

**APPLICATION OF IRON BASED LDH (Mg/Fe LDH)  
WITH TiO<sub>2</sub> PHOTOCATALYSIS FOR AQUEOUS  
SELENIUM POLLUTION CONTROL**

BY

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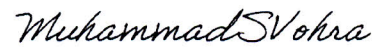
This thesis, written by **Ahmed Ismail Adam** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CIVIL ENGINEERING**.



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2020

## **Dedication**

**| To my parents, brothers, sisters, and friends |**

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## LIST OF ABBREVIATIONS

|             |   |                                   |
|-------------|---|-----------------------------------|
| <b>WHO</b>  | : | World Health Organization         |
| <b>LDH</b>  | : | Layered Double Hydroxide          |
| <b>CLDH</b> | : | Calcined Layered Double Hydroxide |
| <b>RO</b>   | : | Reverse Osmosis                   |
| <b>PCD</b>  | : | Photocatalytic Degradation        |
| <b>MB</b>   | : | Methylene Blue                    |
| <b>MV</b>   | : | Methyl violet                     |
| <b>MG</b>   | : | Malachite green                   |
| <b>SDS</b>  | : | Sodium dodecyl sulfate            |
| <b>DMP</b>  | : | Dimethyl phthalate                |

## ABSTRACT

Full Name : Ahmed Ismail Adam  
Thesis Title : Application of Iron-Based LDH (Mg/Fe LDH) with TiO<sub>2</sub>  
Photocatalysis for Aqueous selenium Pollution Control  
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Selenium is present in respective contaminated water streams in different forms, such as selenite ( $\text{SeO}_3^{2-}$ ), selenate ( $\text{SeO}_4^{2-}$ ), and selenocyanate ( $\text{SeCN}^-$ ). These species cause risk to human and aquatic life. This research applied a combined photocatalytic degradation (PCD) and adsorption using TiO<sub>2</sub>-Mg/Fe LDH to remove aqueous selenocyanate. First, the adsorption capacity of LDH for selenium species ( $\text{SeO}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{SeCN}^-$ ) was investigated by studying the effect of calcination temperature of LDH, adsorbent dosage, and concentration of selenium species. The adsorption isotherm showed that the Langmuir model fitted well for selenite and selenocyanate removal with an adsorption capacity of 4.7 mg/g and 1.47 mg/g, respectively. For selenate, the Freundlich model was the best-fitted model with an adsorption capacity of 3 mg/g. The adsorption kinetics showed that the adsorption of selenite, selenate, and selenocyanate followed the pseudo-second-order model. The adsorption result showed that the maximum removal efficiency for selenite and selenate was achieved for LDH calcined at 500 °C and 1.5 g/l of LDH dosage. For selenocyanate, the maximum removal efficiency was obtained for LDH calcined at 250 °C and 1.5 g/l of LDH dosage. For the PCD experiment, the removal efficiency of  $\text{SeCN}^-$  using TiO<sub>2</sub> modified by LDH was investigated by studying the effect of weight ratio of LDH:TiO<sub>2</sub> (w/w), dosage of adsorbent, and selenocyanate concentration. The obtained

results showed that the removal efficiency of  $\text{SeCN}^-$  increased with an increase in the LDH: $\text{TiO}_2$  (w/w) ratio and the adsorbent dosage. However, the removal efficiency decreased with an increase in the selenocyanate concentration. The maximum removal efficiency was obtained at a LDH: $\text{TiO}_2$  (w/w) ratio of 1:1.5, adsorbent dosage 2 g/l, and selenocyanate concentration 2.5 ppm. The  $\text{TiO}_2$ -LDH based combined PCD and adsorption technology showed sufficient removal of respective selenium species.

## ملخص الرسالة

الاسم الكامل: أحمد إسماعيل ادم

عنوان الرسالة: إستخدام طبقات الهيدروكسيد الثنائية المصنعة على اساس الحديد مع ثاني اكسيد التتانيوم في عملية حفيز ضوئي للتخلص من التلوث المائي للسلينيوم

التخصص: هندسة مصادر المياه والبيئة

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يظهر عنصر السلينيوم في المياه الملوثة في عدة اشكال منها : السيلينات ( $\text{SeO}_3^{2-}$ ) , السلينييت ( $\text{SeO}_4^{2-}$ ) و السيلنيوسيانيت ( $\text{SeCN}^-$ ). وجود السيلنيوسيانيت في البيئة يسبب مخاطر على صحة الانسان والبيئة. هذا البحث قام باستخدام تكنولوجيا مدمجة تشمل عملية التحفيز الضوئي والامتزاز باستخدام طبقات الهيدروكسيد الثنائية المعدلة بثاني اكسيد التتانيوم ( $\text{TiO}_2\text{-Mg/Fe LDH}$ ) في وجود الاشعة فوق البنفسجية للتخلص من السيلنيوسيانيت المائية. السيلنيوسيانيت في عملية التحفيز الضوئي يتأكسد الى السيلينات وبعد فترة يتحول الى السلينييت. لذلك تم دراسة السعة الامتزازية لـ  $\text{TiO}_2\text{-Mg/Fe LDH}$  للتخلص من مركبات السلينيوم انفة الذكر في عملية تخلص تنافسية وذلك من خلال دراسة تأثير درجة حرارة تكلس (calcination) طبقات الهيدروكسيد الثنائية ( $\text{Mg/Fe LDH}$ ). أظهرت نتائج Adsorption isotherm أن Langmuir model كان أفضل نموذج ملائم للسلينييت وسيلنيوسيانات بسعة امتصاص تبلغ 4.7 مجم / جم و 1.47 مجم / جم على التوالي. بالنسبة للسيلينات ، كان Freundlich model هو النموذج الأكثر ملائمة بسعة امتصاص 3 مجم / جم. أظهرت Adsorption kinetics أن امتزاز السلينييت والسيلينات والسيلنيوسيانات يتبع pseudo-second-order model. أظهرت نتيجة الامتزاز أن أقصى كفاءة إزالة للسلينييت والسيلينات تم تحقيقها في LDH المكلس عند 500 درجة مئوية و 1.5 جم / لتر من جرة LDH. بالنسبة لسيلنيوسيانات ، أقصى كفاءة إزالة تم الحصول عليها عند LDH المكلسة عند 250 درجة مئوية و 1.5 جم / لتر من جرة LDH. بالنسبة لـ PCD ، تم التحقيق في كفاءة الإزالة لـ LDH المعدل لـ  $\text{TiO}_2$  من خلال دراسة تأثير نسبة الوزن لـ  $\text{LDH: TiO}_2$  w / w ، جرعات الممتز ، وتراكيز السيلنيوسيلنييت. أظهرت النتائج التي تم الحصول عليها أن كفاءة الإزالة تزداد مع زيادة نسبة LDH:  $\text{TiO}_2$  w / w وجرعة الامتزاز. ومع ذلك ، انخفضت كفاءة الإزالة مع

زيادة وتراكيز السيلنيوسيلنيت. أقصى كفاءة إزالة تم الحصول عليها بنسبة (1:1.5) ، جرعة ممتزة 2 جم / لتر ، وتركيز سيلينوسيانات 2.5 جزء في المليون. أظهرت هذه التكنولوجيا المدمجة إزالة كافية لأنواع السيلينيوم.

# CHAPTER 1

## INTRODUCTION

Selenium is a metalloid multi-faceted element, occurring naturally at low concentrations (trace element) and found in minerals, water, air, soil, and earth crust [1], [2]. It is introduced in the environment as a result of human activities such as irrigation (0.140 – 0.4 ppm), mining of gold (0.2 – 33 ppm), refining of phosphate (0.003 – 12 ppm), fossil fuel combustion (0.009 – 0.389 ppm), gas desulfurization (1 – 10 ppm), mining of uranium (1.6 ppm) and crude oil refining (0.008 – 0.056 ppm) [3]. At certain low concentrations ( $< 0.04$  mg/day) selenium is a nutrient for mammals, fish, and birds. However, it is toxic at higher concentration ( $> 0.4$  mg/day) [4]. At trace concentrations, selenium plays an important role in the process of development and normal growth, and also protection from diseases [4]. However, at high concentrations, it causes oxidative stress and toxicity which cause a chronic disease known as selenosis which is related to long-term exposure to contaminated drinking water (ingestion route). The toxicity of selenium refers to reactivity with thiols that causes damage to the DNA [5]. Selenium is present in the environment in different oxidation forms such as selenium ( $\text{Se}^0$ ), selenite ( $\text{SeO}_3^{2-}$ ), selenate ( $\text{SeO}_4^{2-}$ ), and selenide ( $\text{Se}^{2-}$ ). However, selenite and selenate are the predominant forms in natural water bodies. Also, selenite is comparatively more toxic than selenate because of its distribution and mobility [6]. According to WHO the allowable concentration of selenium in drinking water should not exceed 0.01 ppm [7]. Furthermore, selenocyanate ( $\text{SeCN}^-$ ) is one of selenium

forms that is predominantly present in the wastewater streams originating from petroleum refineries, fossil fuels based power plants, and mining industries [8].

Considering its toxicity, different technologies have been used to remove the respective selenium species from contaminated water bodies. The selenium removal efficiency of respective technologies typically depends on selenium speciation and initial concentration. For example, though precipitation has been reported to remove selenite and selenate from the mining wastewater streams, however, this technology did not provide effective removal because of higher solubility of selenite and selenate [9]. Another study used an ion exchange system to remove selenate [10]. The removal of selenate anion using Reverse Osmosis (RO) system has also been used, but at high concentrations the respective membrane setup suffered from fouling [11].

In this work, the use of combined photocatalytic degradation (PCD) and adsorption process using  $\text{TiO}_2\text{-MgFe/NO}_3$  LDH was investigated to remove aqueous selenocyanate. The photocatalysis process uses hydroxyl radical ( $\text{HO}\cdot$ ), which mineralizes and removes even recalcitrant aqueous phase pollutants [12].  $\text{TiO}_2$  has been widely used in photocatalysis process because of its higher stability, strong oxidation power, and inert nature [13]. The Layered Double Hydroxide (LDHs) has also attracted much attention as an adsorbent due to its multi-functional properties [14]. The present work therefore investigated the destruction of selenocyanate complex using  $\text{TiO}_2$  photocatalysis followed by an adsorption based uptake of produced selenium species by the respective LDH matrix. The results from the present work are promising with further details given in the coming sections.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Layered Double Hydroxides (LDHs) and Synthesis methods

Layered Double Hydroxides abbreviate (LDHs) also called hydrotalcite-like compounds which refer to hydrotalcite mineral (magnesium-aluminum hydroxyl carbonate)  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}](\text{CO}_3) \cdot 4(\text{H}_2\text{O})$ , has been given this name because it contains water (hydro) and talc (talcite) are found in nature or can be synthesized [15]. The general formula of LDHs is  $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  divalent and  $\text{M}^{3+}$  trivalent metal cations,  $x$  represents the molar ratio  $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ , and  $A$  represents valence  $n$  of interlayer anion. LDHs have a crystal structure with wide variations depending on the  $\text{M}^{2+}/\text{M}^{3+}$  ratio and nature of cations. The LDHs compounds consist of positively charged brucite-like octahedral sheets with interlayers anions including carbonate that can be used as exchangeable anions, along with molecules of water [16] as shown in figure 2.1.

There are three different methods of LDHs synthesis:

- Co-precipitation method.
- Ion exchange method.
- Reconstruction (hydration) method.

### 2.1.1 Co-precipitation Method

Co-precipitation method is considered to be the most used method. It can prepare different divalent and trivalent cations intercalated anions (organic or inorganic). In this method solution with targeted intercalated anions is added slowly to another solution with divalent and trivalent cations at specific ratios with pH adjustment that leads to co-precipitation of desired product. The process should be performed under thermal conditions that enhance the crystalline structure of the final compound [17].

