ was observed, indicating the intercalating of the PEI chains at the edge of the GO sheet [318]. In the XRD diffraction pattern of LTH, the peaks observed at $2\theta = 11.76^\circ, 23.48^\circ, 34.69^\circ, 39.24^\circ, 46.27^\circ, 60.67^\circ$, and 61.91° corresponding to the crystal planes of (003), (006), (012), (015), (110) and (113) which are in agreement with the characteristic peaks of hexagonal structure of LTH (JCPDS 70-2151) [319]. The crystal size “D”, and the lattice parameters “a” and “c” calculated using the below equations found to be 9 nm, 30 Å, and 23 Å, respectively [319].

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

where h , k and l are the Miller indexes, θ is the diffraction angle, and β is the full width at half maximum. Furthermore, except that the grain size of the GO/LTH decreased to 5 nm, the other structural properties of the PEI@GO/LTH and GO/LTH samples are similar to the LTH sample.

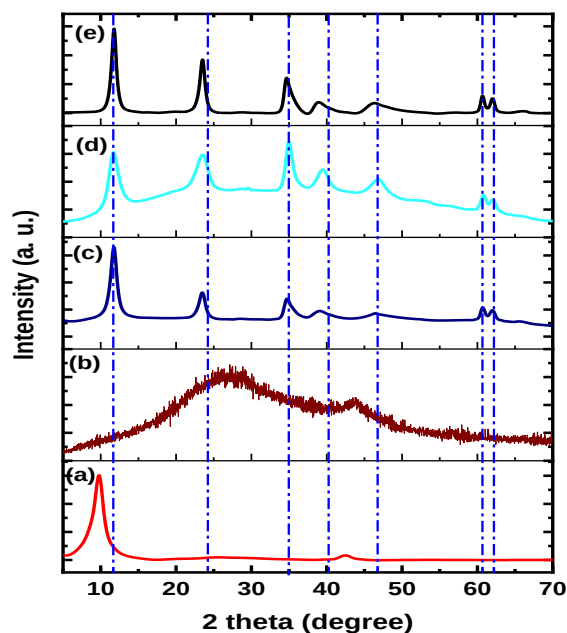


Figure 3-4: XRD patterns for (a) GO, (b) PEI@GO, (c) LTH, (d) GO/LTH, and (e) PEI@GO/LTH.

3.3.2 Adsorbent Screening

In the past few decades, the application of LDHs for the adsorptive removal of various water pollutants has been extensively studied. For instance, Benselka-Hadj Abdelkader et al. [177] studied the adsorption of Acid orange 10 (AO10) on MgFe-LDH and reported an adsorption capacity of 50 mg/g. Moreover, Lafi et al. [174] studied the adsorption of Congo red (CR) on MgAl-LDH and reported an adsorption capacity of 65 mg/g. Despite the unsatisfactory performance of MgAl-LDH and MgFe-LDH reported in the above-mentioned studies, the inclusion of a third metal (e.g., Fe or Al) into the LDH framework (creating MgFeAl-LTH) has the potential to boost its performance. Thus, we synthesized MgFeAl-LTH and used it to adsorb AR1 and BPA from aqueous solutions. As displayed in Figure 3-5, the adsorption capacities of BPA and AR1 on LTH under the utilized

experimental conditions (see the caption of Figure 3-5) are, respectively, 153.6 and 151.2 mg/g, which are higher than those reported in the above-mentioned studies.

Another material that has been utilized in the past couple of decades as an adsorbent for the removal of water pollutants is GO and, thus, it was utilized in this study to adsorb AR1 and BPA. According to the results shown in Figure 3-5, the adsorption capacities of AR1 (26.0 mg/g) and BPA (36.5 mg/g) on GO are very low, which are in agreement with the findings reported by Robati et al. [320] and Wang et al. [321]. With the aim of creating more effective adsorbent, GO/LTH was synthesized and utilized for the adsorptive removal of BPA and AR1. As revealed in Figure 3-5, the GO/LTH significantly outperforms its parental materials for the adsorption of BPA. The BPA adsorption capacity on the GO/LTH nanocomposite reached 190.7 mg/g relative to 36.5 and 153.6 mg/g in the case of GO and LTH, respectively. For AR1 adsorption, the LTH adsorbent outperforms GO and GO/LTH nanocomposites. The AR1 adsorption on LTH reached 151.2 mg/g relative to 25.9 and 140.4 mg/g in the case of GO and GO/LTH.

According to the above results, the intercalation of LTH with GO produces an adsorbent that outperforms both GO and LTH in the adsorption of BPA. While the adsorption of AR1 on LTH has higher performance than both GO and GO/LTH. Another approach to improve the adsorption performance of GO is through its functionalization with amines as reported in a number of recent studies [311,322]. Thus, GO was covalently functionalized with PEI and the PEI-modified GO was used to remove AR1 and BPA from synthetic wastewater samples. Despite the several-fold improvement in the uptake capacities of AR1 (q_e increased from 26.0 to 133.9 mg/g) and BPA (q_e increased from 36.5 to 113.6 mg/g) upon the functionalization of GO with PEI, PEI@GO still underperforms both the GO/LTH

nanocomposite and the pristine LTH. Motivated by the performance of PEI@GO relative to the pristine GO, the PEI@GO/LTH nanocomposite was synthesized and applied to remove BPA and AR1 from synthetic wastewater samples. This composite displayed an astonishing BPA adsorption performance, where the BPA uptake capacity reached 352.0 mg/g. The AR1 uptake capacity also improved and reached 155.5 mg/g. Accordingly, PEI@GO/LTH is superior to other materials (GO, PEI@GO, LTH, and GO/LTH) as investigated in this work. Thus, it will be used to study the effects of operational parameters (i.e., pollutant concentration, contact time, pH, and temperature) in the subsequent sections. However, prior to conducting such investigations, the potential adsorption mechanism(s) of BPA and AR1 on all the synthesized adsorbents in this work has been studied as detailed in the following section.

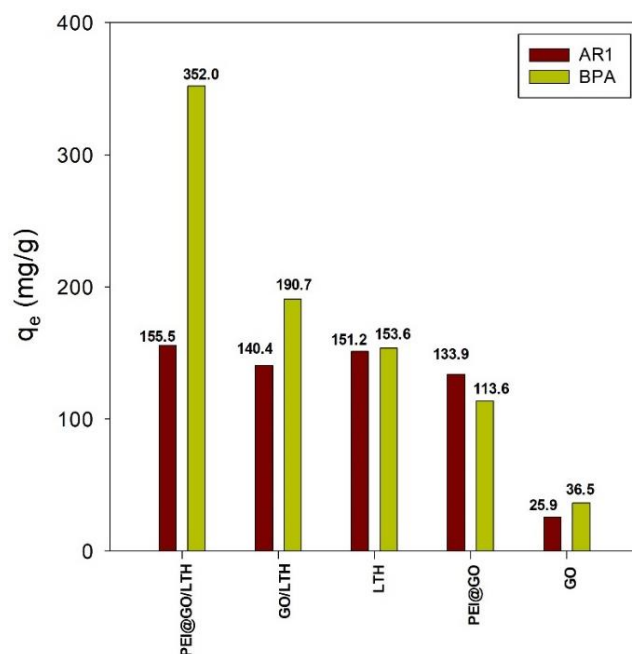


Figure 3-5 : Adsorbent screening of AR1 and BPA adsorption on PEI@GO/LTH, GO/LTH, LTH, PEI@GO, GO obtained at temperature (298 K), initial concentration (100 mg/L), dose (50 mg/L), pH (6), and contact time (20 h).

3.3.3 Potential Adsorption Mechanism(s)

According to the results presented in Figure 3-5, PEI@GO/LTH is the most effective adsorbent for the removal of AR1 and BPA from wastewater samples. To understand the superiority of this adsorbent relative to others, we conducted zeta potential measurements at different pH values and the results are shown in Figure 3-6, which reveals that the point of zero charge (pH_{PZC}) of PEI@GO/LTH, LTH, GO/LTH, PEI@GO, and GO are 10.6, 10.1, 2.5, 2.4, and 2.15, respectively. Accordingly, PEI@GO/LTH and LTH carry a net positive charge at pH 6 (at which the screening experiments were conducted) while the other 3 adsorbents carry a net negative charge. The pH_{PZC} of PEI@GO/LTH was the largest among others which might be the reason the adsorption performance of AR1 and BPA was higher than other adsorbents as shown in Figure 3-5. Furthermore, it implies that the surface charge of PEI@GO/LTH nanocomposite becomes positive as the solution $pH < pH_{PZC}$. However, the zeta potential for LTH is higher than PEI@GO/LTH at pH 6 as shown in Figure 3-6 and it was expected to have higher adsorption than PEI@GO/LTH. However, Figure 3-5 depicts opposite results which indicates that the electrostatic attraction is not the only adsorption mechanism for describing the superiority adsorption of anionic AR1 dye on PEI@GO/LTH. Therefore, other mechanisms such as hydrogen bonding, π - π interactions, and pore filling are playing the major role for the adsorption of AR1 on PEI@GO/LTH, thereby yielding high removal at pH 6. Similar findings of anionic dye adsorption by different LDH nanocomposites were investigated in these studies [171,203]. For BPA adsorption, since its pK_a is 9.6 as reported in [323,324], it is neutral at pH 6, indicating that the electrostatic interaction is not the dominant mechanism in the adsorption of BPA on PEI@GO/LTH. Thus, other adsorption mechanisms such as pore filling, π - π

interactions and hydrogen bonding are responsible for the adsorption of BPA on PEI@GO/LTH. Pioneer studies reported similar behaviors in the adsorption of BPA [325,326] and other aromatics [327,328].

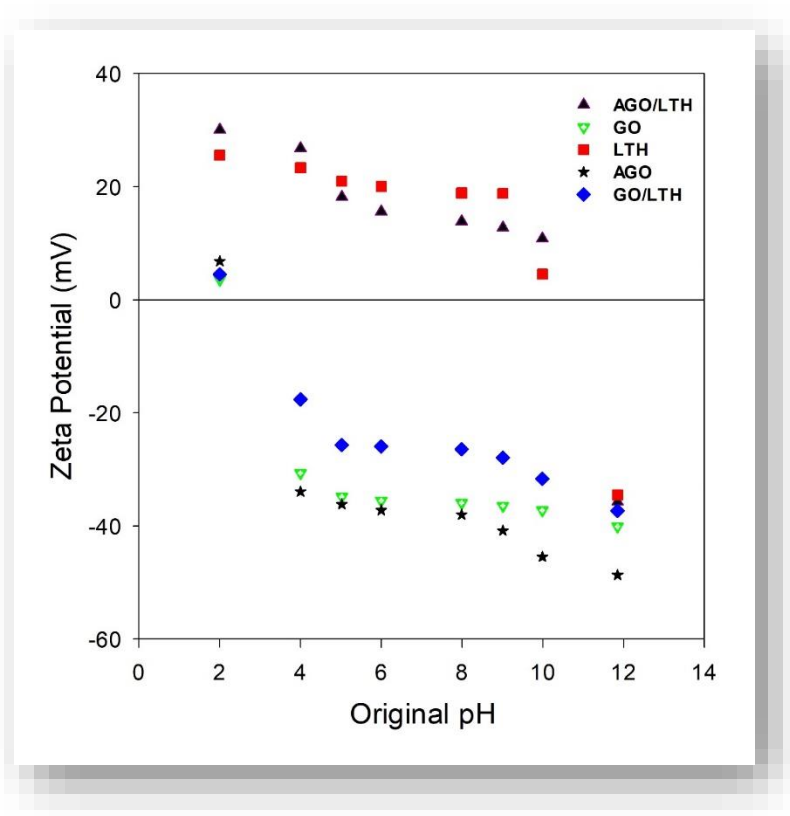


Figure 3-5: Zeta potential analysis for PEI@GO/LTH, PEI@GO, GO, LTH, GO/LTH at temperature (298 K), dose (50 mg/L), and pH from (2-12).

3.3.4 pH Effect

pH of the adsorption medium is one of the most crucial factors because the charges on adsorbents and adsorbates depend on the solution pH. Therefore, we investigated herein the effect of pH on the adsorption of AR1 and BPA on the most effective adsorbent (i.e., PEI@GO/LTH) and the results are displayed in Figure 3-7. As displayed in this figure, the adsorption of AR1 increased almost linearly with increasing the solution pH from 2 to 6

(155.5 mg/g). Afterward, the AR1 uptake capacity by PEI@GO/LTH sharply decreased, reaching the minimum (38.74 mg/g) at pH 12. According to the zeta potential results shown in Figure 3-6, PEI@GO/LTH carries a net positive charge at pH 6 which indicates a strong attraction with anionic AR1 dye.

Similar to AR1, BPA adsorption on PEI@GO/LTH peaked at pH 6 (352.03mg/g), followed by almost a linear sharp decline up to pH 12 at which a q_e value of 17mg/g was obtained. The BPA adsorption capacities at pH 2 (68.3mg/g) and pH 4 (71.8mg/g) were about 5-fold lower than that obtained at pH 6. This indicates that the optimum BPA (and also AR1) adsorption on PEI@GO/LTH is attained at pH 6. Similar trends were observed for BPA [311] and AR1 [329] adsorption on other materials. Additionally, the charge on PEI@GO/LTH was positive at pH 6 as presented in Figure 3-6, while the charge of BPA solution at pH 6 is neutral. Accordingly, the electrostatic potential was not the driven adsorption mechanism of BPA on PEI@GO/LTH at pH 6, thus another adsorption mechanism such as π - π interactions between the BPA and PEI@GO/LTH will describe the adsorption superiority of BPA on PEI@GO/LTH at pH 6 as illustrated in Figure 3-7.

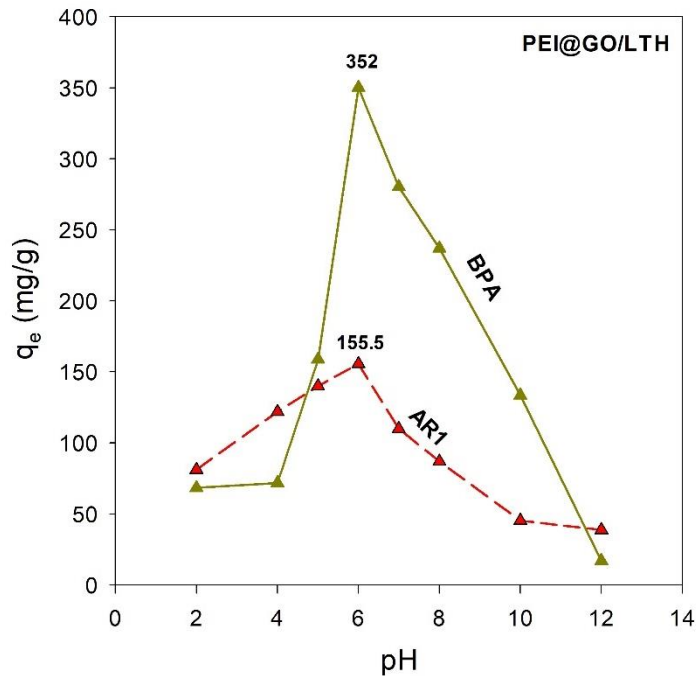


Figure 3-6: pH effect on the adsorption of AR1 & BPA at temperature 298 K, initial concentration 100 mg/L, dose 50 mg/L, and contact time 20 h for AR1 and 8 h for BPA.

3.3.5 Adsorption Isotherms

Adsorption isotherm is a crucial factor for quantizing the maximum adsorption capacity at equilibrium. In this work, experiments data were fitted using different adsorption isotherms as shown in Figure 3-8. The non-linear forms of these models are given in Table 2-13. Figure 3-8a depicts the adsorption isotherm of AR1 on PEI@GO/LTH while the calculated parameters obtained from the nonlinear regression of the experimental data are presented in Table 3-2. The regression curves and the extracted parameters reveal that the Langmuir and Redlich-Peterson models properly fitted the data with R^2 approaching unity (i.e., 0.9948 and 0.9952, respectively). The maximum Langmuir sorption capacity of AR1 on PEI@GO/LTH is 230.9 mg/g as presented in Table 3-2. Moreover, Temkin model fits the

experimental data of AR1 adsorption on PEI@GO/LTH with R^2 (0.9847) and assured the physisorption process as β (44.33 J/mol) value is less than (100 J/mol).

Similar to Figure 3-8a, Figure 3-8b reveals that these models also fitted the BPA adsorption data quite well, where the maximum Langmuir sorption capacity of BPA on PEI@GO/LTH is 585.22 mg/g as shown in Table 3-2, however Redlich-Peterson model accurately fitted the data among other models with R^2 approaching unity (0.994). Furthermore, G values (i.e., 0.967 and 1.78 for AR1 and BPA, respectively) of Redlich-Peterson model were close to 1 indicating that Redlich-Peterson model approaches Langmuir model [330]. Due to the lack of adsorption isotherm studies using the Redlich-Peterson model, Table 3-3 presented the comparison of the maximum adsorption capacities obtained from Langmuir model of AR1 (few studies) and BPA on PEI@GO/LTH with different adsorbents reported in the literature.

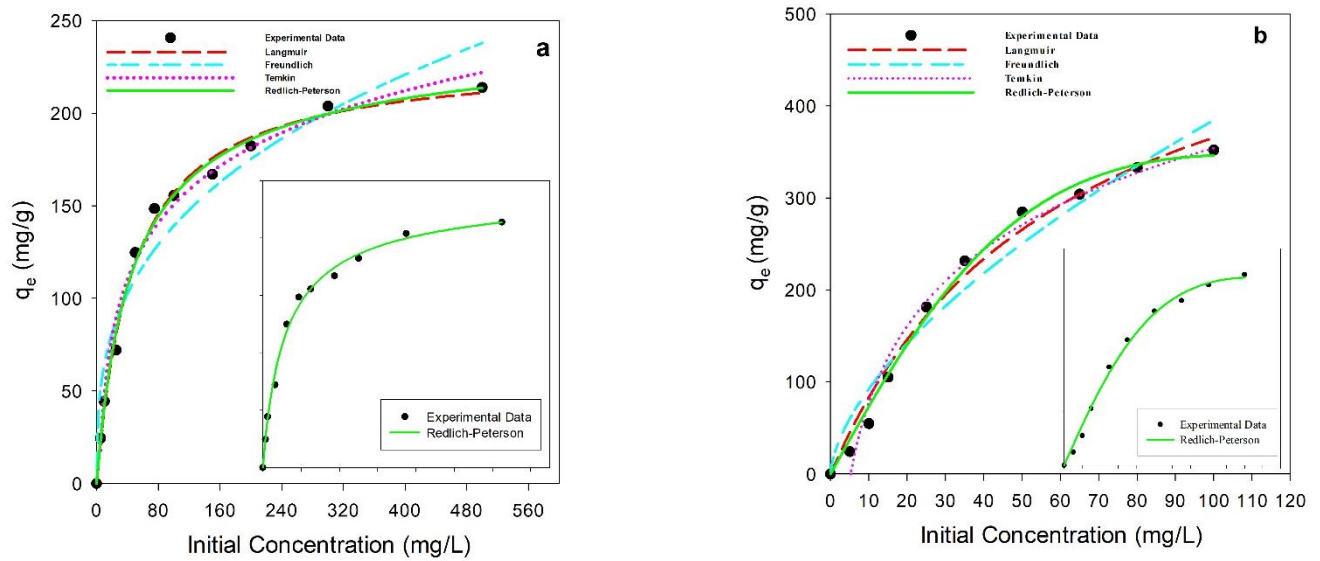


Figure 3-7: Adsorption isotherm of AR1 and BPA on PEI@GO/LTH. Figure (a) represents the adsorption isotherm of AR1 on PEI@GO/LTH. Figure (b) represents the adsorption isotherm of BPA on PEI@GO/LTH at temperature 298 K, dose 50 mg/L, and contact time 8 h.

Table 3-2: Predicted adsorption parameters of AR1 and BPA on PEI@GO/LTH.

Isotherm Model	Parameter	Adsorbate	Adsorbate
		AR1	BPA
Langmuir	$q_{\max}$ (mg/g)	230.9 ± 5.2	585.2 ± 58.7
	k_L (L/mg)	0.021 ± 0.026	0.017 ± 0.084
	R^2	0.9948	0.9856
Freundlich	k_F (mg/g) (L/g) ⁿ	29.9 ± 6.4	22.2 ± 6.6
	1/n	0.333 ± 0.040	0.619 ± 0.072
	R^2	0.9455	0.9591
Temkin	β (J/mol)	44.3 ± 1.9	120.0 ± 6.1
	A_T (L/g)	0.299 ± 0.044	0.191 ± 0.019
	R^2	0.9847	0.9822
Redlich Peterson	k_R (L/g)	5.3 ± 0.7	7.5 ± 0.6
	a_R (L/mg)	0.029 ± 0.011	0.0003 ± 0.001
	G	0.967 ± 0.044	1.780 ± 0.343
	R^2	0.9952	0.994

Table 3-3: Comparison for the maximum sorption capacity of AR1 and BPA obtained from Langmuir model on the synthesized PEI@GO/LTH in this work with the maximum adsorption capacities on different sorbents from the literature.

Adsorbent	Adsorbate $q_{\max}$ (mg/g)		k_L (L/mg)	R^2	Ref.
	AR1	BPA			
CFA	92.6		0.081	0.991	[329]
AS	32.3		0.0533	0.969	[331]
FS	6.6		0.039	0.977	
PEI@GO/LTH	230.9		0.021	0.995	This study
AC		91.9	0.640	0.996	[332]
MBC		342.5	0.023	0.972	[323]
BC		123.8	0.039	0.984	
GO-DEA		334.4	0.011	0.995	[311]
GO		17.3	0.173	0.931	[333]
RGO		80.8	0.287	0.983	
CNTs		46.2	0.116	0.958	[325]
Fe ₃ O ₄		5.08	0.017	0.998	
CPAB/B		27.9	0.011	0.993	[334]
EGIS/B		97.5	0.044	0.988	
CPAB/EGIS/B		119.9	0.046	0.998	
PEI@GO/LTH		585.2	0.017	0.9856	This study

3.3.6 Adsorption Kinetics

To explain the kinetics of AR1 and BPA adsorption on PEI@GO/LTH nanocomposite, the adsorbed amount of AR1 and BPA were measured at various time intervals and the results are illustrated in Figure 3-9. As depicted in this figure, AR1 and BPA adsorption kinetics on PEI@GO/LTH were initially extremely fast and gradually the adsorption rate became slower. To get insight into the dynamic involved in the adsorption and the kinetics of AR1 and BPA on PEI@GO/LTH, various adsorption kinetic models such as Pseudo first order, Pseudo second order, Avrami, and Elovich were applied as shown in Figure 3-9, while the calculated kinetic parameters are listed in Table 3-4. It is illustrated in Figure 3-10, Elovich model failed to fit the experimental data for both AR1 and BPA adsorption on PEI@GO/LTH.

Moreover, the Pseudo first order model reasonably tracked the data of AR1 adsorption on PEI@GO/LTH, while it poorly fitted the data of the adsorption of BPA on PEI@GO/LTH nanocomposite. Like Pseudo first order model, Pseudo second order model nicely fitted the data of BPA adsorption with R^2 approaching unity (0.996), while it fitted the AR1 adsorption data with ($R^2 = 0.9899$). Furthermore, Avrami model with correlation coefficient ($R^2 = 0.995$) fitted the data of AR1 and BPA adsorption on PEI@GO/LTH.

To conclude, the calculated AR1 equilibrium sorption capacities on PEI@GO/LTH for Pseudo first order, Pseudo second order, and Avrami models were, 150.24, 163.9, and 150.244 mg/g respectively, while the experimental AR1 equilibrium sorption capacity was 155.51 mg/g at 100 mg/L. According to these results, Pseudo first order and Avrami models

are the most accurate models which described the AR1 adsorption kinetics on PEI@GO/LTH with 3.39 % deviation from the calculated value.