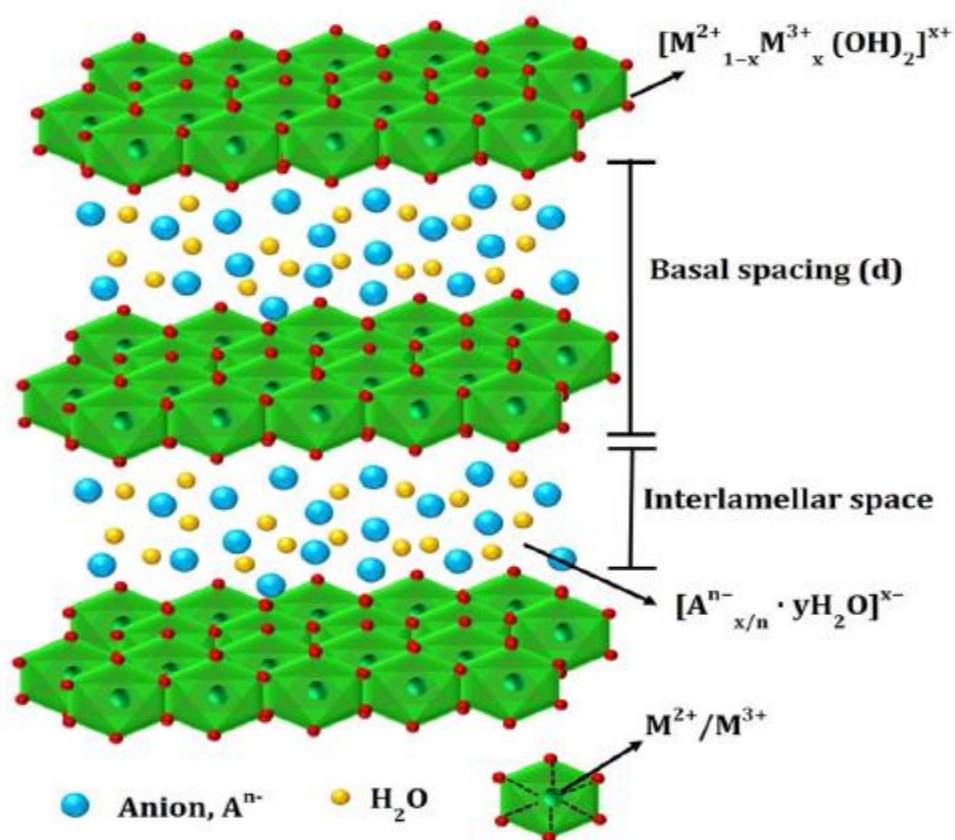


Figure 2.1 LDHs Structure [16]

### **2.1.2 Ion Exchange Method**

LDH is initially synthesized by co-precipitation method using anions chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), and carbonate ( $\text{CO}_3^{2-}$ ), which can be exchanged with other specific anions. The process must be performed under inert atmospheric conditions to avoid the intercalation of  $\text{CO}_3^{2-}$ . The electrostatic forces between metallic cations sheets and anions exchange play a role in the synthesis process [16].

### **2.1.3 Reconstruction (hydration) method**

In this method, LDH is synthesized using calcination and rehydration (in the presence of nitrogen gas). Heating the LDHs at high temperatures ranged from 400 °C to 500 °C that leads to removal of water molecules and undesired intercalated anions in the interlayers [18].

## **2.2 Photocatalytic Degradation (PCD)**

The photocatalytic degradation process is one of the most efficient, effective, and desirable technologies in the area of wastewater treatment because it has many advantages such as use of inert and stable  $\text{TiO}_2$  photocatalyst, higher degradation of target pollutants, and application of PCD at ambient temperature and pressure conditions [19]. The process is initiated when photons of a specific wavelength excite semiconductor photocatalyst causing the electrons transfer from the valence band to the conduction band and that creates electrons hole pairs ( $e^-/h^+$ ), as shown in figure 2.2. The process eventually produces hydroxyl radicals ( $\text{OH}^\bullet$ ), which are powerful oxidizing agents. However, the process has some issues such as accumulation of nanoparticles and recombination of  $e^-/h^+$  species which result in reducing  $\text{OH}^\bullet$  radical formation and decreasing photocatalytic reactivity

[20]. Many studies have demonstrated that Degussa P25 TiO<sub>2</sub> is a very promising photocatalyst [21].

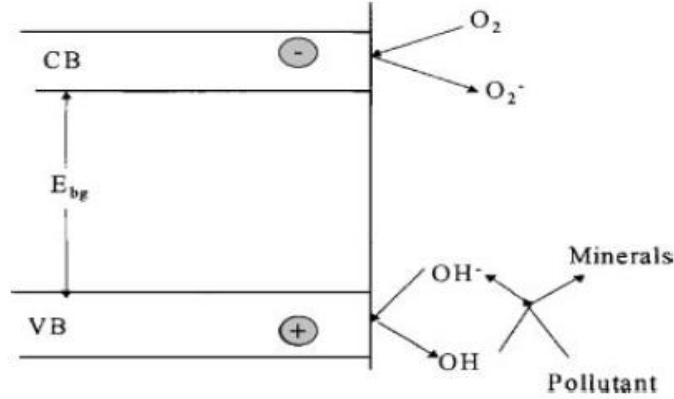
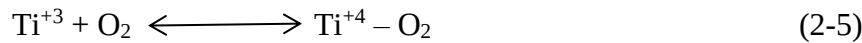
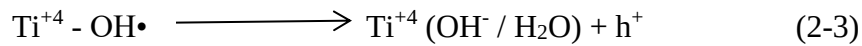
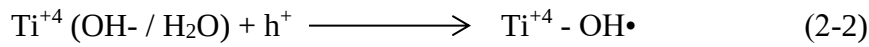


Figure 2.2 The processes occurring during the PCD process [22]

The equations below explain the excitation process and trapping of  $e^-/h^+$  pair on the surface of photocatalyst [22].



The LDHs structure may improve the efficiency of the photocatalysis process via various factors including preventing the recombination of  $e^-/h^+$  pairs, and preventing the accumulation of nanoparticles. Also, LDHs can be obtained by simple synthesis [14].

## 2.3 Selenite and Selenate in Water

According to the selenium pE-pH stability diagram, in the natural aerated water, selenite in form ( $\text{HSeO}_3^-$ ) is favorable at pH values from 3 to 8 [23]. Torres et al. [24] reported that selenate ( $\text{SeO}_4^{2-}$ ) is present at high pH values and oxidation conditions. In aqueous solutions, selenite oxidizes to selenate slowly, and selenite can be present in nonequilibrium conditions. At neutral pH, the adsorption of selenate onto clays and oxides is weak.

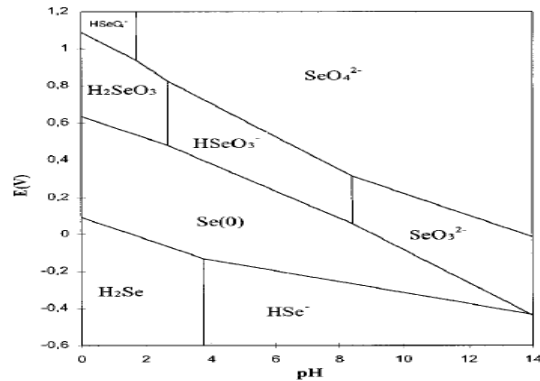


Figure 2.3 Selenium pH diagram at 25 °C and selenium concentration  $10^{-7}$  M [23]

## 2.4 Previous Studies

### 2.4.1 Removal of Selenite and Selenate using LDHs

Das et al. [25] used calcined and uncalcined Mg-Fe LDH intercalated  $\text{CO}_3^{2-}$  to remove selenite. Co-precipitation method was used to synthesize LDH with molar ratio ( $\text{Mg:Fe}$ ) = (2:1) and calcined LDH was obtained by heating LDH at 500 °C. The characterization results showed that the calcined LDH had more specific surface area than uncalcined LDH because the high temperature conditions destroyed the interlayers and removed the water molecules. The selenite removal efficiency using calcined LDH was 64% whereas it was

54% for the uncalcined LDH. The low adsorption of uncalcined LDH related to strong intercalation between carbonate anions in the interlayer and metals hydroxide layers. The highest selenite removal (64%) was achieved at pH 6, because of the adsorption of anions on the surface of oxides by ligand exchange. The adsorption depends on the electrostatic force to attract the selenite to the surface of LDH. Hence the calcination of LDH at a specific temperature increases its specific surface area and low pH yields more selenite removal because the surface of LDH is positively charged.

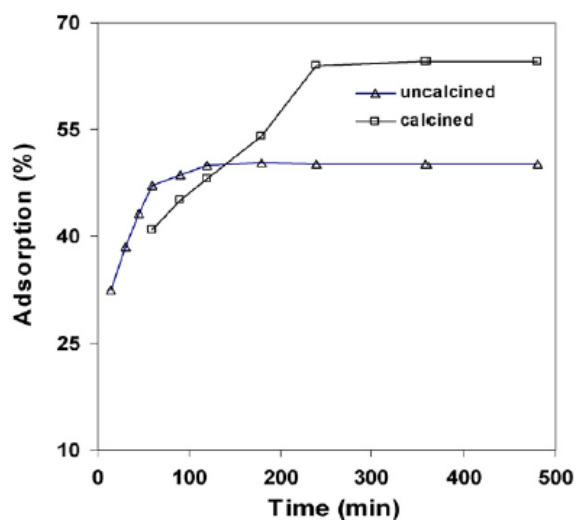


Figure 2.4 The removal efficiency of selenite with time for both calcined and uncalcined LDH [25]

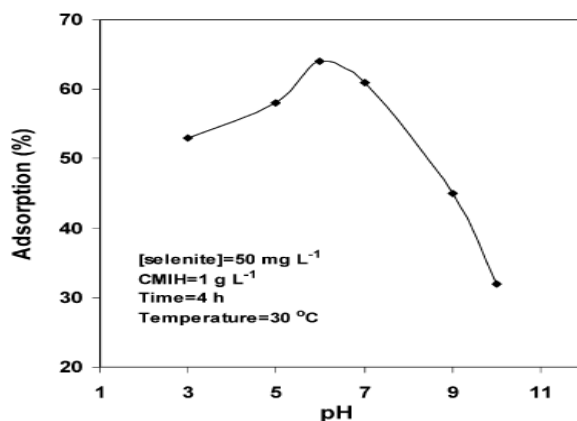


Figure 2.5 The removal efficiency with pH [25]

Mandal et al. [26] investigated the removal of selenite in aqueous solution by using different types of LDH (Zn-Al, Mg-Al, and Zn-Fe) intercalated  $\text{Cl}^-$ . The study used different molar ratios ( $\text{M}^{2+} : \text{M}^{3+}$ ) (1, 2, 3: 0.33). The LDH were synthesized using the co-precipitation method. The influence of molar ratio on selenite adsorption showed that the adsorption of selenite increased with an increase in the molar ratio up to 2 (2:0.33), and above 2, the adsorption of selenite decreased. Also, the results showed that Zn-Fe LDH is less effective compared to Mg-Al LDH and Zn-Al LDH because in case of former only adsorption was dominant whereas in case of Mg-Al LDH and Zn-Al LDH both adsorption and ion exchange with  $\text{Cl}^-$  were applicable. The effect of pH results showed that from pH 3.4 to 7.4, the adsorption was almost constant. At pH less than 2 the adsorption decreased whereas at pH higher than 7.4, the adsorption decreased because of competition between  $\text{OH}^-$  and selenite anions. The study showed that the optimum adsorbent dosages to achieve removal efficiency above 90% was from 0.5 to 4 g/l. It is concluded that that Mg-Al and Zn-Al LDH intercalated with  $\text{Cl}^-$  are more efficient to remove selenite.