For BPA adsorption, the predicted equilibrium sorption capacities using Pseudo first order, Pseudo second order, and Avrami models were, 338.97 mg/g, 369.36 mg/g, and 348.49 mg/g, respectively, while the experimental BPA adsorption capacity on PEI@GO/LTH at 100 mg/L was 352.03 mg/g indicating that the Avrami model is the best model for fitting the data of BPA adsorption kinetics on PEI@GO/LTH which was deviated from the calculated sorption capacity by 1.01%. Recent published study reported similar findings in the BPA adsorption [311]. The equilibrium adsorption capacities of AR1 and BPA at 100 mg/L on PEI@GO/LTH were compared with different sorbents reported in the literature using different kinetic models as presented in Table 3-5.

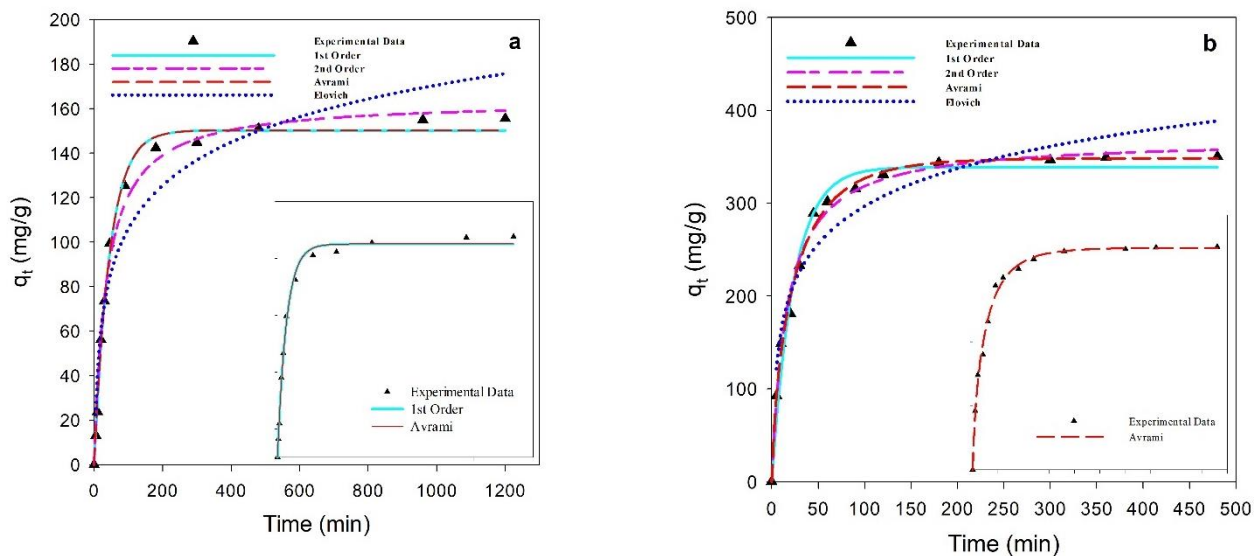


Figure 3-8: Kinetics of AR1 and BPA on PEI@GO/ LTH. Figure (a) the kinetic adsorption of AR1 on PEI@GO/LTH at pH 6 for 20 h, initial concentration = 100 mg/L, and dose 50 mg/L, and temperature 298 K, where Avrami and 1st order models are overlapped as shown in Figure (a) indicating that they are well fitted for the experimental results and they have similar R^2 . Figure (b) the kinetic adsorption of BPA on PEI@GO/LTH at pH 6 for 8 h, dose 50 mg/L, and temperature 298 K, where Avrami model is the accurate model for fitting the experimental data.

Table 3-4: Predicted Kinetic Parameters of AR1 and BPA on PEL@GO/LTH.

Kinetic Model	Parameter	Adsorbate	Adsorbate
		AR1	BPA
1st Order	q_e (mg/g)	150.2 ± 2.0	339 ± 6.5
	k_1 (1/min)	0.022 ± 0.001	0.043 ± 0.003
	R^2	0.9950	0.9822
2nd Order	q_e (mg/g)	163.9 ± 3.63	369.4 ± 5.8
	k_2 g/(mg .min)	0.0002	0.0002
	R^2	0.9899	0.996
Avrami	q_e (mg/g)	150.2 ± 2.2	348.5 ± 4.6
	k_{av} (1/min ⁿ)	0.022 ± 0.003	0.026 ± 0.003
	n	0.999 ± 0.072	0.738 ± 0.042
	R^2	0.9950	0.9950
Elovich	α (mg.min/g)	0.016 ± 0.008	0.027 ± 0.016
	β	0.036 ± 0.371	0.017 ± 0.172
	R^2	0.9229	0.9101

Table 3-5: Comparison for the equilibrium kinetic sorption capacity of AR1 and BPA on the prepared PEI@GO/LTH in this work with some previous studies using different adsorbents.

Adsorbent	Adsorbate q_e (mg/g)		Kinetic Model	k_1 (1/min)	k_2 g/mg /min	k_{av}/n $\text{min}^{-n}/-$	R^2	Ref.
	AR1	BPA						
CFA	91.7		2 nd order		0.003		0.998	[329]
HNTs-SA-PAMAM	120.5		2 nd order		0.043		0.999	[335]
CIV	32.9		1 st order	0.019			0.901	[336]
PEI@GO/LTH			Avrami			0.022/0.999	0.995	This study
	155.5		1 st order	0.022			0.995	
rGO-MNPs		78.7	2 nd order		0.095		0.999	[337]
BC		10.9	1 st order	0.011			0.992	[323]
MBC		10.2	2 nd order		0.016		0.988	
GO-DEA		187.9	Avrami			0.003/0.468	0.985	[311]
GO		9.5	2 nd order		0.020		0.999	[333]
RGO		11.8	2 nd order		0.070		0.999	
MMT		4.4	2 nd order		0.756		1	[338]
PEI@GO/LTH		339	Avrami			0.026/0.738	0.995	This study

3.3.7 Thermodynamic Adsorption of AR1 and BPA on PEI@GO/LTH

Adsorption thermodynamic study was conducted in this work to examine the nature of the adsorption of AR1 and BPA on PEI@GO/LTH nanocomposite. This study was performed at four different temperatures (i.e., 283.15 K, 298.15 K, 313.15 K, and 328.15 K) to investigate the impact of AR1 and BPA adsorption. Accordingly, the thermodynamic parameters including ΔS^o (standard entropy change), ΔH^o (standard enthalpy change), and ΔG^o (standard free change) were calculated using equations (3-1 – 3-3) [3].

$$K_d^o = \frac{C_{Ae}}{C_e} \quad (3-1)$$

$$\Delta G^o = -RT \ln K_d^o \quad (3-2)$$

$$\ln K_d^o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (3-3)$$

Where K_d^o is the equilibrium constant, C_{Ae} (mg/L) is the adsorbed concentration by the adsorbent at equilibrium, C_e (mg/L) is the remaining concentration at equilibrium, R (8.314 J/mol.K) is the universal gas constant, and T (K) is the absolute temperature. Plots of $\ln K_d^o$ against $1/T$ for the adsorption of AR1 and BPA on PEI@GO/LTH to obtain ΔH^o and ΔS^o from the slope and y intercept, respectively, are shown in Figure 3-10, and summarized in Table 3-6.

As shown in Table 3-6, the negative values of the standard entropy change (ΔS^o) of the adsorption of AR1 and BPA on PEI@GO/LTH indicate the decrease of the randomness during the process of adsorption. Furthermore, the negative values of the standard enthalpy change (ΔH^o) imply an exothermic and physical adsorption process of AR1 and BPA into PEI@GO/LTH. The positive values of the standard free energy ΔG^o calculated using

equation (3-2), show that the adsorption is more preferable as the temperature decreases [334,339]. Therefore, the results indicate that the adsorption of BPA is more favorable than AR1 adsorption by PEI@GO/LTH as ensured by the adsorption capacity (q_e) listed in Table 3-6.

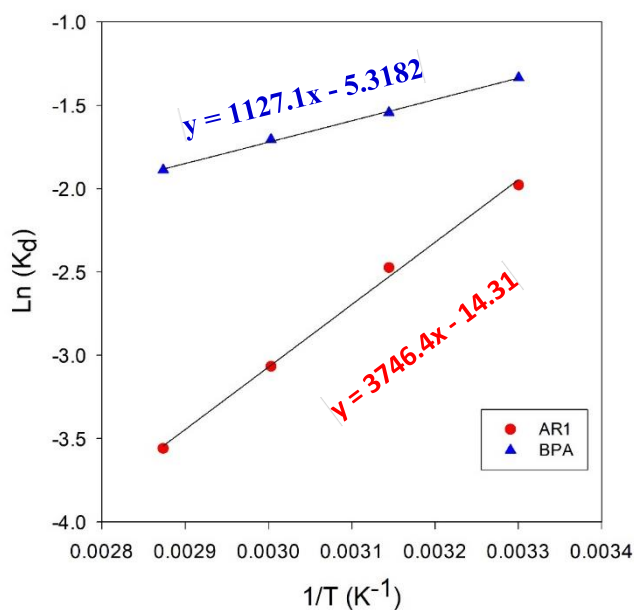


Figure 3-9: Plot of the adsorption equilibrium constant against the invers of the absolute temperature of the adsorption of AR1 and BPA on PEI@GO/LTH at pH 6, initial concentration 100 mg.L⁻¹, dose 50 mg.L⁻¹, and time 20 h for AR1 and 8 h for BPA.

Table 3-6: Thermodynamic parameters of the adsorption of AR1 and BPA on PEI@GO/LTH.

Pollutant	T(K)	q_e (mg/g)	ΔS^o (J/mol.K)	ΔH^o (kJ/mol)	ΔG^o (kJ/mol)
AR1	283.15	243.08	-118.973	-31.148	2.540
	298.15	155.51			4.324
	313.15	89.05			6.109
	328.15	55.35			7.894
BPA	283.15	416.78	-44.216	-9.371	3.149
	298.15	352.03			3.812
	313.15	307.96			4.475
	328.15	262.94			5.139

CHAPTER 4

Adsorptive Potential of GO/BENT/LTH for the Removal of Methyl Orange and 2 Nitrophenol from Synthetic Water

Samples

In this study, graphene oxide (GO), bentonite (BENT), and layered triple hydroxide (LTH) nanomaterials were intercalated with each other to create a novel GO/BENT/LTH nanocomposite by the co-precipitation method. This tertiary nanomaterial was utilized to remove Methyl Orange (MO) and 2-Nitrophenol (2NP) pollutants from synthetic water samples, and it exhibited astonishing performance in the adsorption of MO and 2NP. Moreover, the impacts of several key parameters including contact time, MO and 2NP initial concentration, pH, thermodynamics have been studied for the adsorption performance of MO and 2NP on GO/BENT/LTH. The equilibrium results were fitted to four isotherm models (i.e., Langmuir, Freundlich, Temkin, and Redlich-Peterson), where Langmuir and Redlich-Peterson models accurately fitted the data for the adsorption of MO and 2NP. Furthermore, the kinetic results exhibit that, the adsorption of MO and 2NP on GO/BENT/LTH was very well described by Avrami model with sorption capacity of 705.4 and 545 mg/g, respectively. Hydrogen bonding, π - π dispersions, and pore filling were potentially the driven mechanisms of the MO and 2NP sorption. Moreover, the adsorption thermodynamic studies reveal that as the temperature increases, the adsorption becomes

not favorable and the adsorption nature is exothermic. The obtained results verify that GO/BENT/LTH could be used as a promising adsorbent to remove or mitigate dyes and phenols from wastewater.

4.1 Introduction

Shortages in freshwater supply are experienced by several regions in the world due to the growth in population and industrial activities [340]. Pollution of freshwater resources due to the discharge of harmful materials to the environment is another key factor in exacerbating the freshwater shortage problem, in addition to the impact of such pollution on public health and the ecosystem [1,3,34,282,300]. Furthermore, the majority of domestic and industrial wastewater is immediately released into water streams either without any kind of treatment or merely after primary treatment [341]. Thus, there are number of environmental issues that can arise from the discharge of untreated wastewater into water bodies, including the consumption of the dissolved oxygen for the satisfaction of biochemical oxygen demand (BOD) in wastewater and hence, minimize the dissolved oxygen needed by aquatic creatures in the water stream. Moreover, it contains several harmful substances and dangerous microbes that can dwell in the human intestinal system and cause sickness, endangering human health [340], large amount of odorous fumes may be produced as a result of the decomposition of the chemical compounds in wastewater [342], and other consequences which are harmful to human health and ecosystem [5,14] such as causing cancer to human cells [301,302], and blocking sunlight from penetrating water samples.

Due to the intricacy of their aromatic structures, high stability, and consequently weak biodegradability, organic dyes are among the contaminants found in wastewater and can

have a variety of negative impacts on the environment and human health even at low concentrations [3,5–15]. The yearly production of organic dyes is about 0.07×10^7 tons, and 0.1×10^3 tons [12,15–17] of synthetic dyes are released into the environment each year as effluent [18,19]. In addition, the usual sources of organic dyes are oil refining, pharmaceuticals, textile, and food industries [1,3,6,9,11,12,14,16,24–34]. The existence of dyes in water streams at higher concentration than the allowable limits causes severe impacts to human health and aquatic life (i.e., carcinogenicity, mutagenesis, changing water color, etc.) [35–38].

Similar to dyes, phenols consider to be one of the most dangerous organic contaminants detected in various local wastewater [40]. Although, the concentration of the released phenolic compounds in wastewater into the environment might approach 10^3 (mg/L) [41], the production of these organics continues to rise with time, which threaten the bio-system balance, and human health [47–51]. As a result, the concentration of the released phenols into water bodies should be lower than 1 (mg/L) [45,46].

Prior to water discharge or reuse, it is crucial to get rid of or at least significantly lower the concentrations of organic contaminants (to allowable discharge levels) in order to comply with the applicable environmental rules and protect animals and flora. Therefore, it is utmost to promote efficacious wastewater treatment technologies. Numerous wastewater methods, including physical methods (i.e., coagulation [93], filtration [303,304], sedimentation, etc.), chemical methods (i.e., Chemical precipitation [343], adsorption [96,305,306], etc.), mechanical methods (i.e., filters, screening [343], etc.), and biological methods (i.e., disinfection, dichlorination [94], etc.) have been used to remediate

synthetic organic pollutants (i.e., dyes, phenols, etc.) encountered into water bodies. Despite the unsatisfactory of some of these methods, adsorption is considered to be one of the most conventional and attractive methods because it is simple, inexpensive, and efficacious in removing organic dyes and phenols to extremely low concentrations [99,100]. Accordingly, creating promising, and attractive sorbent is a need to improve the performance of the adsorption process.

In this work, we synthesized GO/BENT/LTH nanocomposite to remediate toxic pollutants (MO and 2NP) from aqueous solution. This innovative nanocomposite (GO/BENT/LTH) outperforms its pristine materials (i.e., LTH, GO, BENT, GO/LTH, LTH/BENT, and GO/BENT). Various characterization techniques were used to examine the crystallinity, morphology, and functional groups of the created GO/BENT/LTH nanocomposite. Moreover, the impacts of the operation parameters including time, initial concentration, pH, temperature have been investigated for the removal of MO and 2NP. Additionally, studies of the zeta potential have been conducted to explain the potential mechanism (s) of the adsorption.

4.2 Materials and Methods

4.2.1 Materials

The following items were purchased from Sigma Aldrich and used without further purification: 2 - Nitrophenol (2NP), Methyl orange (MO), magnesium nitrate hexahydrate, aluminum nitrate nonahydrate, ferric nitrate nonahydrate, bentonite, graphite powder, potassium permanganate, sulfuric acid (98%), hydrogen peroxide (30%), hydrochloric acid

(37%), sodium hydroxide, sodium carbonate, potassium hydroxide, and phosphoric acid (85%).

4.2.2 Synthesis of LTH, GO/LTH, LTH/BENT, and GO/BENT/LTH

To synthesize LTH, the co-precipitation technique was applied. Two solutions, solution A (27.9 mM Na_2CO_3 and 334.8 mM NaOH) and solution B (111.6 mM $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 11.16 mM $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 44.64 mM $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were prepared. After that, 100 mL of distilled water was adjusted with solution A to pH 10 and then solutions A and B were simultaneously drop-wise added. The pH of the mixture was maintained at 10–12 by regulating the pace at which solutions A and B were added while it was being constantly agitated at room temperature. The resultant suspension was further agitated for an additional 17 h at room temperature. The resulting suspension was centrifuged at 8000 rpm and rinsed at least seven times with distilled water to remove excess salts. The produced LTH was then ground into a fine powder after being dried in an oven at 80 °C.

To prepare GO/LTH nanocomposite, a predetermined amount of GO (the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ /GO mass ratio was fixed at 6) was added to 150 mL of distilled water and agitated for 30 minutes at room temperature to disperse the GO. The pH of the GO suspension was then adjusted to 10–11 using solution A. The GO suspension was then sonicated for one hour at 50% amplitude. Finally, the same steps as in the preparation of the pristine LTH described above were used to obtain the GO/LTH nanocomposite.

For the preparation of BENT/LTH, the same steps as for GO/LTH synthesis were followed but BENT was used in replace of GO.

For the synthesis of GO/BENT/LTH, GO/BENT nanocomposite was prepared by adding 1.05 g of bentonite to 200 mL of distilled water and agitated for 30 minutes at room temperature to well disperse the BENT. The pH of BENT suspension was then manipulated to be within 10–11 using solution A. The BENT suspension was then sonicated for one hour at 50% amplitude. The same amount of GO (1.05 g) was added to the BENT dispersion and sonicated for one hour at 50% amplitude. Finally, similar procedures as the synthesis of LTH were applied, while keeping the ratio of $(\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/(\text{BENT}+\text{GO}) = 3)$.

4.2.3 Adsorption Experiments

To assess the adsorption performance of GO/BENT/LTH under different conditions, several adsorption tests were conducted. First, using MO and 2NP as dye and phenolic pollutant models, the performance of GO/BENT/LTH was compared to that of GO, BENT, LTH, GO/LTH, GO/BENT, and BENT/LTH. These adsorbent screening tests were conducted under the following conditions: pollutant (MO or 2NP) initial concentration = 100 mg.L^{-1} , adsorbent dose = 50 mg.L^{-1} , initial pH = 6, temperature = 298.15 K, speed of shaking = 250 rpm; and contact time = 20 h. After each experiment, 5 mL of each sample was filtered and subjected to UV-Vis spectroscopic analysis to determine the concentration of residual pollutants. These screening tests showed that the GO/BENT/LTH nanocomposite was superior, hence it was used in further investigations (i.e., effects of the variation of adsorbate concentrations, variation of time, the synthetic wastewater initial pH, and thermodynamics).

The experimental adsorption isotherms were established by varying the initial concentrations of MO and 2NP (in the range of 0-500 mg.L⁻¹), while maintaining all other variables constant; these experimental adsorption isotherms were regressed using four adsorption isotherm models (Langmuir, Freundlich, Temkin, and Redlich-Peterson) as shown in Table 2-13.

While the adsorption kinetics characteristics may be predicted using the models (Pseudo first order, Pseudo second order, Elovich, and Avrami) as shown in (Table 2-14) by varying the contact duration between the GO/BENT/LTH nanocomposite and the two adsorbates. The process temperature and the initial pH of the aqueous solutions in the isotherms and kinetic studies were fixed at 298.16 K and 6, respectively.

To determine the effects of thermodynamics and pH on the adsorptive removal of MO and 2NP, the temperature was changed from 283.15 to 328.15 K, during which the pH_i was maintained at 6, while the pH was changed from (2–12) at a fixed temperature of 298.15 K.

4.2.4 Zeta Potential Measurements

In order to assess the 2NP and MO adsorption mechanisms on the GO/BENT/LTH nanocomposite and other used adsorbents (i.e., GO, BENT, LTH, GO/LTH, GO/BENT, and BENT/LTH), zeta potential measurements were carried out. For these measurements, dissolved gases such as CO₂ and O₂ were removed by first purging aqueous solutions containing 1 mM NaCl as the background electrolyte with N₂ for 3 min. The original pH of these aqueous solutions was then varied using either 100 mM HCl or NaOH to obtain

the desired value (2, 4, 5, 6, 8, 9, 10, and 12). After adding the GO/BENT/LTH at a dosage of 50 mg.L⁻¹ to each of the aforementioned samples, the prepared pH solutions were again purged with N₂. After the addition of GO/BENT/LTH, the samples were put on the shaker, and they were shaken at 250 rpm for one day. Each sample was then subjected for 7 min of sonication at 25% amplitude followed by zeta potential measurements. For all other adsorbents analyzed in this study, the aforementioned process was repeated.

4.3 Results and Discussion

4.3.1 GO/BENT/LTH Nanocomposite Characterization

a. FT-IR Analysis

Figure 4-1(A&B) displayed the FTIR spectra (500-4000 cm⁻¹) of the seven adsorbents synthesized in this study. The main peaks of graphene oxide (GO) as observed in Figure 4-1A appear in 3392, 1714, 1649, 1193, and 1076 cm⁻¹. The peaks at 3392 and 1714 cm⁻¹ can be ascribed to the hydroxyl group (OH) and stretching mode of carbonyl group (C=O), respectively. The remaining peaks centered at 1649, 1193 and 1076 cm⁻¹ are attributed to the alkene (C=C), carboxylic acid (C-OH), and epoxy (C-O-C) groups, respectively [313]. The peaks centered at 3392 and 1356 cm⁻¹ for LTH adsorbent can be attributed to the hydroxyl group (OH) and the nitrate anions interaction with the layer or the translational mode of Fe-OH and Mg-OH [314,315], respectively. For BENT adsorbent, FTIR spectra displayed a peak centered at 3618 cm⁻¹ which can be ascribed to the OH stretching vibration of the Si-O-H group, while the peaks centered at 3421 and 1625 cm⁻¹ are ascribed to the stretching mode of H-O-H on the Si surface. The peak centered at 1000 cm⁻¹ is attributed

to stretching mode of Si-O-Al [133]. The GO/LTH spectrum shows similar functional groups as the parent LTH. For GO/BENT sample, the FTIR spectra showed that the peak on GO centered at 1076 cm^{-1} is shifted to the peak centered at 1002 cm^{-1} on GO/BENT. Moreover, the peak centered at 3421 cm^{-1} (H-O-H on the Si surface) on BENT disappeared in the formation of GO/BENT indicating that hydrophobicity of GO/BENT increased. For LTH/BENT sample, the OH stretching vibration of the Si-O-H group located at 3618 cm^{-1} and the peak centered at 1356 cm^{-1} indicating the existence of BENT and LTH, respectively in the binary composite LTH/BENT. For the tertiary GO/BENT/LTH, the stretching modes (OH), and (Si-O-Al) located at 3392 , 1000 cm^{-1} , respectively indicating the success forming of the tertiary GO/BENT/LTH from its pristine.