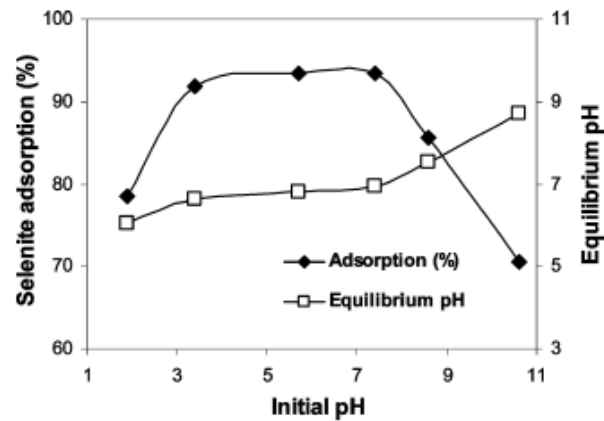


Figure 2.6 The reduction of selenite concentration with time [26]

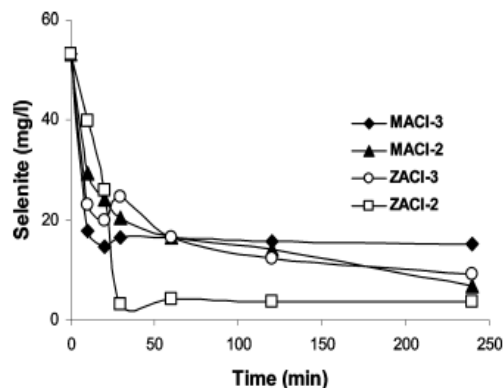


Figure 2.7 The effect of pH on the removal of selenite [26]

Vinicius et al. [27] investigated the removal of selenite and selenate using calcined Mg-Al LDH (hydrotalcite) intercalated with sulfate, nitrate, and phosphate. The results (figure 2.5) showed selenite and selenate were removed by the outer-sphere complexation mechanism. Selenite showed the highest affinity to the adsorption site,. The authors mentioned that high adsorption related to low affinity ( $b_2$ ,  $K_2$ ) and low adsorption related to high affinity ( $b_1$ ,  $K_1$ ). But there are some exceptions like selenite with phosphate and selenate with sulfate that can refer to similar structure between sulfate and selenate, which change the affinity of adsorption sites. It is concluded that the ion exchange removal process between the intercalated anions and pollutants, which hold the same charge may provide low adsorption because of the competition.

| Anion              | $K_1$ | $b_1$ | $n_1$ | $K_2$ | $b_2$ | $n_2$ | $R^2$  | RMSE | HI     | MF     |
|--------------------|-------|-------|-------|-------|-------|-------|--------|------|--------|--------|
| Selenite           |       |       |       |       |       |       |        |      |        |        |
| $\text{NO}_3^-$    | 237   | 60.0  | 4.04  | 10.3  | 503   | 1.49  | 0.9980 | 8.85 | 0.3209 | 0.0015 |
| $\text{SO}_4^{2-}$ | 651   | 48.4  | 2.82  | 28.6  | 446   | 1.55  | 0.9987 | 7.14 | 0.2353 | 0.0047 |
| $\text{PO}_4^{3-}$ | 26.9  | 92.0  | 11.3  | 95.2  | 461   | 0.75  | 0.9958 | 12.8 | 0.2804 | 0.0039 |
| Selenate           |       |       |       |       |       |       |        |      |        |        |
| $\text{NO}_3^-$    | 845   | 149   | 1.40  | 47.7  | 510   | 1.96  | 0.9964 | 13.0 | 0.3360 | 0.0017 |
| $\text{SO}_4^{2-}$ | 44.9  | 200   | 5.88  | 139   | 409   | 1.07  | 0.9997 | 4.16 | 0.3190 | 0.0142 |
| $\text{PO}_4^{3-}$ | 74.1  | 79.2  | 6.69  | 68.0  | 550   | 1.59  | 0.9932 | 17.9 | 0.2928 | 0.0266 |

$K_1$  and  $K_2$  ( $\text{L meq}^{-1}$ ): constants related to the sorbate-sorbent affinity parameter;  $b_1$  and  $b_2$  ( $\text{meq kg}^{-1}$ ): maximum sorption capacity;  $n_1$  and  $n_2$ : heterogeneity index of the sorption sites;  $R^2$ : determination coefficient; RMSE: root mean square error; HI: hysteresis index; MF: mobilization factor.

Figure 2.8 The parameters of the Langmuir and Freundlich model [27]

You et al. [28], used Mg-Al LDH and Zn-Al LDH with anions nitrate, carbonate, sulfate, and phosphate to remove selenite in aqueous solution. LDHs prepared by the Co-precipitation method with different molar ratios. The results showed that the increase in the molar ratio of (Mg:Al) up to (4:1) leads to decrease removal efficiency, and that refers to the reduction in the electrostatic force between the positively charged layers when Mg substituted with Al in LDH structure. The removal of selenite onto Mg-Al LDH is more than Zn-Al LDH, and that because of the big atomic weight of Zn, which decreases the ion exchange capacity. Also, the affinity of selenite is lower in Mg-Al LDH. The effect of pH had investigated, and the results showed that adsorption of selenite stayed constant between pH= 5 and 10, then increased when pH increased and that returns to the high affinity of OH<sup>-</sup> comparing to other monovalent anions. Zn-Al LDH showed less adsorption at low pH than Mg-Al LDH because of the high affinity of OH<sup>-</sup>. Also, the adsorption process declined at a pH low than 4.5 because of the dissolution of LDH. Also, the author mentioned that when the initial pH is low, the equilibrium pH increases because of LDH dissolution and result in releasing OH<sup>-</sup> and when initial pH is high, the equilibrium pH decreases, and that refers to direct adsorption of OH<sup>-</sup> from solution by LDH. Using different competitive anions played a rule in selenite removal, nitrate showed the highest adsorption then, carbonate, sulfate, and finally phosphate, and that can return it to the affinity of this anions to LDH, phosphate showed the highest affinity in Mg-Al LDH followed by sulfate and carbonate respectively. It is concluded that Mg-Al LDH with monovalent anion is more efficient in adsorption of selenite.

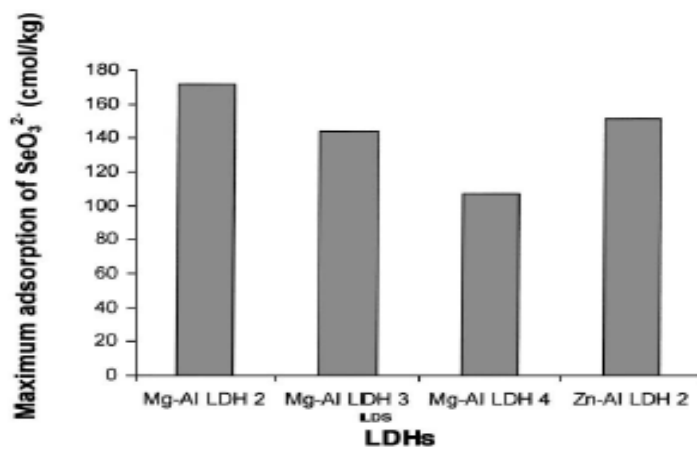


Figure 2.9 The adsorption capacity of different LDHs to remove selenite[28]

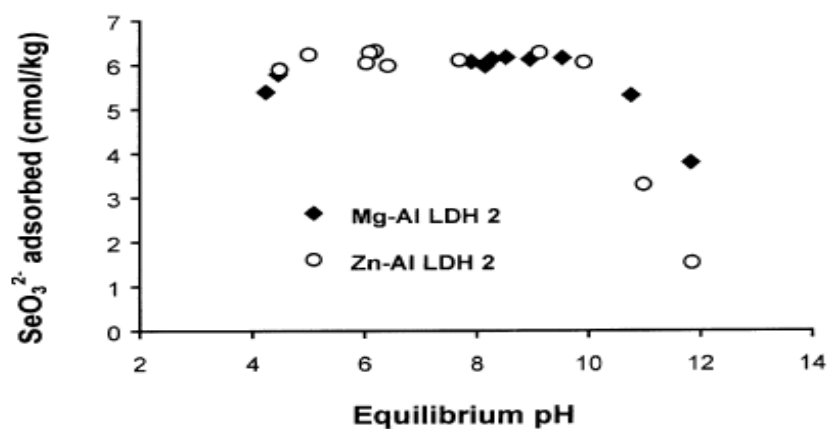


Figure 2.10 The adsorption of selenite with equilibrium pH [28]

Different Studies used different LDHs to remove selenite and selenate are summarized in table 2.1.

[Table 2.1 The removal of selenite and selenate using different LDHs]

| LDHs                                                                                                       | Pollutant             | Method/Calcination                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | Ratio ( $M^{+2}/M^{+3}$ )                                                                                                                                                     | Dosage                             | Concentration                                                             | pH of solution                            | Comment                                                                                                                                  | Ref  |
|------------------------------------------------------------------------------------------------------------|-----------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|---------------------------------------------------------------------------|-------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|------|
| Mg/Fe-LDH loaded cellulose fiber                                                                           | Selenite and selenate | Co-precipitation/0C°                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 3:1                                                                                                                                                                           | 5 mg of Mg/Fe-LDH loaded cellulose | 0.01 mg/l                                                                 | Selenite (3.8-8.0) and Selenate (5.8-7.0) | The high removal obtained related to selenium speciation through different pH values and surface charge of the adsorbent.                | [29] |
| Mg/Al-CO <sub>3</sub> LDH (static and dynamic adsorptive)                                                  | Selenite and Selenate | Alkoxide free sol-gel                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | -                                                                                                                                                                             | 2 g/l                              | 168 mg/g <sub>dw</sub> for Se (IV) and 103 mg/g <sub>dw</sub> for Se (VI) | 5                                         | The presence of phosphate and sulfate on the adsorbate did not affect the dynamic adsorptive of selenite and selenate.                   | [30] |
| Two types of Ca/Al LDH: monosulfaluminate (AFm-SO <sub>4</sub> ) and Friedel's salt (AFm-Cl <sub>2</sub> ) | Selenite              | AFm-SO <sub>4</sub> synthesized using a mixed solution of CaSO <sub>4</sub> ·2H <sub>2</sub> O and C3A. C3A produced by a heating mixture of CaCO <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> with a molar ratio of 10 for 72 h at 1300C°. Then the solution kept for 42 days under suspension after that the product filtered and dried in the glove box. AFm-Cl <sub>2</sub> was synthesized using a mixture of C3A and CaCl <sub>2</sub> ·6H <sub>2</sub> O with the same molar ratio. | AFm-SO <sub>4</sub> and AFm-Cl <sub>2</sub> were prepared using the molar ratio (0.7-1) of CaSO <sub>4</sub> ·2H <sub>2</sub> O/ CaCl <sub>2</sub> ·6H <sub>2</sub> O and C3A | -                                  | 0.01-1 mM                                                                 | 12.4 (pH of LDH)                          | Results showed AFm-Cl <sub>2</sub> achieved the highest removal because of monovalent anions easier to exchange than divalent anions.    | [31] |
| Fe/Al-Cl LDH/ZVI and Fe/Al-SO <sub>2</sub> LDH/ZVI                                                         | Selenate              | Nitrate AlCl <sub>3</sub> /Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> pre-treatment method to coat ZVI grains using LDH                                                                                                                                                                                                                                                                                                                                                                  | -                                                                                                                                                                             | -                                  | 20 ppm and 120 ppm                                                        | 7.1-7.3                                   | Fe/Al-Cl LDH/ZVI was more efficient than Fe/Al-SO <sub>2</sub> LDH/ZVI and that refers to competition between similar anions charges (Se | [32] |

|                           |                                |                          |                                                                                                        |        |                                                                  |                |                                                                                                                                                                                                                      |      |
|---------------------------|--------------------------------|--------------------------|--------------------------------------------------------------------------------------------------------|--------|------------------------------------------------------------------|----------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
|                           |                                |                          |                                                                                                        |        |                                                                  |                | (VI) and SO <sub>4</sub> ), which reduce the removal efficiency.                                                                                                                                                     |      |
| Mg/Al-CO <sub>3</sub> LDH | Selenate (existing of sulfate) | Fine inorganic sol – gel | -                                                                                                      | 2 g/l  | 470 mg (Se)/l with initial concentration of sulfate 46.5 mg(S)/l | 8.5, 7 and 4.5 | Sulfate slightly affected the removal of selenate at pH 8.5 and no effect at pH 4.5 and for pH 7 the removal efficiency decreases by 37%.                                                                            | [33] |
| Ca/Al LDH                 | Selenate (caustic solution)    | Co-precipitation/0C°     | 22 mmol of CaO·Al <sub>2</sub> O <sub>3</sub> added to 22 mmol of CaCl <sub>2</sub> ·6H <sub>2</sub> O | 40 g/l | 200 mg/l                                                         | -              | Removal of selenate affected by temperature. The maximum removal efficiency achieved at 30 C°. At temp ranged from (30-70) C° the removal be high. Increasing the temp till 80 C° decreasing the removal efficiency. | [34] |

### 2.4.2 Removal of Selenocyanate

Meng et al. [35], studied the removal of selenocyanate from oil refinery wastewater using elemental iron Fe (0). At pH 6 more than 97% of selenocyanate was removed within 3 h (figure 2.7). The elemental iron removed selenocyanate by forming elemental selenium Se (0) and ferrous selenide. The chemical reaction between elemental iron and selenocyanate included de-selenation of selenocyanate and electrochemical reduction of elemental selenium Se (0) to selenide.