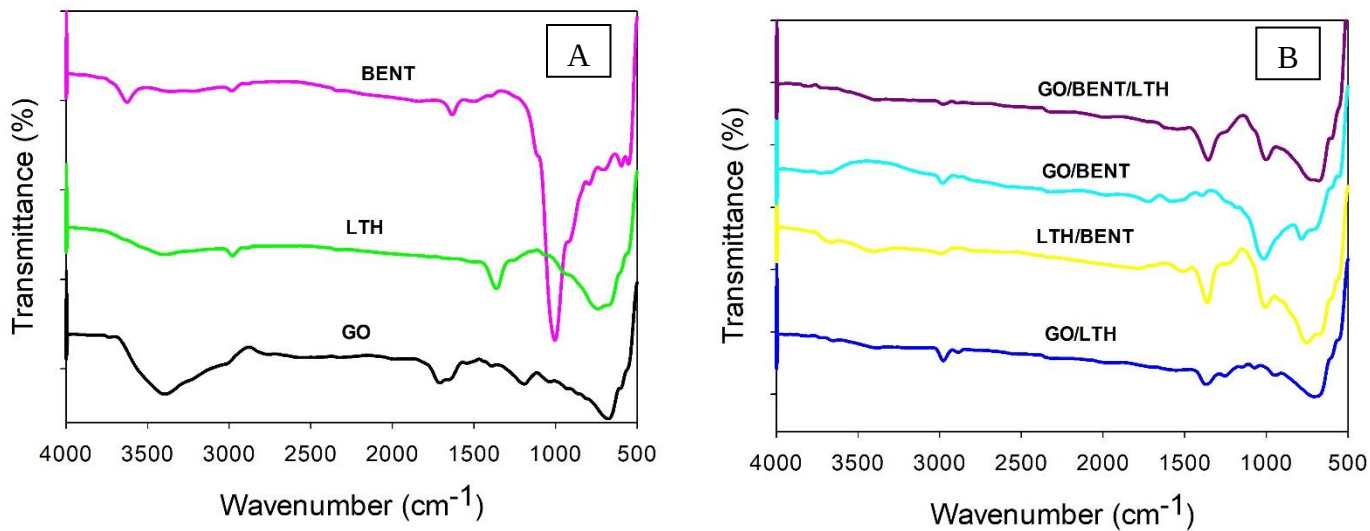


Figure 4-1: FTIR Spectra of the synthesized adsorbents in this work. (A) LTH, GO, and BENT, (B) GO/LTH, LTH/BENT, GO/BENT, and GO/BENT/LTH adsorbents.

b. SEM and EDX Analysis

Figure 4-2 displays the morphologies of all adsorbents synthesized in this work which were characterized using scanning electron microscope (SEM). Figure 4-2a represents the morphology of graphene oxide (GO) which illustrates different sized of dense flakes, while the morphology of LTH where the LTH surface composes of nanosheets connected with orderly nanoparticles is shown in Figure 4-2b. The SEM of BENT adsorbent (Figure 4-2c) displays that the surface of BENT consists of compact and rough macroparticles. After forming GO/LTH, the SEM shows that the dense flake surface of GO turned into uniform thickness and tiny nanosheets as observed in Figure 4-2d. Furthermore, the morphology of LTH/BENT (Figure 4-2e) depicts the rock-like particles of BENT anchoring the sheets of LTH sample. The SEM image (Figure 4-2f) displays that the surface of the sample is smooth and has some cracks due to the exfoliation of BENT layers during the addition of GO and ascribed to the intercalating of GO into BENT [344]. The last SEM image (Figure 4-2g) for the tertiary GO/BENT/LTH composite shows that the morphology surface consists of thin plates (lamellae).

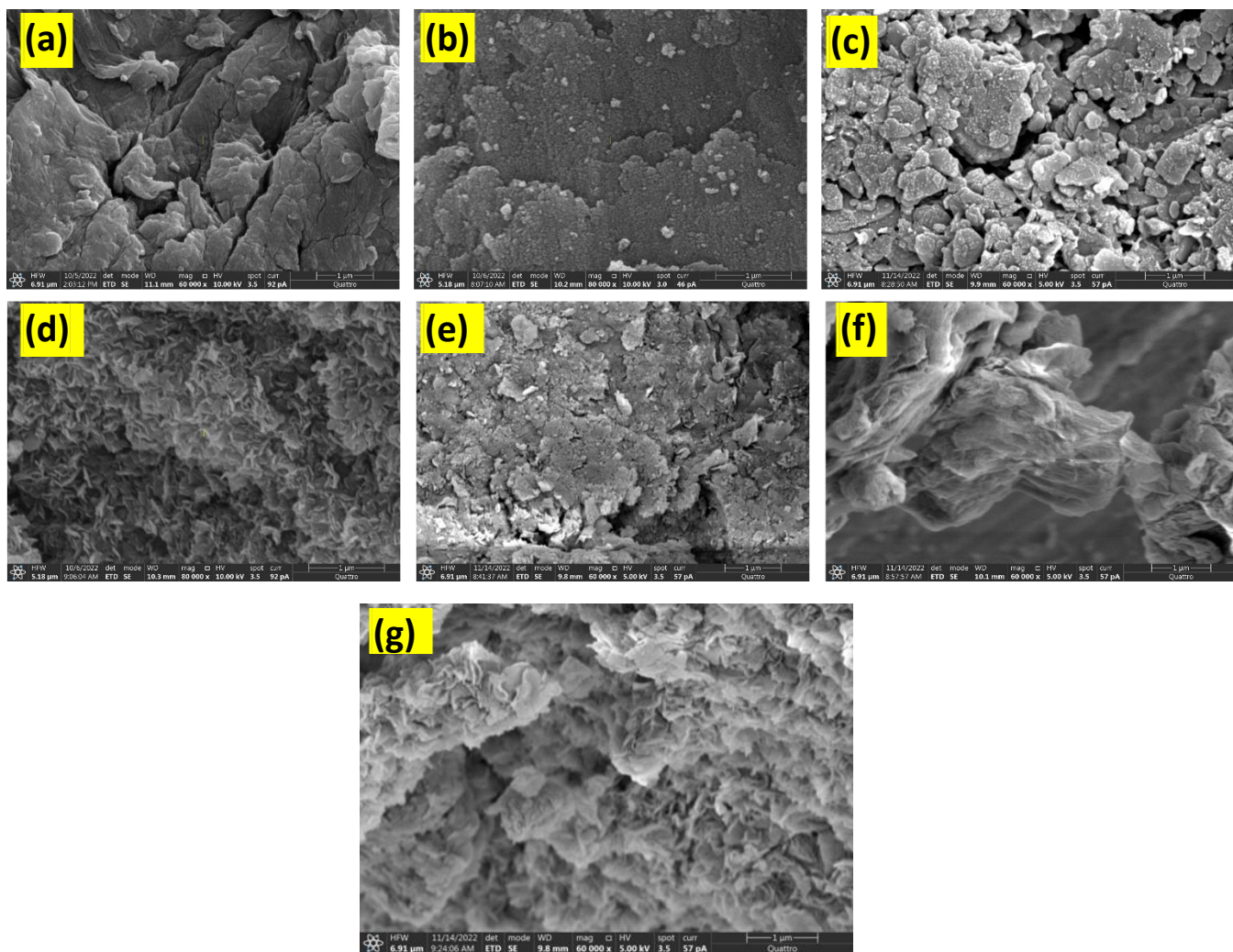


Figure 4-2: SEM images of (a) GO, (b) LTH, (c) BENT, (d) GO/LTH, (e) LTH/BENT, (f) GO/BENT, and (g) GO/BENT/LTH.

To ensure the availability of the elements in the synthesized composites, EDS characterization was conducted. Table 4-1 summarizes the atomic percentages of all elements that appear in all prepared adsorbents.

Table 4-1: EDS characterization of the synthesized adsorbents in this work.

Atomic % /Adsorbent	GO	LTH	BENT	GO/LTH	LTH/BENT	GO/BENT	GO/BENT/LTH
C	64.30	22.90	-	39.20	31.13	56.70	31.34
O	35.70	52.20	-	43.40	54.04	36.40	48.96
N	-	5.30	-	2.80	-	-	5.40
Mg	-	13.00	3.34	9.90	7.69	0.18	6.08
Al	-	5.20	23.35	3.90	3.78	1.30	3.23
Fe	-	1.40	4.89	0.80	1.02	0.31	1.38
Si	-	-	62.94	-	2.22	4.64	2.28
Na	-	-	4.16	-	0.00	0.25	1.21
K	-	-	0.45	-	0.04	0.07	0.00
Ca	-	-	0.87	-	0.09	0.15	0.12
C/O	1.80	0.44	-	0.90	0.58	1.56	0.64
C/N	-	4.32	-	14.00	-	-	5.81
Al/Fe	-	3.71	4.78	4.88	3.70	4.14	2.33
Mg/(Fe+Al)	-	1.97	0.12	2.11	1.60	0.11	1.32

c. XRD Analysis

The XRD patterns for the synthesized adsorbents in this work are displayed in Figure 4-3.

The diffraction patterns for GO adsorbent illustrates two distinct peaks centered at $2\theta = 9.65^\circ$, and 42.60° which corresponds to the crystal planes of (002) and (101), respectively. The GO interlayer distance “ $d = 0.901 \text{ nm}$ ” was computed using Bragg’s law. Similar findings were reported in these studies [316,317]. As can be observed for the XRD patterns of LTH, six main peaks observed at $2\theta = 11.76^\circ$, 23.48° , 34.69° , 39.24° , 46.27° , 60.67° , and 61.91° ,

which correspond to (003), (006), (012), (015), (110), and (113) crystal planes. Similar characteristic peaks of LTH (hexagonal structure) were reported in [319]. Moreover, the XRD for GO/LTH is similar to the diffraction patterns of LTH, except that the size decreases to 5 nm. For the XRD of BENT sample, the (001) plane is at the peak centered at $2\theta = 6.4^\circ$, while the diffraction patterns for GO/BENT shows peaks centered at $2\theta = 7.3^\circ$ and 42.6° , corresponding to (001) and (101) planes, indicating that GO was successfully intercalated with BENT. Upon the formation of GO/BENT, the GO/BENT interlayer distance “ d ” reduced from 1.38 nm of BENT to 1.2 nm as calculated using Bragg’s law. For LTH/BENT and GO/BENT/LTH samples, their XRD patterns are similar to that of LTH except the peak appeared at $2\theta = 26.7^\circ$ which corresponds to the pattern of the quartz phase, indicating BENT composites of quartz phase [344,345].

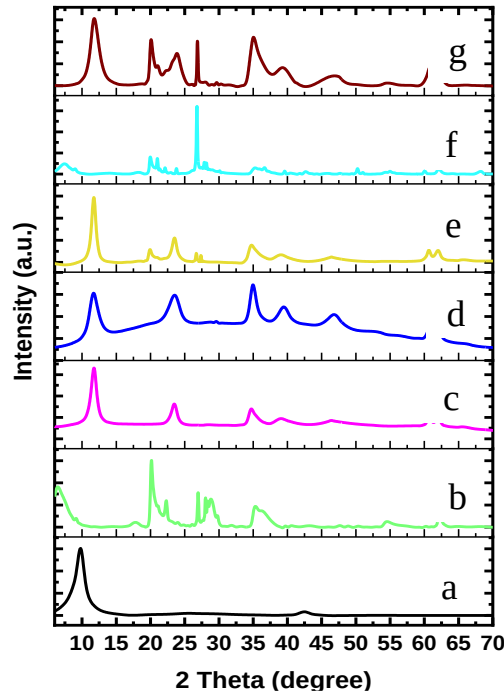


Figure 4-3: (a) XRD spectra of LTH, GO, and BENT, (b) XRD spectra of GO/LTH, LTH/BENT, GO/BENT, and GO/BENT/LTH.

4.3.2 Adsorbent Screening

The use of LDH materials for the adsorptive removal of various water contaminants has been thoroughly studied during the last few decades. For example, Bharali et al. [172] studied the adsorption of Congo red (CR) on NiAl-LDH and reported sorption capacity of 65 mg/g. Furthermore, Huang et al. [168] examined the adsorption of Reactive Red dye (RR) on MgFe-LDH and reported an adsorption capacity of 150.03 mg/g. Although LDH performed poorly in the studies indicated above, adding a third metal to the LDH framework (producing ternary LDH) has the potential to improve its performance. As a result, we synthesized LTH and used it to the adsorptive removal of MO and 2NP from aqueous solutions. As displayed in Figure 4-4, the sorption capacities of MO and 2NP on LTH are 479.8 and 177.3 mg/g, respectively, which are higher than those reported in the research cited above.

GO is another material that has been used in recent years as an adsorptive material for the removal of pollutants from aqueous solutions. In this study, GO was used to remove MO and 2NP. The results displayed in Figure 4-4 indicate that the adsorption capacities of MO and 2NP on GO are 503.5 mg/g and 334.6 mg/g, respectively. Furthermore, BENT was used recently as a sorbent for the removal of adsorbates from aqueous media. For instance, Espantaleón et al. [346] studied the adsorption of Acid Yellow (AY), Acid Blue (AB), and Acid Red (AR) on natural BENT and reported adsorption capacities of 24.9, 92.7, and 29.1 mg/g, respectively. Moreover, Ahmadi et al. [347] reported 95 % removal of phenol using BENT clay. Therefore, it was utilized in this work to uptake MO and 2NP. As depicted in Figure 4-4, the adsorption capacities of MO and 2NP on BENT are 608.1 and 257.8 mg/g, respectively. With the goal to create more influential adsorbents to adsorb MO and 2NP

from aqueous solution, LTH/BENT, GO/LTH, and GO/BENT were synthesized. According to Figure 4-4, LTH/BENT (649.6 mg/g), and GO/LTH (570.4 mg/g) perform better than their parental adsorbents (BENT = 608.1 mg/g and LTH = 479.8 mg/g) and (GO = 503.5 mg/g and LTH = 479.8 mg/g), respectively, while GO/BENT composite (238 mg/g), underperforms its individual materials (GO = 503.5 mg/g and BENT = 608.1 mg/g) for the removal of MO.

For the adsorption of 2NP, Figure 4-4 illustrates that BENT (257.8 mg/g) outperforms the composite LTH/BENT (254.1 mg/g), where GO (334.6 mg/g) outperforms the composites GO/LTH (197.4 mg/g) and GO/BENT (301.7 mg/g). According to the aforementioned results, LTH/BENT composite significantly outperformed its individual materials for the adsorption of MO, while GO-based material tackled a higher adsorption capacity than the composites for the removal of 2NP. Motivated by an astonishing performance of LTH compared to LDH, creating a ternary composite assembling the pristine materials (i.e., GO, BENT, and LTH) is another way to enhance the adsorption of MO and 2NP from aqueous solution. Therefore, GO/BENT/LTH nanocomposite was synthesized and employed to adsorb MO and 2NP from wastewater samples. As depicted in Figure 4-4, this nanocomposite showed spectacular removal performance, where the MO and 2NP adsorption capacity reached 706.2, and 510.1 mg/g, respectively. Consequently, GO/BENT/LTH tackles the highest adsorption capacity compared to other adsorbents (LTH, GO, BENT, GO/LTH, LTH/BENT, and GO/BENT) as discussed in this study. Therefore, this nanocomposite will be utilized to study the effect of other parameters including initial concentration of MO and 2NP, contact time, temperature, and pH.

However, before conducting any further studies, the adsorption mechanism(s) of MO and 2NP on all synthesized materials in this study has been investigated in section 4.3.3.

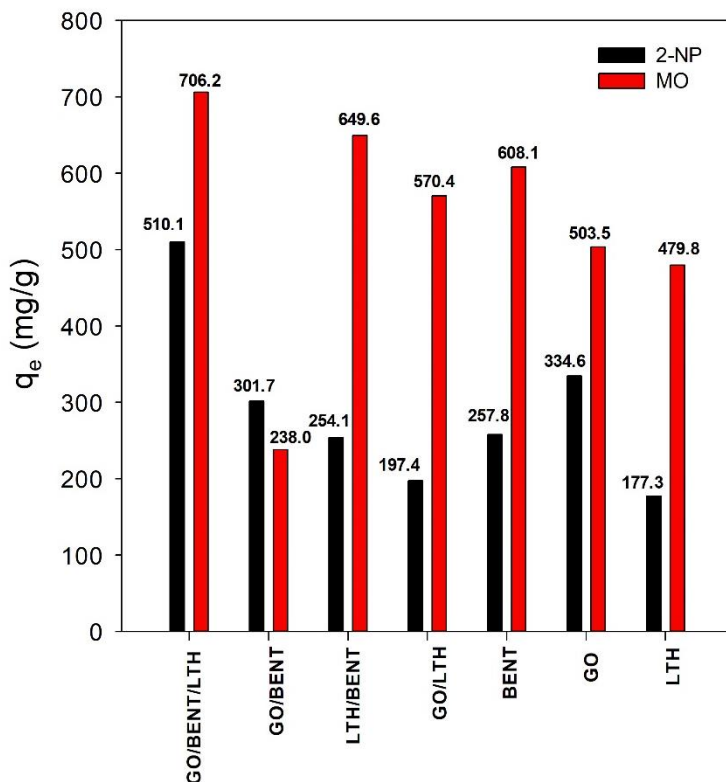


Figure 4-4: Adsorbent screening results of 2-NP and MO removal on GO/BENT/LTH, GO/BENT, LTH/BENT, GO/LTH, BENT, GO, and LTH conducted at $C_0 = 100 \text{ mg.L}^{-1}$, $T = 25^\circ \text{C}$, $t = 20 \text{ h}$, dose = 50 mg.L^{-1} , and $\text{pH} = 6$.

4.3.3 Potential Adsorption Mechanism(s)

As discussed above, the ternary composite GO/BENT/LTH was an astonishing adsorbent for the adsorption of MO and 2NP from synthetic wastewater samples as illustrated in Figure 4-4. To thoroughly realize why this nanocomposite was superior compared to the parental materials, zeta potential measurements have been conducted at different values of pH as presented in Figure 4-5 which shows the point of zero charge of all synthesized adsorbents in this work (i.e., $\text{GO}_{(\text{PZC})} = 2.2$, $\text{LTH}_{(\text{PZC})} = 10.12$, $\text{BENT}_{(\text{PZC})} = 2.1$, $\text{GO/LTH}_{(\text{PZC})}$

= 2.45, LTH/BENT_(PZC) = 4.8, GO/BENT_(PZC) = 2.4, and GO/BENT/LTH_(PZC) = 2.9).

Consequently, LTH is the only adsorbent among others that holds a net positive charge at pH 6 where the experiments of screening were conducted.

Although, GO/BENT/LTH nanocomposite outperformed the other adsorbents for the removal of 2NP and the anionic MO as shown in Figure 4-4, its pHPZC is 2.9 which means that it carries a net negative charge and small zeta potential at pH 6. However, LTH has the largest pHPZC (10.12) as presented in Figure 4-5 which is supposed to have the highest adsorption capacity among others, which explains that the electrostatic attraction was not the driven potential for the removal of anionic MO dye. Accordingly, other potential adsorption mechanisms including pore filling, π - π stacking interaction, and hydrogen bonding are potentially contributing for the removal of MO on GO/BENT/LTH. Similar findings were reported in these studies [14,348,349].

For the removal of 2NP by GO/BENT/LTH, it is neutral at pH 6 since its value of pKa is 7.2 [350], which reveals that hydrogen bonding, π - π dispersions, and pore filling (2NP molecules were adsorbed within the pores of GO/BENT/LTH) are the most likely potential adsorption mechanisms candidates. Wu et al. [351] studied the adsorption of p-nitrophenol (PNP) on aluminum metal organic framework/rGO and reported an agreement results. In addition, other studies reported similar behavior for the adsorption of BPA [325,326].

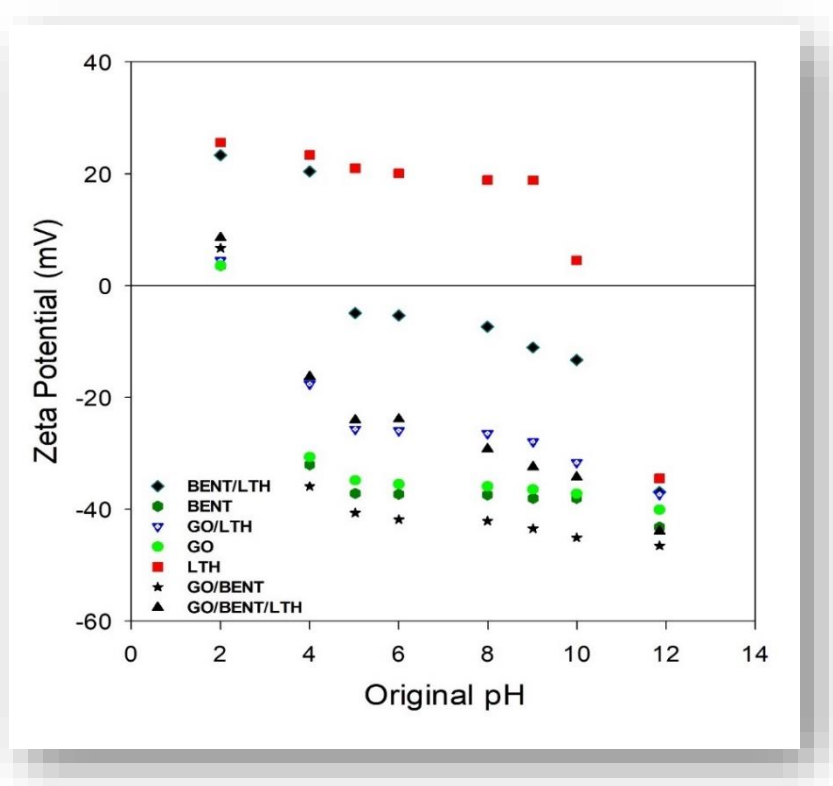


Figure 4-5: Zeta potential measurements for LTH, GO, BENT, GO/LTH, LTH/BENT, and GO/BENT/LTH under these conditions: $T = 25\text{ }^{\circ}\text{C}$, $\text{pH} = 6$, and $\text{dose} = 50\text{ mg.L}^{-1}$.

4.3.4 pH Effect

In this section, we discussed the influence of pH solution on the removal of 2NP and MO over the selective sorbent (i.e., GO/BENT/LTH) because it is considered as one of the most important parameters in the removal process. This study was conducted with conditions (i.e., initial phenol and dye concentration of 100 mg.L^{-1} and the amount of GO/BENT/LTH used was 5 mg) over the pH ranges of 2-12. Figure 4-6 shows the results of the pH effect on the removal of 2NP and MO by GO/BENT/LTH, which illustrates that the adsorption capacities of both MO (706.2 mg/g) and 2NP (510.1 mg/g) are higher at pH 6. For both anionic dye and phenol, these enhancements of the adsorption capacities at pH 6 on

GO/BENT/LTH were most likely ascribed to the pore filling hydrogen bonding, and π - π dispersions.

At pH 4, a decrease in the adsorption capacities of MO and 2NP on GO/BENT/LTH has been noticed with 572.3 and 251.9 mg/g, respectively. This decrease in the removal of MO on GO/BENT/LTH at pH 4 attributed to the electrostatic repulsion between the adsorbent and adsorbate molecules since MO pKa is 3.4 as reported in [352], while 2NP pKa is 7.2 as reported in [213], indicates that the charge of 2NP is neutral at pH 4. More decreases at pH 2, the adsorption of MO and 2NP reaches 443.4 and 53.4 mg/g, respectively. This decreasing in the adsorption as the pH decreases might be attributed to the dissolution of the adsorbent at pH 2, hence it lowers the adsorption capacity due to the unavailability of the active sites on the GO/BENT/LTH surface as stated in [353,354]. Similar trend was observed as increasing the pH from 6 to 12, where the adsorption capacities for both 2NP and MO on GO/BENT/LTH decreased from (510.1 to 127.4 mg/g) and (706.2 to 32.8 mg/g), respectively. This decrease can be ascribed to the electrostatic repulsion between the negative charges on the adsorbent and the adsorbate. Similar findings are found in [172,311,354]. Accordingly, further studies were conducted at pH 6.

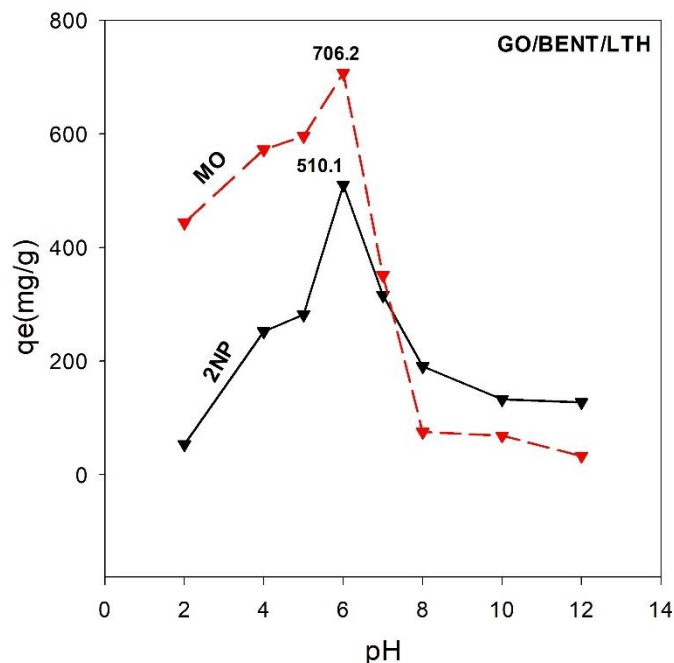


Figure 4-6: Influence of pH on the adsorption of 2-NP and MO over GO/BENT/LTH under these conditions: $T = 25\text{ }^{\circ}\text{C}$, $C_0 = 100\text{ mg.L}^{-1}$, volume= 100 mL, pH ranges from (2-12), and dose= 50 mg.L^{-1} .