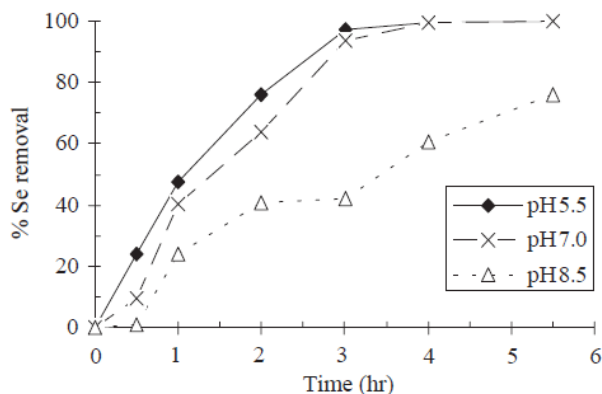


Figure 2.11 The removal of selenocyanate as a function of pH [35]

Kazeem et al. [36], investigated the removal of selenocyanate using the electrocoagulation (EC) technology. The obtained results represented that removal of selenocyanate increased with an increase in the applied current from 0.4 A to 1.2 A but decreased when the initial concentration of selenocyanate increased from 10 mg/l to 50 mg/l and pH of the solution increased from 4 to 8. The mechanism of the removal is oxidizing selenocyanate to selenite and selenate then adsorb them into aluminum hydroxides or iron hydroxides generated at the anode. Also, the author reported that zeta potential of steel electrode showed changes in the surface charge of the sludge from positive at pH = 4 to negative at pH = 8 whereas,

this change created a negative effect in the adsorption process. The characterization showed iron hydroxide had more adsorption capacity than aluminum hydroxide.

Gallup [8], investigated the removal of selenocyanate from refining water and wastewater using precipitation and ion exchange. Selenocyanate reacted and precipitated with lead, gold, cadmium, copper, thallium, silver, and mercury. The precipitates showed not well characterization, in addition to the low solubility of this compound, which may form with selenocyanate complexes become difficult to remove. Also, the metals almost are arranged in the same way during the disposing of selenium, and that makes treatment expensive.

### **2.4.3 Applications of Mg/Fe-LDH as adsorbent**

SUN et al. [37], studied the removal of phosphate using a different molar ratio of uncalcined and calcined Mg/Fe LDHs. The obtained Mg/Fe LDHs were prepared with molar ratio ranged from 1:2 to 5:1 then heated to 300 °C for 3 h. This temperature considers the optimum calcination temperature to increase the adsorption capacity of LDH [38]. The authors investigated the effect of molar ratio on adsorption capacity and found that calcined LDH adsorbed more than uncalcined for all molar ratio. The highest adsorption was at molar ratio 3:1, and that refers to the contribution of ferric ( $\text{Fe}^{3+}$ ) ions, which improve the purity and structure of Mg/Fe LDH when the ratio of Mg:Fe increased from 0.5 to 3. However, increasing this ratio will decrease the adsorption because of the repulsion forces between the cationic metals, also repulsion between interlayers' anionic species. The optimum molar ratio of Mg:Fe is 3 for both uncalcined and calcined LDH [39]. It is concluded that Mg/Fe LDH prepared with molar ratio (3:1) followed by calcination at 300 °C for 3h had provided the highest adsorption of phosphate.

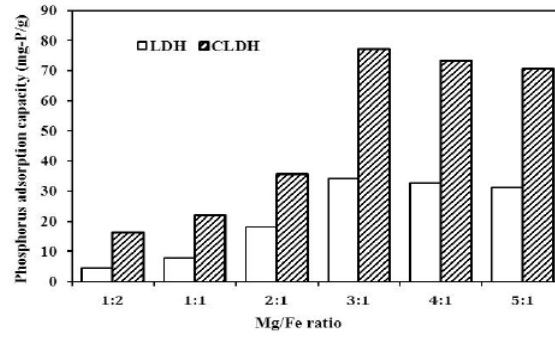


Figure 2.12 The adsorption capacity of phosphate of different Mg:Fe ratio [37]

Peng et al. [40], investigated the removal of arsenate in aqueous solution using calcined Mg/Fe-LDHs synthesized from three different molar ratios (3-5:1). According to the authors, the LDHs were heated at different temperatures for different times and found, the calcination at 350 °C for 5 h is the optimum condition whereas, the TEM characterization showed many numbers of pores on the surface of LDH. Furthermore, the BET characterization results showed that calcined LDH with molar ratio (4:1) has a specific surface area of 144 m<sup>2</sup>/g, which made it the best and fastest in adsorption of arsenate compared to the other molar ratio (3:1) and (5:1) with specific surface area 108 and 130 m<sup>2</sup>/g respectively.

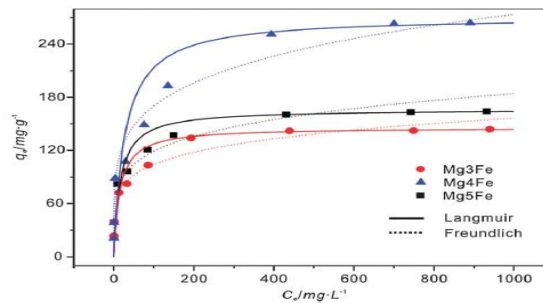


Figure 2.13 The adsorption isotherm of arsenate on calcined Mg/Fe-LDH [40]

Xue et al. [41], investigated the removal of nitrate using Mg/Fe-LDH modified wheat straw biochar in liquid phase precipitation. The characterization results showed that the specific

surface area of biochar was  $182 \text{ m}^2/\text{g}$  and for Mg/Fe-LDH modified biochar was  $3.9 \text{ m}^2/\text{g}$ , the author suggested the incorporation of Mg/Fe-LDH may fill or clogged pores of biochar. The adsorption kinetics appeared that adsorption process with time passed through two phases; fast phase, which achieved 74% of removal during 3h as shown in figure 2.14, then slow phase with adsorption capacity  $0.086 \text{ mg/g/h}$  before equilibrium. Rapid adsorption, according to the author, refers to the high anion exchange capacity of LDH, and slow adsorption refers to pores' series and biochar surface. The effect of coexisting ions had studied and found that sulfate and phosphate had a very small effect (figure 2.15) can be ignored and that because of the ion sieve effect formed between interlayers of Mg/Fe-LDH. It is concluded that Mg/Fe-LDH has high adsorption capacity to remove nitrate when modified biochar which can distribute LDH particles very well to obtain higher sorption of pollutants.

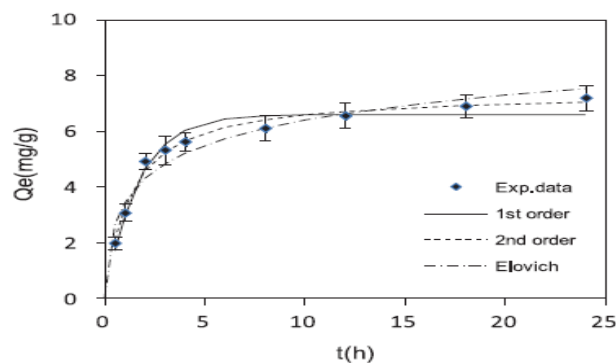


Figure 2.14 The adsorption kinetic of nitrate with time [41]

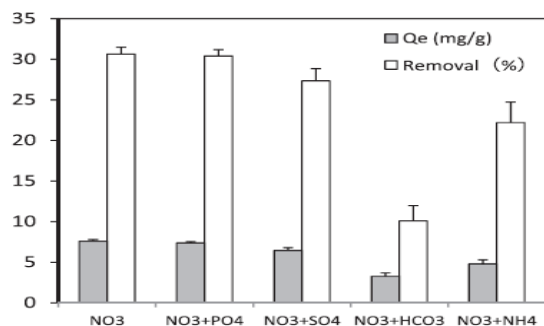


Figure 2.15 The influence of coexisting ions on the removal of nitrate [41]

Elmoubarki et al. [42], studied the removal of textiles dyes (Methylene blue (MB), Methyl orange (MO), and Malachite green (MG)) in aqueous solutions using uncalcined and calcined Ni/Fe-LDH and Mg/Fe-LDH. LDHs had synthesized using the Co-precipitation method and followed by calcination at 400 °C and 500 °C for 3h. The calcined LDH achieved higher adsorption than uncalcined because of the reconstruction of the LDH structure. The investigation of the pH effect showed, increasing pH of the solution leads to a decline in the removal of MO gradually. The highest removal obtained at pH 3 and pH 10 provided the lowest removal (figure 2.16). At low pH, hydrogen ions  $H^+$  dominant and make the surface of LDH positive charge, which generates electrostatic forces with anionic dyes, so neutral or weak acid conditions consider the optimal to adsorb MO.

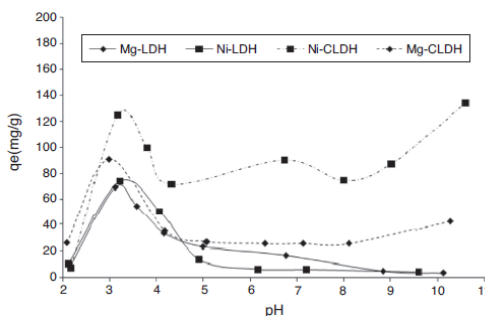


Figure 2.16 The influence of pH solution on the removal of MO into LDHs [42]

For MB and MG, the removal efficiency increases with increasing pH of the solution. At pH 10 Ni/Fe- LDH achieved removal up to 35  $mg.g^{-1}$  and 90  $mg.g^{-1}$  for MB and MG respectively, and for Mg/Fe-LDH removal reached up to 10  $mg.g^{-1}$  and 100  $mg.g^{-1}$  for MB and MG respectively figures (2.17- 2.18). It is concluded that when pH of solution is less than zero charge point, the hydrogen ions promote electrostatic attraction force with negatively charged pollutants, and when pH of solution is more than point zero charge, the hydroxide ions are dominant which is favorable to adsorb the cationic pollutants.

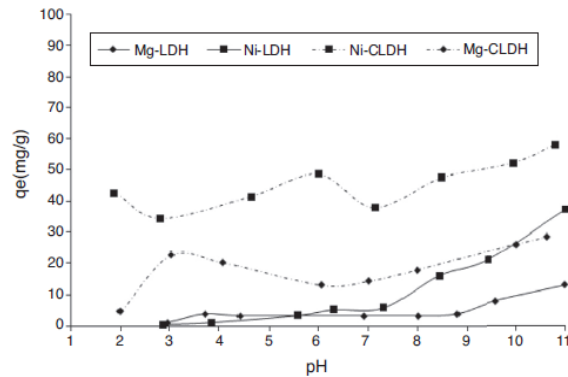


Figure 2.17 The influence of pH on the removal of MB onto LDHs [42]

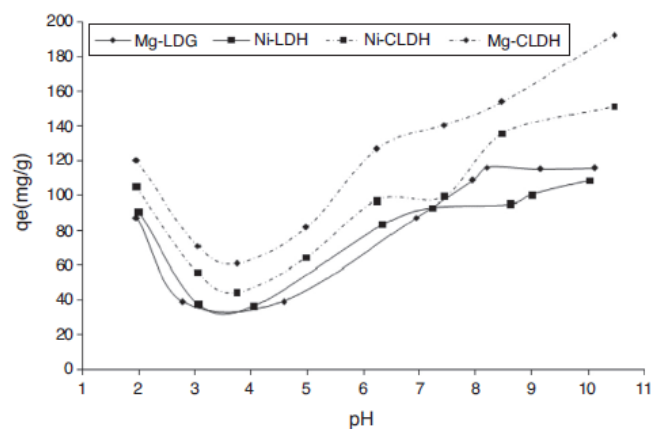


Figure 2.18 The influence of pH solution on the removal of MG onto LDHs [42]

Ashekuzzaman and Jiang [43], applied calcined and uncalcined Mg/Fe-LDH as advanced treatment units in the wastewater treatment plant to remove and recover phosphate. The adsorbent Mg-Fe/Cl-LDH was synthesized using the co-precipitation method followed by calcination at 450 °C for 2 h. The result showed that calcined LDH with dosage 2 g/l at pH from 3 to 7.5 achieved phosphate removal efficiency up to 99% (figure 2.19). The pH effect was also investigated at different pH values from 3 to 11 (figure 2.20), and the respective results indicated tht the speciation of phosphate plays an important role in the adsorption process. For pH 3 to 11,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  are dominant species and it is the  $\text{H}_2\text{PO}_4^-$

anions (at pH 3-7.5) that are adsorbed easily by ion exchange with  $\text{Cl}^-$  ions in the interlayers of LDH. An increase in pH caused decreased removal because of high competition between  $\text{OH}^-$  and  $\text{HPO}_4^{2-}$  ions. It is concluded that the speciation of a phosphate with pH affects its removal efficiency using LDH.

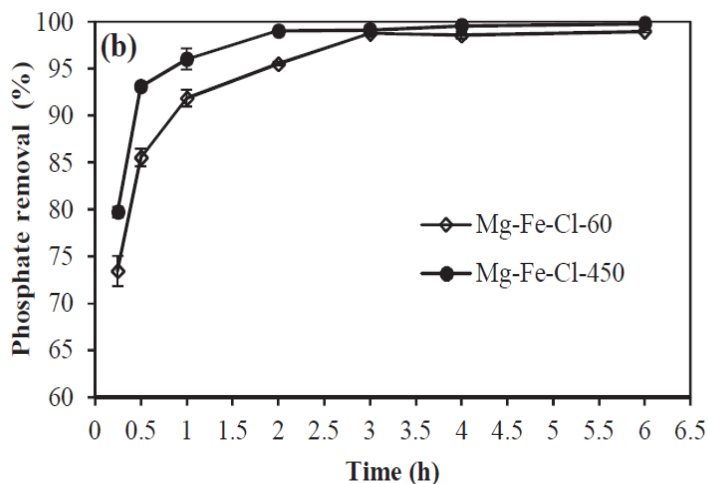


Figure 2.19 The removal efficiency of phosphate as a function of time [43]

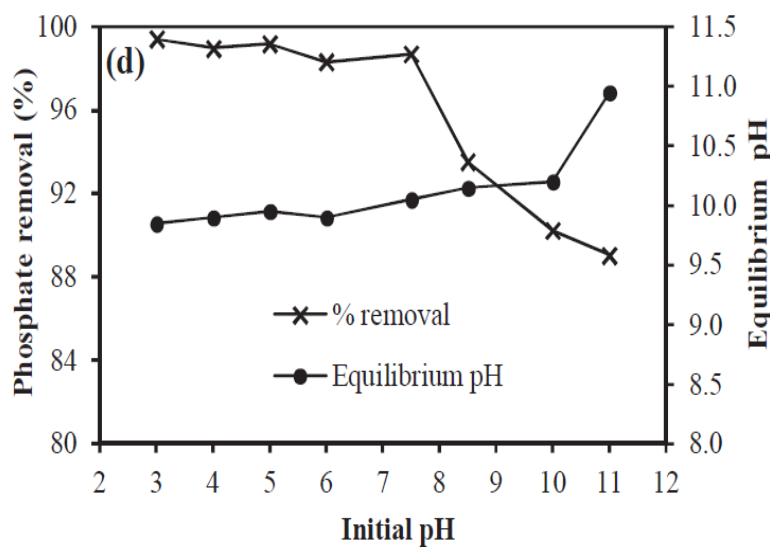


Figure 2.20 The removal efficiency of phosphate as a function of pH [43]

Table 2.2 summarizes the use of Mg/Fe LDH as an adsorbent with different pollutants.

[Table 2.2 Different applications of Mg/Fe LDH as adsorbent]

| LDH                   | Pollutant | Method/Calcination        | Ratio<br>(M <sup>+2</sup> /M <sup>+3</sup> ) | Surface<br>Area         | Dosage                          | Conc                          | Solution<br>pH    | Comment                                                                                                                                                                                                                                                                | Ref  |
|-----------------------|-----------|---------------------------|----------------------------------------------|-------------------------|---------------------------------|-------------------------------|-------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Mg/Fe<br>hydrotalcite | Selenite  | Co-precipitation / 0 C°   | 2:1                                          | 59 m <sup>2</sup> /g    | 1g/l – 5 g/l                    | 50 mg/l                       | 3 to 10           | The removal increases with increasing dosage and decreasing the pH. At pH more than zero charge point of LDH, the adsorption had taken place, whereas the author referred that to the combined effect between chemical (anion exchange) and electrostatic interaction. | [44] |
| Mg/Fe<br>hydrotalcite | Arsenate  | Co-precipitation / 0 C°   | 3:1                                          | 1.448 m <sup>2</sup> /g | (0.1, 0.5, 1, 5, 10 and 15) g/l | (0.1, 0.3, 0.5, 1 and 2) mg/l | 3, 5, 7, 9 and 12 | Mg/Fe LDH has high removal efficiency, whereas it reduced the concentration of arsenate from 0.33 mg/l to 0.01 mg/l. The initial pH of the solution has a weak effect on the removal.                                                                                  | [45] |
| Mg/Fe LDH             | Orange G  | Co-precipitation / 500 C° | Various (2-5)                                | -                       | (0.1-1.8) g/l                   | (300-500) mg/l                | 3 to 13           | CLDH showed adsorption capacity more than LDH. The removal increased with increasing dosage. The initial pH of the solution did not affect the removal of CLDH.                                                                                                        | [46] |

|                                              |                       |                                      |            |                                                            |                  |                          |         |                                                                                                                                                                                                               |      |
|----------------------------------------------|-----------------------|--------------------------------------|------------|------------------------------------------------------------|------------------|--------------------------|---------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Mg/Fe LDH                                    | Congo red             | Separate nucleation and aging / 0 C° | 3:1        | -                                                          | 30 mg            | 100 mg CR/ 10 ml         | 1 to 10 | Mg/Fe LDH is essentially efficient in the removal of congo red. Removal decreasing with increasing pH of the solution.                                                                                        | [47] |
| Mg/Fe LDH with organic and inorganic ligands | Arsenite              | Co-precipitation / 0 C°              | 2:1        | -                                                          | 100 mg           | 0.00005 to 0.00875 mol/l | 4 to 10 | Mg/Fe LDH is efficient in the removal of arsenite at acidic pH more than alkalinity pH. PO <sub>4</sub> is preventing adsorption of arsenite more than the other ligands.                                     | [48] |
| Mg/Fe LDH                                    | Acid Brown 14 dye     | Co-precipitation / 500 C°            | 3:1        | LDH= 35.4 m <sup>2</sup> /g<br>CLDH= 131 m <sup>2</sup> /g | 0.1 g/l to 1 g/l | (0.5 – 50) mg/l          | 4 to 11 | CLDH achieved higher removal than LDH because of the high adsorption capacity. In CLDH, the initial pH of the solution did not affect the removal. The removal increased with increasing in adsorbent dosage. | [49] |
| Mg/Fe LDH                                    | Fluoride and Arsenate | Co-precipitation / (300 to 500) C°   | 1, 3 and 5 | CLDH 5,400 =145.3 m <sup>2</sup> /g                        | -                | 50 mg/l                  | 3 to 11 | CLDH with molar ratio 5, 400 C° calcination, and pH = 7 achieved highest removal efficiency with adsorption capacity 50.91 and 50.24 mg/g for fluoride and arsenate respectively.                             | [50] |

|                                                                            |                    |                          |             |                                                                        |          |                      |             |                                                                                                                                                                                                  |      |
|----------------------------------------------------------------------------|--------------------|--------------------------|-------------|------------------------------------------------------------------------|----------|----------------------|-------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| Mg/Fe LDH in a combination of adsorption modeling and solid-state analysis | Arsenate           | Co-precipitation / 0 C°  | 2:1         | 40.1 m <sup>2</sup> /g                                                 | 1 g/l    | 10 <sup>-4</sup> M   | 5.5 and 8.5 | The highest adsorption obtained at pH = 5.5. the adsorption influenced by anion exchange which formed the outer-sphere complexes.                                                                | [51] |
| Mesoporous Mg/Fe LDH nanoparticles                                         | Indigo carmine dye | Sol-gel route using CTAB | -           | 85.5 m <sup>2</sup> /g                                                 | -        | (13.98 - 55.92) mg/l | 9.5         | The maximum adsorption was 62.8 mg/g at pH = 9.5                                                                                                                                                 | [52] |
| Mg/Fe LDH                                                                  | Tungsten ion       | -                        | 3:1 and 5:1 | Fe-HT 3 = 6.5 m <sup>2</sup> /g<br><br>Fe-HT 5 = 3.2 m <sup>2</sup> /g | 0.05 g/l | 100 mg/l             | 2 to 12     | LDH with molar ratio 3 adsorbed more than LDH with molar ratio 5. The adsorption had done using ion-exchange, electrostatic force, and inner-sphere complex. The optimum pH for both LDHs was 2. | [53] |

#### **2.4.4 Photocatalytic Degradation (PCD) applications**

Vohra [54] investigated the removal of selenocyanate using  $\text{TiO}_2$  mediated photocatalytic degradation in the presence of UV light. The results showed that at pH 4, 6, and 10 the disappearance of selenocyanate results because of complex destruction followed by the formation of selenite and selenate (as the released elemental selenium is first oxidized to selenite that is further oxidized to selenate. At pH higher, selenite removal decreased due to electrostatic repulsion between negative surface charge of  $\text{TiO}_2$  and negative charge of selenite. It is concluded that  $\text{TiO}_2$  removes selenocyanate by complex destruction at basic and acidic pH.

Paredes et al. [55], investigated the removal of phenol using calcined and uncalcined Mg-Al LDH mixed with  $\text{TiO}_2$  in the photocatalysis degradation process. Mg-Al LDH was prepared using the sol-gel method and intercalated with  $\text{NO}_3^-$ . The optimum weight ratio of  $\text{TiO}_2$  and LDH was (1:1), which yielded the highest removal efficiency. Using  $\text{TiO}_2$  photocatalysis, the degradation of phenol was 72%, whereas using LDH with irradiation, the degradation was only 15%. However mixed  $\text{TiO}_2$  and LDH showed a linear increase in phenol degradation and achieved 93% removal efficiency after 2 hours. The mixed  $\text{TiO}_2$  and LDH system increased phenol removal efficiency by 21%. It is concluded that during  $\text{TiO}_2$  photocatalysis addition of LDH has positive effect on phenol removal because of, 1) increased generation of oxidant i.e., hydroxyl radicals ( $\text{OH}^\bullet$ ), and 2) increased adsorption of target pollutant.

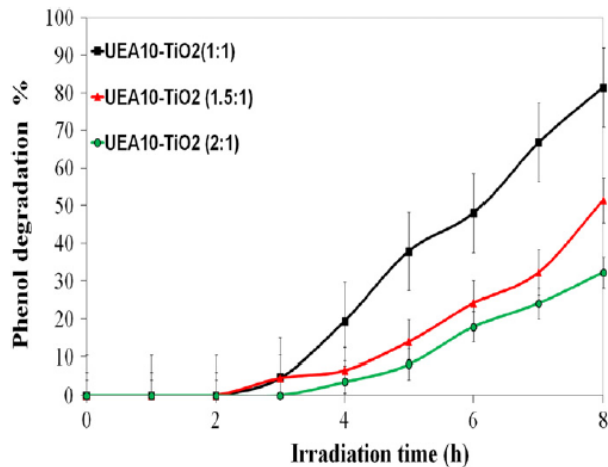


Figure 2.21 Effect of the molar ratio (LDH:TiO<sub>2</sub>) in the removal of phenol [55]

Seftel et al. [14], studied different LDH samples modified by TiO<sub>2</sub> during photocatalytic degradation for the removal of phenol and methylene blue. Four LDHs (Zn-Al LDH, Cu-Zn-Al LDH, Zn-Fe LDH, and Cu-Zn-Fe-Ti LDH) were prepared using co-precipitation method that were modified with TiO<sub>2</sub>. The experiments were performed using UV and visible light sources. The study investigated TiO<sub>2</sub>-LDH system at different pH. The zero-point charge of respective LDH was 6.5, above which the surface of adsorbent becomes negatively charged and favorable to adsorb and remove the pollutants (figure 2.22). The results showed the maximum removal efficiency at pH 10. For photocatalytic degradation, the LDHs containing Fe<sup>3+</sup> achieved maximum removal (90%) after 5 hours. For methylene blue, the TiO<sub>2</sub> with Zn-Fe LDH provided the highest removal efficiency (figure 2.23).