4.3.5 Adsorption Isotherms

To understand the distribution of the adsorption equilibrium of MO and 2NP between the GO/BENT/LTH phase and the aqueous solution, studies of the adsorption isotherm were investigated. As listed in Table 2-13, the isotherm models (i.e., Langmuir, Freundlich, Temkin, and Redlich-Peterson) were employed to fit the experimental data of the adsorption of MO and 2NP on GO/BENT/LTH as shown in Figure 4-7. The obtained parameters of the adsorption of MO and 2NP from the non-linear models are summarized in Table 4-2. As illustrated in Figure 4-7A, the isotherm data of MO removal on GO/BENT/LTH are very well fitted by Redlich-Peterson and Langmuir models with R^2 close to unity (i.e., 0.9986 and 0.9972, respectively). The maximum adsorption capacity of the adsorption MO on GO/BENT/LTH obtained from Langmuir model is 3740.8 mg/g as

shown in Table 4-2. Furthermore, Figure 4-7A and the calculated parameters elucidate that Freundlich model nicely fitted to the data of the adsorption of MO on GO/BENT/LTH with R^2 equal 0.9868, while Temkin model poorly tracked the experimental data with R^2 equal 0.8513.

Moreover, Figure 4-7B illustrates that, these isotherm models properly fitted the 2NP sorption data and it reveals that Redlich-Peterson and Langmuir models produce the best data fittings with similar R^2 approaching unity (0.9965), where the maximum Langmuir adsorption capacity of 2NP on GO/BENT/LTH is 2347.5 mg/g and the Redlich-Peterson isotherm exponent (G) is 0.999 which is very close to 1 implying that Redlich-Peterson model is approaching the Langmuir model [330]. Similar to Figure 4-7A, Temkin model not properly fitted the experimental data of the adsorption of 2NP on GO/BENT/LTH with R^2 equal 0.8957. The comparison of the maximum sorption capacities of MO and 2NP using the synthesized GO/BENT/LTH in this work and various materials from the literature is presented in Table 4-3. All these results are obtained from Langmuir model due to lack of studies using Redlich-Peterson.

Table 4-2: Predicted isotherm Parameters of 2NP and MO on GO/BENT/LTH.

Pollutant	Langmuir			Freundlich			
	q _{max} (mg/g)	b (L.mg ⁻¹)	R ²	k _F (mg/g) (L/g) ⁿ	1/n	R ²	
MO	3740.8 ± 204.8	0.004 ± 0.026	0.9972	31.4 ± 6.8	0.677 ± 0.038	0.9868	
	Temkin			Redlich Peterson			
	β (J.mol ⁻¹)	A _T (L.g ⁻¹)	R ²	k _R (L.g ⁻¹)	a _R (L.mg ⁻¹)	G	R ²
	414.0 ± 61.2	0.096 ± 0.033	0.8513	7.5 ± 0.3	0.00	1.536 ± 0.205	0.9986
Pollutant	Langmuir			Freundlich			
	q _{max} (mg/g)	b (L.mg ⁻¹)	R ²	k _F (mg/g) (L/g) ⁿ	1/n	R ²	
2NP	2347.5 ± 109	0.005 ± 0.041	0.9965	37.1 ± 7.3	0.603 ± 0.035	0.986	
	Temkin			Redlich Peterson			
	β (J.mol ⁻¹)	A _T (L.g ⁻¹)	R ²	k _R (L.g ⁻¹)	a _R (L.mg ⁻¹)	G	R ²
	313.8 ± 37.9	0.109 ± 0.032	0.8957	8.3 ± 1.1	0.0043 ± 0.004	0.999 ± 0.162	0.9965

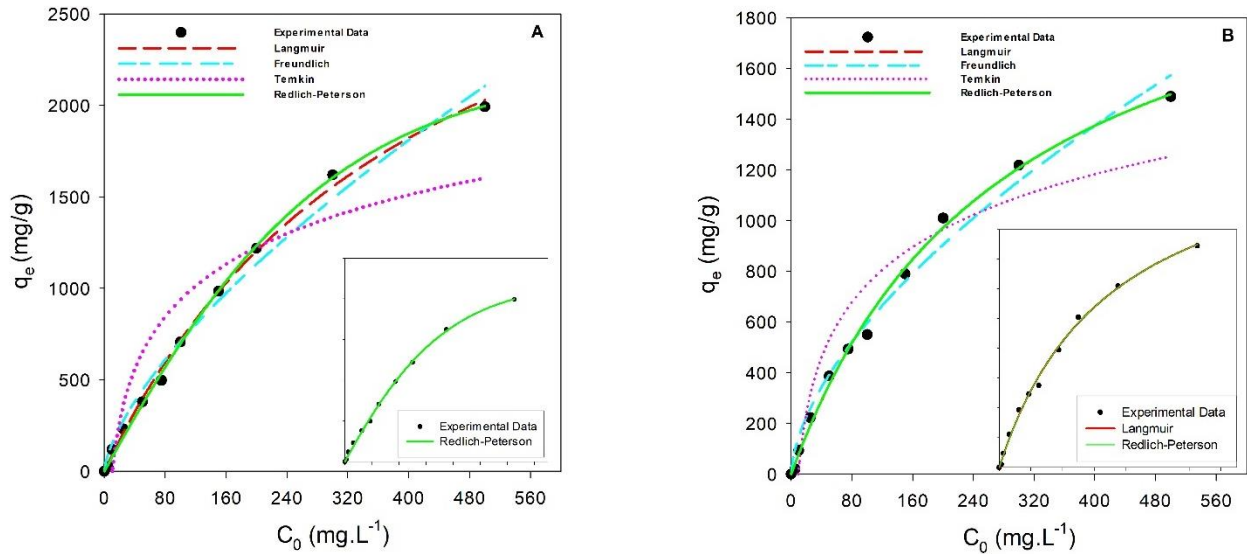


Figure 4-7: Effect of the adsorption isotherm of MO and 2NP using GO/BENT/LTH. Figure (A) the adsorption isotherm of MO on GO/BENT/LTH where Redlich-Peterson model (R-P) produces the most accurate fitting. Figure (B) the adsorption isotherm of 2NP on GO/BENT/LTH where Redlich-Peterson (R-P) and Langmuir (L) models produce the most accurate fitting. All conducted at $T=25^\circ\text{C K}$, shaking time = 1200 min, and dose = 50 mg.L⁻¹.

Table 4-3: Comparison of the maximum adsorption capacity of MO and 2NP into GO/BENT/LTH and other adsorbents from the literature from Langmuir model.

Sorbent	$Q_{\max}$ ($\text{mg}\cdot\text{g}^{-1}$)		b ($\text{L}\cdot\text{mg}^{-1}$)	R^2	Reference
	MO	2NP			
rGO/Ni/MMO	210.8		0.049	0.977	[355]
BP	21		11.4	0.934	[356]
OP	20.5		16.5	0.954	
Au/ZnAl-LDO	627.5		-	0.999	[357]
CuMgAl₄ - LDH	123.5		0.199	0.985	[358]
MgNiAl – LDH - CO₃	118.5		0.035	0.972	[167]
MgNiAl – LDH - C	375.4		0.025	0.991	
CANF	416		0.147	0.999	[359]
RGO–Ni–Cr – CO₃ LDH	312.5		0.051	0.997	[360]
CoFe-LDH	>1206		-	0.988	[361]
Fe₃O₄/MIL-101(Al_{0.9}Fe_{0.1})/NH₂	355.8		0.100	0.982	[362]
G-LDH	443.5		0.050	0.980	[155]
G-LDO	1062.3		0.210	0.980	
Fe₃O₄@GO	28.6		0.61	0.998	[363]
NiFeTi-LDH	32.6		0.379	0.967	[364]
Uncalcined MgAlNi-BaFe	746.3		0.012	0.890	[365]
Calcined MgAlNi-BaFe	740.7		0.014	0.928	

ZnAl-LDH	1309.3	229.1	0.999	[166]
(γ-Fe₂O₃)/chitosan	28.9	0.190	0.996	[366]
NiAlTi-LDH	1250	0.039	0.964	[367]
Bentonite/LDH	61.8	15.640	0.818	[368]
LDH	32.3	0.087	0.963	[201]
ZIF-67	75.6	0.088	0.992	
ZIF-67 composite	180.5	0.035	0.974	
GO/BENT/LTH	3740.8	0.004	0.997	This work
Zn-Al-LDH	312.6	0.019	0.990	[369]
Mg-Fe-LDH	394.15	0.005	0.999	
MWCNTs	476.2	0.018	0.990	[370]
MWCNTs-COOH	256.4	0.050	0.990	
HCP	350	0.024	0.979	[371]
HCP-N	426	0.008	0.932	
GO/BENT/LTH	2347.5	0.005	0.997	This work

4.3.6 Adsorption Kinetics

Adsorption is frequently mediated by a chemical interaction between functional groups on the surface of the adsorbent and the adsorbate. There are several kinetic models that have been used to represent the order of adsorbate-adsorbent interactions. In this work, four kinetic models (i.e., Pseudo first order, Pseudo second order, Elovich, and Avrami) were

employed as shown in Figure 4-8 and the calculated kinetic parameters are presented in Table 4-4.

Figure 4-8A shows the adsorption kinetics of MO on GO/BENT/LTH at 100 mg.L^{-1} , where the kinetic models mentioned above are properly fitted the experimental data of MO adsorption on GO/BENT/LTH. Avrami and Pseudo first order models demonstrated high accurate data fitting with R^2 of 0.9987 and 0.9985. Moreover, the predicted equilibrium adsorption capacity of MO on GO/BENT/LTH using Avrami and Pseudo first order models are 750.4, and 701.2 mg/g, respectively while the MO experimental equilibrium adsorption capacity on GO/BENT/LTH at 100 mg.L^{-1} is 706.2 mg/g which indicated that, Avrami model exhibited the best data fitting for the adsorption kinetics of MO on GO/BENT/LTH as illustrated in Figure 4-8A.

Similar to the adsorption kinetics of MO on GO/BENT/LTH, Figure 4-8B represents the adsorption kinetics of 2NP on GO/BENT/LTH using different kinetic models. As shown in Figure 4-8B, the 2NP adsorption kinetics on GO/BENT/LTH are initially very fast, and progressively the rate of adsorption gets slower. From the kinetic parameters listed in Table 4-4 and the regression curves shown in Figure 4-8B, they reveal that Avrami model exhibited high performance of 2NP adsorption on GO/BENT/LTH with R^2 approaching unity (0.9980) and equilibrium sorption capacity of 545 mg/g which is deviated from the 2NP experimental sorption capacity (510.1 mg/g) at 100 mg.L^{-1} by 6.84%. Al-Qadri et al. [311] reported that Avrami model fits the experimental data of the adsorption of BPA on GO-DETA. Table 4-5 below lists the comparison of the MO and 2NP equilibrium adsorption capacity on GO/BENT/LTH with different materials reported from the literature at 100 mg.L^{-1} .