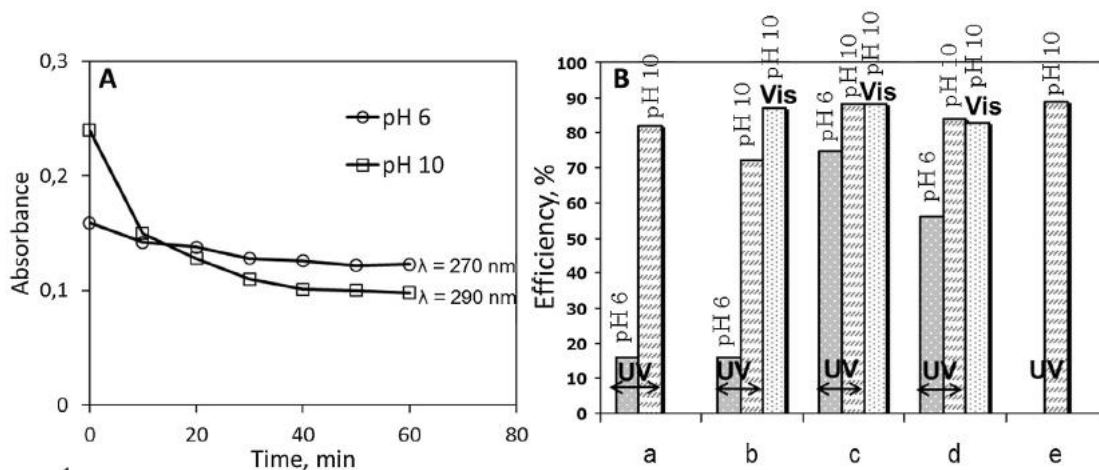


Figure 2.22 The removal of phenol on different LDHs as a function of pH[14]

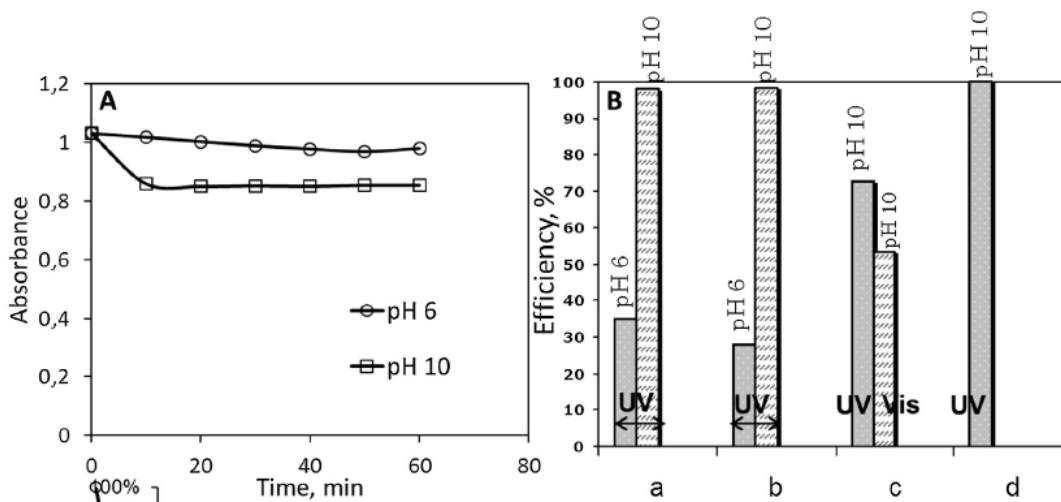


Figure 2.23 The removal of MB on different LDHs as a function of pH[14]

Parida and Mohapatra [56] investigated use of Zn-Fe LDH intercalated with  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{2-}$  during photocatalytic degradation (visible light based) to remove methyl violet (MV) and malachite green (MG) along with the effect of pH (figure 2.24). The Zn-Fe/ $\text{CO}_3$  LDH yielded the highest removal efficiency of 99% followed by 75% and 66% for Zn-Fe/ $\text{Cl}$  LDH and Zn-Fe/ $\text{NO}_3$  LDH, respectively. The superiority of  $\text{CO}_3^{2-}$  was ascribed to several

factors such as small crystal size, the ability to transfer electrons rapidly, and good pore size distribution.

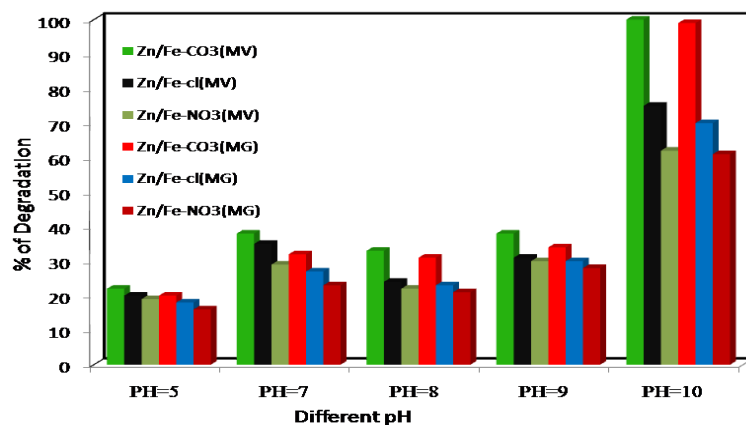


Figure 2.24 The removal of azo dyes into LDH as a function of pH [56]

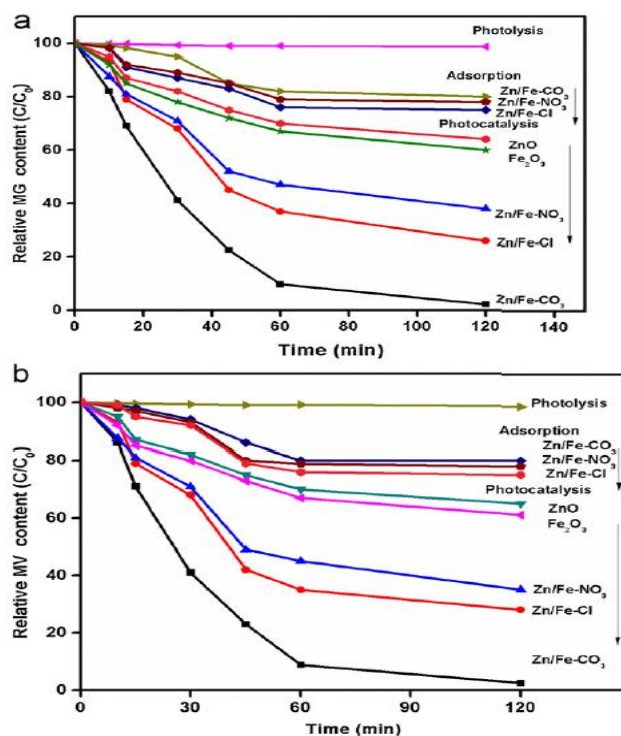


Figure 2.25 The removal of (a) methyl violet and (b) malachite green as a function of time [56]

Table 2.3 illustrates the use of TiO<sub>2</sub> LDH during photocatalytic degradation (PCD) to remove different pollutants.

Table 2.3 Different applications of TiO<sub>2</sub> mediated LDH in photocatalytic degradation

| PCD                                                                                           | Pollutant        | Method                                                                                                                                                                                                                                                     | Ratio (LDH: TiO <sub>2</sub> )         | Dosage                | Conc                     | Comment                                                                                                                                                                                                                                                                                                                                                                        | Ref  |
|-----------------------------------------------------------------------------------------------|------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------|-----------------------|--------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| TiO <sub>2</sub> – Zn/Al LDH with solar light                                                 | Rhodamine B      | Different concentrations of TiO <sub>2</sub> (1%, 2%, and 3% mass) with 0.67M of Na <sub>2</sub> CO <sub>3</sub> were loaded into calcined Zn/Al LDH (500 C°), then dried for 12 h at 100 C°.                                                              | 1%, 2% and 3% mass of TiO <sub>2</sub> | 50 mg                 | 10.02 µmol/l             | The author concluded from this study that suited amount TiO <sub>2</sub> can confirm the stability of the photocatalytic system, prevent undesired LDH memory effects, and improving photocatalytic performance in solar light. Also, the author concluded advantages of TiO <sub>2</sub> – Zn/Al LDH novelty: simple preparation, low cost, high photodegradation efficiency. | [57] |
| (1) Calcined Mg/Al-LDH in TiOSO <sub>4</sub> .xH <sub>2</sub> O and (2) Calcined Mg/Al/Ti-LDH | Methyl-blue (MO) | For (1) the material got by mixing LDH with 0.01 M of TiOSO <sub>4</sub> .xH <sub>2</sub> O for 1h under vigorous stirring. For (2), the three cationic elements mixed with ratio (Mg: Al: Ti) (3:0.5:0.5) using Co-precipitation method then calcination. | (Mg: Al: Ti) = (3:0.5:0.5)             | 4 ×10 <sup>-5</sup> M | (1) 1 g/l<br>(2) 0.5 g/l | Calcined Mg/Al/Ti-LDH had shown a powerful photocatalytic effect because of the good distribution of TiO <sub>2</sub> nanoparticles on the LDH and removed up to 93 % of methyl blue.                                                                                                                                                                                          | [58] |
| LDH-VB9-TiO <sub>2</sub>                                                                      | methylene blue   | 100 mg of LDH -VB9 added to 10 ml of DIW under sonication for 15 min. Same steps for TiO <sub>2</sub> , then they mixed for 30 min under sonication and dried for 24 h.                                                                                    | 1:1                                    | 10 mg/l               | 100 mg                   | The author reported that LDH-VB9-TiO <sub>2</sub> in nanosheet structure has a significant effect on the photodegradation process.                                                                                                                                                                                                                                             | [59] |

|                                        |                          |                                                                                                                                                                                                                                                            |                              |              |         |                                                                                                                                                                                                                                                                                                     |      |
|----------------------------------------|--------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|--------------|---------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| TiO <sub>2</sub> /Zn-LDH nanoparticles | phenol                   | 1.5 g of calcined LDH mixed by stirring with 0.01 M/L of TiOSO <sub>4</sub> under the presence of nitrogen, then dried followed by calcination at 800 °C.                                                                                                  | 1:1                          | 0.425 mmol/l | 0.5 g   | The author concluded that TiO <sub>2</sub> /Zn-LDH improved the photodegradation performance because the nanostructure of the material enhanced light-harvesting and generation of electron-hole pairs.                                                                                             | [60] |
| Organic LDH/TiO <sub>2</sub>           | Dimethyl phthalate (DMP) | The hydrothermal method had been followed. 1 g/l of TiO <sub>2</sub> was added drop-Wiseley to 1 g/l of LDH in suspension for 24 h. The obtained material calcined at 500 °C for 4h then added to 10 g/l of SDS in stirring for 24 h at 60 °C and pH = 10. | 4:1, 4:2, 4:3, 4:4, 3:4, 2:4 | 50 µmol/l    | 0.4 g   | The impregnate of DMP into Organic LDH/TiO <sub>2</sub> and his hydroxyl groups produced significant effects that resulted in improving the photocatalysis degradation process.                                                                                                                     | [61] |
| CeO <sub>2</sub> /ZnTi-LDH             | phenol                   | 1 g of calcined Zn/Ti-LDH (550 °C for 14 h) had added to 0.1 M of Ce (SO <sub>4</sub> ).4H <sub>2</sub> O at pH =9 then dried and followed by calcination at 750 °C for 8 h.                                                                               | -                            | 50 mg/l      | 0.5 g/l | The composition of this type of LDH provided significant effects in the photodegradation performance. The structure of LDH provided advantages like manipulation of LDH composition and supplement of key cations, moreover, it provided a good distribution of metal cations on the layers of LDH. | [62] |

|                                                                                          |        |                                                                                                                                                           |      |         |       |                                                                                                                                                                                                                                                                                                      |      |
|------------------------------------------------------------------------------------------|--------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|------|---------|-------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|
| TiO <sub>2</sub> -Mg/Al LDH, TiO <sub>2</sub> -Mg/Fe LDH and TiO <sub>2</sub> -Zn/Al LDH | phenol | TiO <sub>2</sub> mixed with calcined LDH (550 °C for 3.5 h) in ethanol at a weight ratio (1:10) in vigorous stirring for 3 h then dried at 100 °C for 2 h | 1:10 | 10 mg/l | 1 g/l | The results showed TiO <sub>2</sub> -Zn/Al LDH was the best from a one-time test and TiO <sub>2</sub> -Mg/Fe LDH is the best after 10 times of testing. The uptake of phenol onto TiO <sub>2</sub> -Zn/Al LDH and TiO <sub>2</sub> -Mg/Fe LDH was close and better than TiO <sub>2</sub> -Mg/Al LDH. | [63] |
|------------------------------------------------------------------------------------------|--------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|------|---------|-------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|

From the above literature review, it can be concluded that the removal of selenite and selenate onto LDH is increased for calcined LDH, which provided a high adsorption capacity resulting from the removal of interlayer anions and water molecules. An increase in the LDH dosage also increased the removal efficiency. The removal of selenite and selenate transpired via adsorption and ion-exchange and was function of point of zero charge of LDH and solution pH. Higher removal was noted at pH values less than the point of zero charge, because at these pH values the positive surface sites made it favorable to adsorb anionic pollutants. However, as per the existing literature review, no study has investigated selenocyanate ( $\text{SeCN}^-$ ) removal efficiency using LDH. Furthermore the application of  $\text{TiO}_2\text{-Mg/Fe}$  LDH system to remove selenocyanate is also not reported. However, considering the possible efficiency of combined  $\text{TiO}_2\text{-Mg/Fe}$  LDH photocatalysis and adsorption system for aqueous phase selenocyanate treatment, it is of interest to explore this research study.

## CHAPTER 3

### OBJECTIVES

#### 3.1 Objectives

The objective of this work is to investigate combined adsorption and photocatalytic degradation using  $\text{TiO}_2\text{-MgFe/NO}_3$  LDH to remove aqueous phase selenocyanate. Photocatalytic degradation using  $\text{TiO}_2$  generates hydroxyl radicals ( $\text{OH}^\bullet$ ), which oxidize selenocyanate to selenite and selenate [54], which then can be adsorbed onto LDH. So, the specific objectives are:

- 1- To investigate photocatalytic degradation of selenocyanate using  $\text{TiO}_2\text{-Mg/Fe}$  LDH.
- 2- To optimize photocatalytic degradation using different dosages of  $\text{TiO}_2\text{-Mg/Fe}$  LDH, at different weight ratios ( $\text{LDH}:\text{TiO}_2$ ), and different concentrations of selenocyanate.
- 3- To investigate the adsorption of selenite, selenite, and selenocyanate onto  $\text{Mg/Fe}$  LDH.
- 4- To optimize adsorption based removal using different  $\text{Mg/Fe}$  LDH dosages, different calcined LDH, and different concentrations of selenite, selenite, and selenocyanate.

|

## CHAPTER 4

### MATERIALS AND METHODOLOGY

#### 4.1 Materials

All chemicals used in this work were of high purity reagent-grade quality (> 95%). The chemicals include magnesium nitrate hexahydrate, and ferric nitrate (sigma Aldrich Co Germany), potassium selenate, sodium selenite, and potassium selenocyanate (Aldrich USA), titanium dioxide powder (P25 DEGUSSA Germany), potassium cyanide, cyanate, nitrate, sodium carbonate, sodium bicarbonate, sodium hydroxide, and hydrochloric acid.

Some hardware used included standard pH meter, physical balance, magnetic stirrer, Pyrex conical flasks, Pyrex round-bottom flask, Pyrex bottles, shaker, centrifuge, furnace, Ion Chromatograph, and UV reactor for photocatalytic degradation (PCD) as illustrated in figure 4.1. The PCD reactor (Pyrex glass) had a height 30 cm, and a diameter 7 cm, with a glass sleeve to hold the UV lamp.

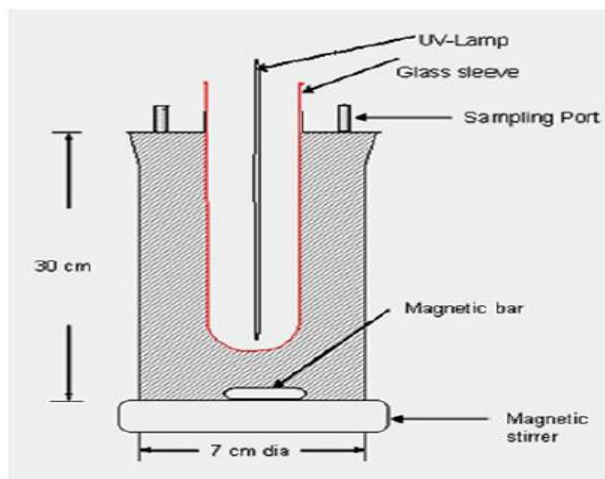


Figure 4.1 Reactor setup for photocatalytic degradation [54]

## **4.2 Method**

### **4.2.1 LDH synthesis**

LDH was synthesized using the co-precipitation method at Mg:Fe molar ratio of 3:1, using 3.85 g of magnesium nitrate and 2.02 g of ferric nitrate that were added to 50 ml of DI water in a round-bottom flask, which was then heated for 15 min in oil bath heater at temperature 60 °C along with stirring at 600 rpm. After that 1M NaOH was added dropwise to increase the pH up to  $10 \pm 0.5$ . This was followed by the reflux procedure at 90 °C and 900 rpm. After 24 hours the sample was collected for centrifugation then washed 2 times with water and ethanol to remove impurities and centrifuged each time and dried in an oven at 80 to 90 °C for 48 hours. The obtained material was grinded to powder and then calcined at 250 and 500 °C and stored.

### **4.2.2 TiO<sub>2</sub> modified LDH Preparation**

TiO<sub>2</sub> modified LDH was prepared with different weight ratios (TiO<sub>2</sub>: LDH): (1:0.5), (1:1), and (1:1.5). For all ratios, appropriate amounts of LDH (10 mg/l) and TiO<sub>2</sub> (10 mg/l) were suspended separately in glass beakers under vigorous stirring for 10 min, then the TiO<sub>2</sub> solution was added slowly to LDH solution and kept in suspension for 48 h, and then centrifuged & then dried at 80 °C for 24 h. The obtained material was heated for 5 hours at 250 °C for calcination then stored.

### **4.2.3 Adsorption Experiments**

Stock solutions of selenocyanate, selenate, and selenite (1000 ppm) were prepared using high purity reagents (as mentioned above) that were subsequently used to prepare the synthetic wastewater samples for respective adsorption (and also the photocatalysis)

studies. The experiments were divided into three batches. Each batch included 9 bottles (each with 10 ml sample). A 10 ml blank sample was also taken. All bottles were covered using aluminum foil to prevent reaction between selenium species and external light. The initial pH of the samples was measured and then the desired amounts of LDH and calcined LDH were added. The bottles were placed on the shaker at a rotational speed of 250 rpm for 6 days. On the 6<sup>th</sup> day, the final pH of samples was measured, then the samples were collected using clean and sterilized syringes, filtered through 0.2  $\mu\text{m}$  membrane filter, and stored before analysis.

#### **4.2.4 Photocatalytic degradation (PCD) Experiments**

First, a stock solution of selenocyanate with 1000 ppm concentration was prepared from high purity potassium Selenocyanate reagent. For all PCD experiments, the required selenocyanate concentrations were obtained using the above-mentioned stock solution. For each experiment, 1.1 L of selenocyanate solution was prepared, and 1000 ml was added to the reactor and 100 ml was taken as a blank. The reactor was covered using aluminum foil to prevent reaction with the external light. Two blanks were also collected, one blank before adding  $\text{TiO}_2$ -LDH and another blank 30 min after adding  $\text{TiO}_2$ -LDH along with constant stirring (but before exposure to UV lamp light). The initial pH of the solution was also measured after 30 min of stirring. After that, the photocatalytic degradation was started in the presence of UV light (15 W and wavelength (315 - 400) nm). The samples were collected at different times (0 to 360) min using cleaned and sterilized syringes then filtered through 0.2  $\mu\text{m}$  membrane filter and stored for analysis using the Ion Chromatograph instrument.

#### 4.2.5 Response Surface Methodology (RSM)

Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes. Its used when various variables potentially affect some performance measure or quality characteristic of the process. The performance measure represents a **response**, and the variables represent **independent variables** [64].

In this work, RSM was used to make the Design of Experiment for both Adsorption experiments and Photocatalytic Degradation experiments to achieve the objectives of this study. For the adsorption experiments, the following independent variables were employed; calcination temperature, adsorbent dosage, and concentration of selenium species. For the photocatalysis experiments the variables were the weight ratio, adsorbent dosage and concentrations of selenocyanate. The central composite design RSM with a face-centered single center point approach was used to create design of experiment for the adsorption (table 4.1) and for photocatalytic degradation systems (table 4.2).

Table 4.1 Design of Experiment for the Adsorption Experiments

| Calcination (°C) | Dose (g/l) | SeO <sub>3</sub> (ppm) | SeO <sub>4</sub> (ppm) | SeCN (ppm) |
|------------------|------------|------------------------|------------------------|------------|
| 500              | 1.5        | 7.5                    | 2.5                    | 2.5        |
| 0                | 0.5        | 2.5                    | 2.5                    | 7.5        |
| 500              | 0.5        | 7.5                    | 7.5                    | 2.5        |
| 0                | 0.5        | 2.5                    | 7.5                    | 2.5        |
| 250              | 1          | 5                      | 5                      | 7.5        |
| 250              | 1.5        | 5                      | 5                      | 5          |
| 0                | 0.5        | 7.5                    | 7.5                    | 7.5        |
| 250              | 1          | 7.5                    | 5                      | 5          |
| 500              | 1          | 5                      | 5                      | 5          |
| 500              | 0.5        | 7.5                    | 2.5                    | 7.5        |
| 0                | 1.5        | 7.5                    | 7.5                    | 2.5        |
| 250              | 1          | 5                      | 5                      | 5          |
| 500              | 1.5        | 2.5                    | 2.5                    | 7.5        |
| 0                | 1.5        | 2.5                    | 2.5                    | 2.5        |
| 250              | 1          | 5                      | 2.5                    | 5          |
| 250              | 1          | 5                      | 7.5                    | 5          |
| 0                | 1          | 5                      | 5                      | 5          |
| 0                | 1.5        | 7.5                    | 2.5                    | 7.5        |
| 0                | 0.5        | 7.5                    | 2.5                    | 2.5        |
| 0                | 1.5        | 2.5                    | 7.5                    | 7.5        |
| 500              | 1.5        | 7.5                    | 7.5                    | 7.5        |
| 250              | 1          | 5                      | 5                      | 2.5        |
| 500              | 0.5        | 2.5                    | 2.5                    | 2.5        |
| 250              | 0.5        | 5                      | 5                      | 5          |
| 500              | 0.5        | 2.5                    | 7.5                    | 7.5        |
| 250              | 1          | 2.5                    | 5                      | 5          |
| 500              | 1.5        | 2.5                    | 7.5                    | 2.5        |

Table 4.2 Design of Experiment for the Photocatalytic Degradation Experiments

| Ratio | Dose (g/l) | SeCN (ppm) |
|-------|------------|------------|
| 1.5   | 1          | 7.5        |
| 1     | 2          | 5          |
| 0.5   | 2          | 2.5        |
| 1     | 1.5        | 7.5        |
| 1     | 1.5        | 2.5        |
| 0.5   | 2          | 7.5        |
| 1     | 1.5        | 5          |
| 1.5   | 2          | 7.5        |
| 0.5   | 1          | 2.5        |
| 0.5   | 1.5        | 5          |
| 1.5   | 2          | 2.5        |
| 1.5   | 1.5        | 5          |
| 1     | 1          | 5          |
| 0.5   | 1          | 7.5        |
| 1.5   | 1          | 2.5        |

#### 4.2.6 Analytical Method

The ion chromatograph equipment (Metrohm, Switzerland) equipped with conductivity and amperometric detectors and anion Dual 2 IC column was used to analyze (SeCN<sup>-</sup>), Selenite (SeO<sub>3</sub><sup>2-</sup>), Selenate (SeO<sub>4</sub><sup>2-</sup>), Nitrate (NO<sub>3</sub><sup>-</sup>), Cyanate (OCN<sup>-</sup>) and Cyanide (CN<sup>-</sup>). The amperometric detector was used to detect Cyanide (CN<sup>-</sup>). For the conductivity detector, the eluent composition was 3 mM of NaHCO<sub>3</sub> and 2.7mM of Na<sub>2</sub>CO<sub>3</sub>. Cyanide was analyzed using the amperometric detector with 100 mM of NaOH as eluent. The IC system was calibrated using calibration standards with various concentrations prepared from the stock solutions.