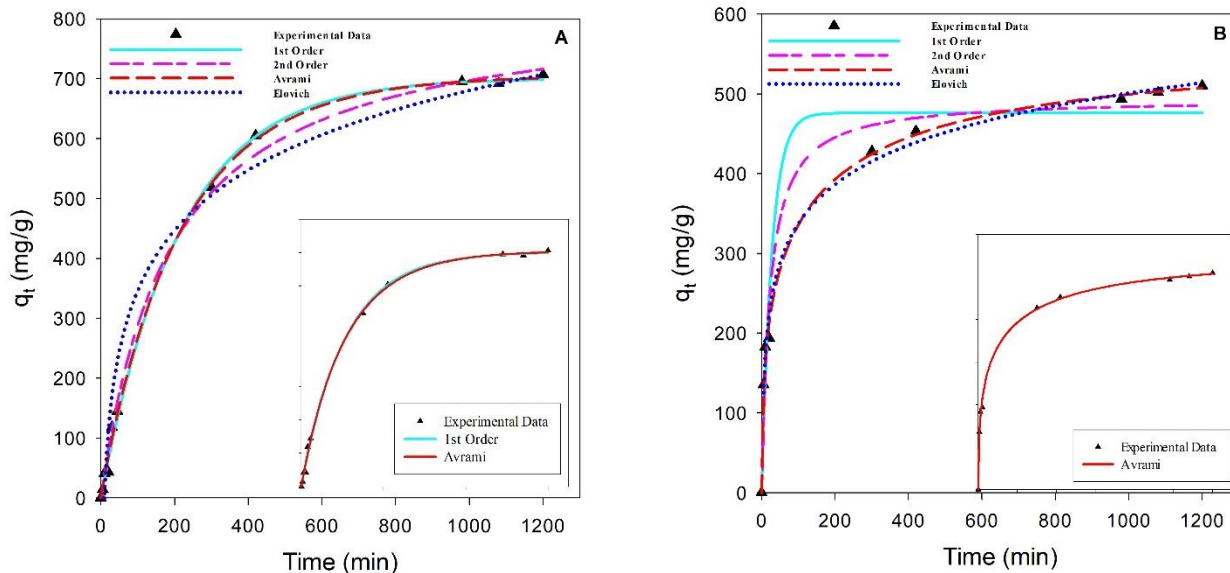


Figure 4-8: Contact time effect of the adsorption of MO and 2NP using GO/BENT/LTH. Figure (A) represents the kinetics of MO on GO/BENT/LTH at pH 6, temperature 25 °C, initial concentration 100 mg.L⁻¹, and dose 50 mg.L⁻¹ where Avrami and 1st order models produce the best data fittings ($R^2 = 0.9987$, and $R^2 = 0.9985$ respectively) of MO adsorption on GO/BENT/LTH. Figure (B) represents the kinetics of 2-NP on GO/BENT/LTH at pH 6, temperature 25 °C, initial concentration 100 mg.L⁻¹, dose 50 mg.L⁻¹ where Avrami and 1st order models produce the best data fittings ($R^2 = 0.9980$) of 2NP adsorption on GO/BENT/LTH.

Table 4-4: Predicted Kinetic Parameters of 2-NP and MO on AGO/BENT/LTH.

Pollutant	1 st Order			2 nd Order			
	q _e (mg/g)	k _{PFO} (min ⁻¹)	R ²	q _e (mg/g)	k _{PSO} (g.mg ⁻¹ .min ⁻¹)	R ²	
MO	701.2 ± 8	0.005	0.9985	827.1 ± 20.2	0.00001	0.9968	
	Elovich			Avrami			
	α (mg.min.g ⁻¹)	β	R ²	q _e (mg/g)	k _{Av} (min ⁻ⁿ)	n _{Av}	R ²
	0.001	0.007 ± 0.103	0.9656	705.4 ± 8.8	0.004	0.955 ± 0.036	0.9987
Pollutant	1 st Order			2 nd Order			
	q _e (mg/g)	k _{PFO} (min ⁻¹)	R ²	q _e (mg/g)	k _{PSO} (g.mg ⁻¹ .min ⁻¹)	R ²	
2NP	476.2 ± 18.7	0.036 ± 0.007	0.9591	494.5 ± 15.6	0.00009	0.9773	
	Elovich			Avrami			
	α (mg.min.g ⁻¹)	β	R ²	q _e (mg/g)	k _{Av} (min ⁻ⁿ)	n _{Av}	R ²
	0.017 ± 0.004	0.014 ±0 .384	0.9920	545 ± 22.7	0.001 ± 0.001	0.413 ± 0.028	0.9980

Table 4-5: Comparison of the kinetic adsorption capacity of MO and 2NP into GO/BENT/LTH and other adsorbents from the literature.

Material	Q _e (mg/g)		Kinetic Model				R ²	Ref.
	MO	2NP		k _{PFO} (min ⁻¹)	k _{PSO} g.mg ⁻¹ .min ⁻¹	k _{Av} / n min ⁻ⁿ /-min ⁻¹		
rGO/Ni/MMO	87.7		PSO		0.0003		0.997	[355]
CuMgAl ₄ - LDH	79.2		PSO		0.0021		0.998	[358]

Ni–Cr – SDBS - LDH	152	PSO	0.0006	0.996	[360]
MWCNT	123.5	PSO	0.0020	0.999	[372]
Fe₃O₄@GO	32.7	PSO	0.0031	0.995	[363]
Fe₃O₄/MIL-101(Al_{0.9}Fe_{0.1})/NH₂	111.4	PSO	0.0001	0.999	[362]
GO/BENT/LTH	701.2	PFO	0.005	0.999	This work
	705.4	AV	0.004/0.955	0.999	
Zn-Al-LDH	123	PSO	0.0006	0.913	[369]
Mg-Fe-LDH	86.7	PSO	0.0030	0.998	
MWCNTs (C₀=120 ppm)	109.9	PSO	0.0020	1.000	[370]
MWCNTs-COOH (C₀=130 ppm)	122	PSO	0.0018	1.000	
HCP	238	PSO	0.1760	0.999	[371]
HCP-N	385	PSO	0.1130	0.999	
GO/BENT/LTH	545	AV	0.001/0.413	0.998	This work

4.3.7 Thermodynamic Adsorption of MO and 2NP on GO/BENT/LTH

The nature of the adsorption process of 2NP and MO on GO/BENT/LTH can be determined by studying the adsorption thermodynamics. In this work, four temperatures (10 °C, 25 °C, 40 °C, and 55 °C) were tested to study the effect of the temperature on 2NP and MO adsorption. The thermodynamic parameters (i.e., ΔH^o , ΔS^o , and ΔG^o) were calculated using Eq. 4-1 and Eq. 4-2 [373] as follows and summarized in Table 4-6:

$$\ln K_d^o = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (4-1)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (4-2)$$

Table 4-6: Thermodynamic parameters of the adsorption of 2NP and MO into GO/BENT/LTH.

Adsorbate	ΔS^o (J/mol.K)	ΔH^o (kJ/mol)	ΔG^o (kJ/mol)			
			283.15 (K)	298.15 (K)	313.15 (K)	328.15 (K)
2NP	-41.648	-9.751	2.041	2.666	3.291	3.915
			q_e (mg/g)			
			591.32	510.05	443.90	383.29
Adsorbate	ΔS^o (J/mol.K)	ΔH^o (kJ/mol)	ΔG^o (kJ/mol)			
			283.15 (K)	298.15 (K)	313.15 (K)	328.15 (K)
MO	-121.443	-34.851	-0.464	1.357	3.179	5.001
			q_e (mg/g)			
			1126.69	706.19	447.44	287.87

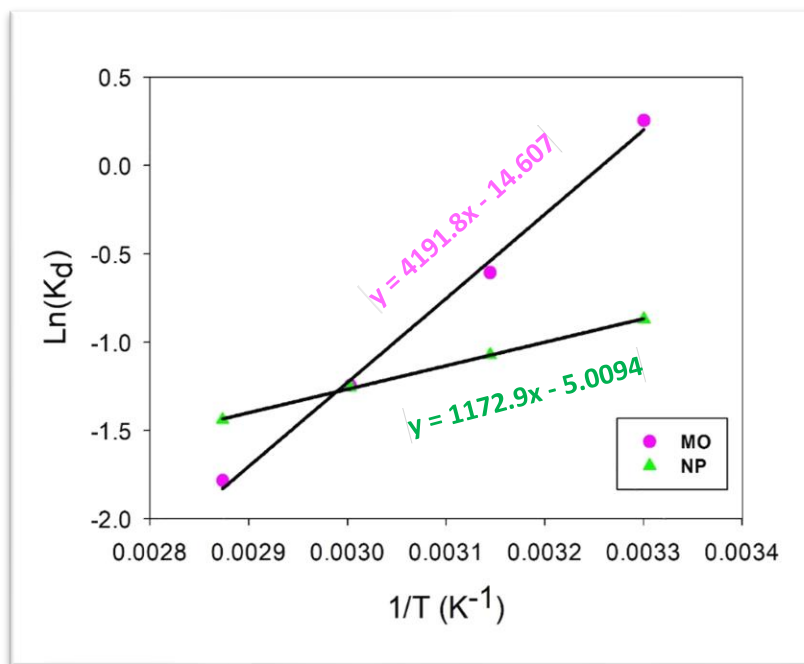


Figure 4-9: Plot of $\ln(K_d)$ versus $1/T$ of the 2NP and MO adsorption by GO/BENT/LTH at pH 6, initial concentration 100 mg.L^{-1} , dose 50 mg.L^{-1} , and time 20 h.

As illustrated in Figure 4-9, the slope and y-intercept of the plot of $(\ln K_d^0 \text{ Vs } 1/T)$ represent the enthalpy change (ΔH^0) and the entropy change (ΔS^0) for the adsorption of MO and 2NP into GO/BENT/LTH. The obtained thermodynamic parameters (ΔH^0 and ΔS^0) were plugged in Eq. 4-2 to calculate the Gibbs free energy (ΔG^0).

According to the results presented in Table 4-6, the negative ΔH^0 and ΔS^0 values for the removal of 2NP and MO, imply that the adsorption process is a physical exothermic and the order increases during the adsorption [12]. Moreover, it is shown that as the temperature decreases, the positive ΔG^0 values decrease, indicating that the adsorption is more favorable at lower temperatures for the adsorption of 2NP and MO on GO/BENT/LTH.

CHAPTER 5

Conclusion and Recommendations

5.1 Conclusions

To conclude, the removal of the four pollutants (i.e., AR1, BPA, MO, and 2NP) from wastewater using the novel adsorbents (i.e., PEI@GO, and GO/BENT/LTH) was considered in this work. The highest adsorption capacities of these pollutants were attained at pH 6 using the PEI@GO/LTH and GO/BENT/LTH nanocomposites. The adsorption capacity of BPA and AR1 on PEI@GO/LTH was 352.0 and 155.5 mg/g, respectively, while the adsorption capacity of MO and 2NP on GO/BENT/LTH was 706.2 and 510.1 mg/g, respectively. Moreover, the adsorption isotherms were nicely fitted by Redlich-Peterson model for the removal of the four pollutants using both adsorbents, while the adsorption kinetics were accurately fitted by Avrami model. Thermodynamic results demonstrated that the nature of the adsorption is exothermic and the adsorption is more favorable at low temperatures. These findings indicate that these two nanocomposites are promising, effective, abundant, and excellent for the removal of dyes and phenols from wastewater samples.

5.2 Recommendations

LTH composites are one of the newest, most promising fields of research, particularly for water purification. LDHs have seen a rise in interest in water treatment applications because of their thermal and chemical stability. As a result, from an academic point of view, these materials have been designated as being appropriate for use in water treatment.

There are some suggestions that can be utilized for future aspects:

- a. Water purification using LDH composites is still in the Lab scales, therefore, a clear need exists to estimate the actual process challenges encountered LDH composites utilization including industrial scale cost effective preparation and reusability.
- b. LDH or LDH composites have only been investigated so far for single pollutant systems (dyes, heavy metals, or phenols). Testing the effectiveness of these materials in wastewater containing several toxic pollutants, such as dyes and heavy metals, dyes and phenols, or heavy metals and phenol, is highly suggested because it will move the research much closer to practical applications.
- c. Several studies reported the removal of pollutants from aqueous media using specific LDH composites (carbon, mineral) whereas few studies reported the use of LDH/MOFs, hence more research studies have to be done using LDH/MOFs adsorbent to evaluate its effectiveness on water purification.

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- 1) Onaizi, S. A., Alsulaimani, M., Al-Sakkaf, M. K., **Bahadi, S. A.**, Mahmoud, M., & Alshami, A. (2021). Crude oil/water nanoemulsions stabilized by biosurfactant: Stability and pH-Switchability. Journal of Petroleum Science and Engineering, 198, 108173.
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To be Submitted

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Upcoming Papers: 3 result papers and 1 review paper.