## CHAPTER 5

### RESULTS AND DISCUSSION

#### 5.1 Characterization

##### 5.1.1 XRD of calcined and uncalcined LDHs

The X-Ray diffraction results for the Mg/Fe LDH are shown in figure 5.1. The diffractograms shows peaks at 7.855 Å ( $d_{003}$ ), 3.909 Å ( $d_{006}$ ), 2.646 Å ( $d_{012}$ ), 1.558 Å ( $d_{110}$ ) (2) and 1.529 Å ( $d_{113}$ ) corresponding to  $2\theta = 11.256^\circ$ ,  $22.73^\circ$ ,  $33.847^\circ$ ,  $59.244^\circ$  and  $60.49^\circ$  respectively, which agree with the peaks obtained from previous studies [42], [46]. These peaks indicate that uncalcined LDH has high crystallinity, hexagonal structure with a space group R3m. Also, the crystallinity of LDH is indexed to the rhombohedral structure [42]. The calcined LDH at 250 °C shown in figure 5.2 illustrates peaks at 2.626 Å and 1.567 Å corresponding to  $2\theta = 34.11^\circ$  and  $59.07^\circ$  respectively, which agree with a previous study [65]. After calcination of LDH at 250 °C, the crystallinity reduced which can be noted as the disappearance of the diffraction peak at  $d_{003}$ , which represents the water molecules in the LDH structure. The reduction in crystallinity at high temperature transpire from the removal of interlayer anions and water molecules [37]. For LDH calcined at 500 °C as shown in figure 5.3, the XRD result showed two diffraction peaks at 2.124 Å and 1.494 Å which correspond to angles  $42.53^\circ$  and  $62.09^\circ$ . These peaks are in good agreement with results observed in previous studies [46][42]. At high temperature (500 °C), the interlayer

anions and water molecules were removed, which results in the collapse of LDH structure, and the formation of MgO.

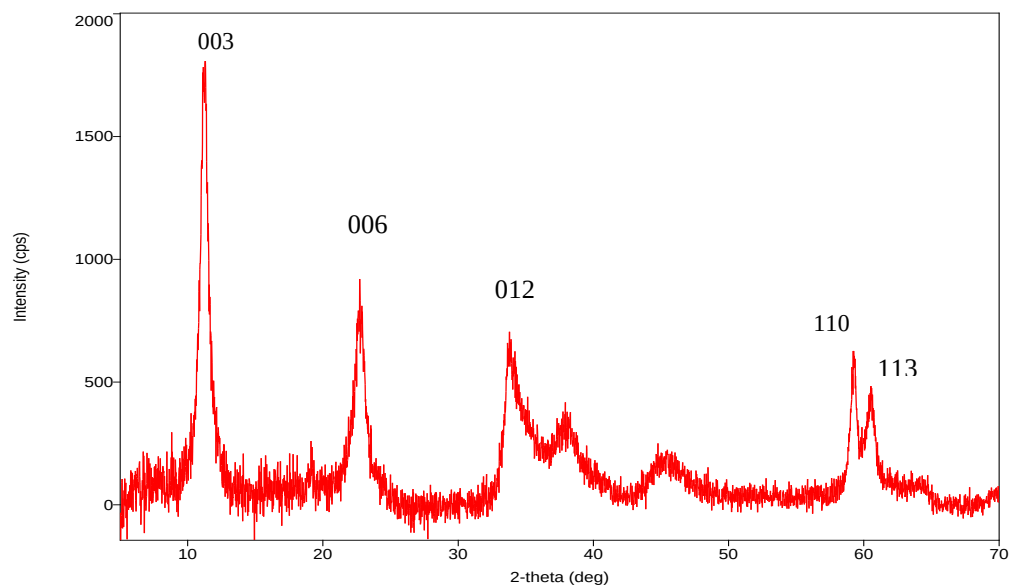


Figure 5.1 XRD of Mg/Fe LDH (uncalcined)

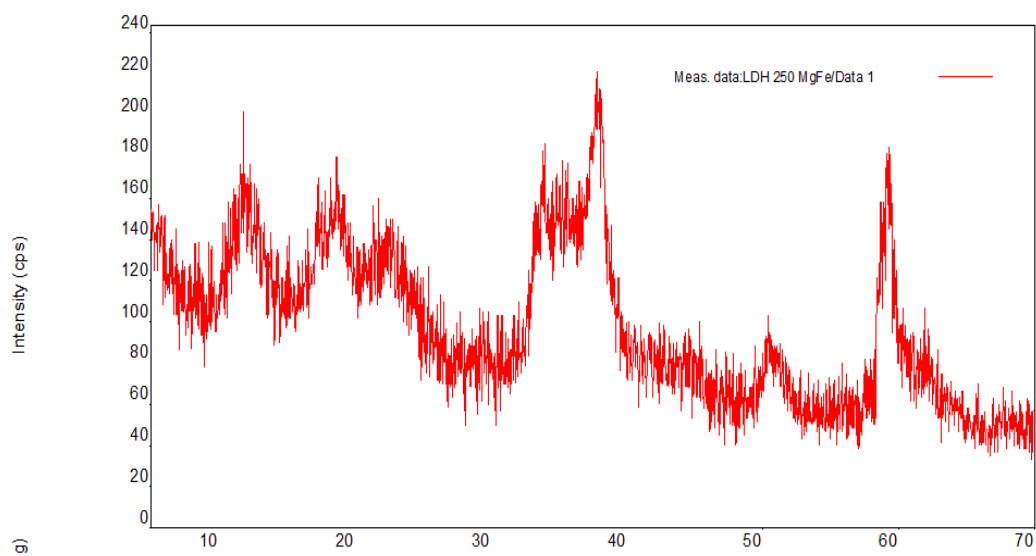


Figure 5.2 XRD of calcined Mg/Fe LDH (250 °C)

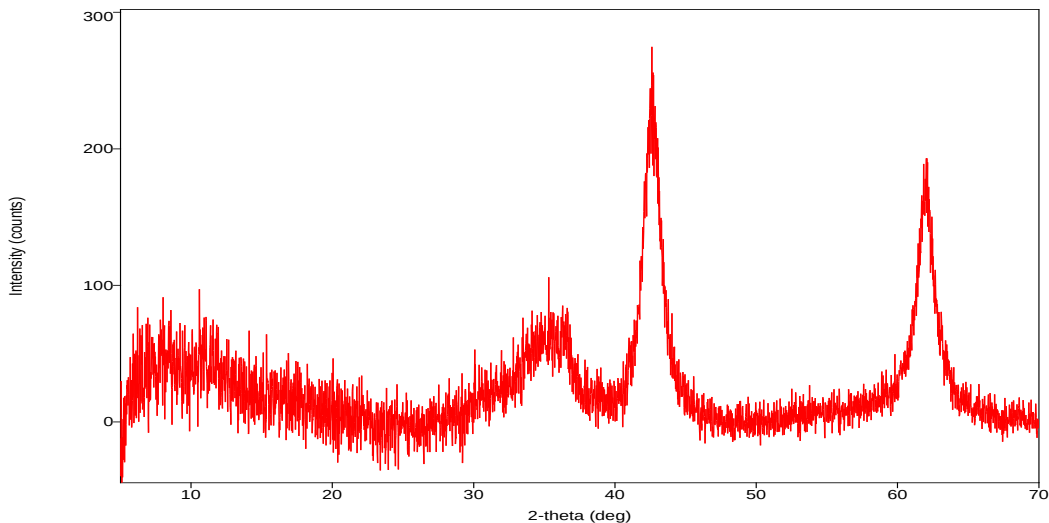


Figure 5.3 XRD of calcined Mg/Fe LDH (500 °C)

### 5.1.2 XRD of TiO<sub>2</sub>

The XRD of TiO<sub>2</sub> (DEGUSSA) shows peaks at  $2\theta = 25.57^\circ, 28.41^\circ, 37.56^\circ, 47.68^\circ, 53.71^\circ, 54.65^\circ, 62.5^\circ, 69.5^\circ, \text{ and } 74.68^\circ$  corresponding to diffraction planes (101), (110), (112), (200), (105), (211), (204), (116), and (215), respectively. These peaks are in good agreement with other peaks obtained from a previous study[66]. The obtained peaks for TiO<sub>2</sub> (DEGUSSA) indicate 75% anatase and 25% rutile.

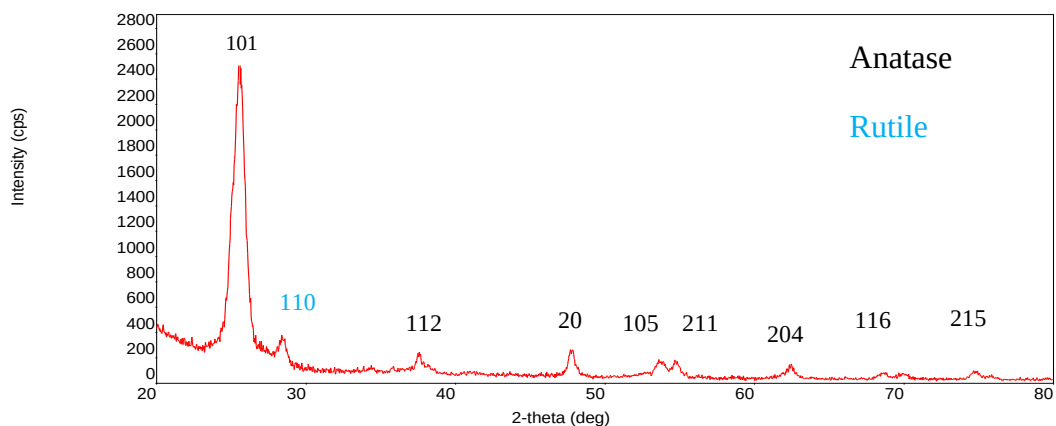


Figure 5.4 XRD of TiO<sub>2</sub> DEGUSSA

### 5.1.3 XRD of TiO<sub>2</sub>-Mg/Fe LDH calcined at 250 °C

The XRD of TiO<sub>2</sub>-Mg/Fe LDH shows many diffraction peaks, and most of these peaks relate to the anatase phase of TiO<sub>2</sub>. These diffraction peaks are 3.56 Å, 2.39 Å, 1.904 Å, 1.705 Å, 1.675 Å, 1.487 Å, and 1.269 Å, which are corresponding to the angles 24.99°, 37.59°, 47.72°, 53.71°, 54.74°, 62.39°, and 74.76° respectively. For Mg/Fe LDH, the diffraction peaks are 7.90 Å, 2.651 Å and, 59.011 Å, which are corresponding to the angles; 11.19°, 33.78°, and 59.011° respectively. The obtained diffractions peaks are in good matching with the other diffraction peaks from the previous study[63].

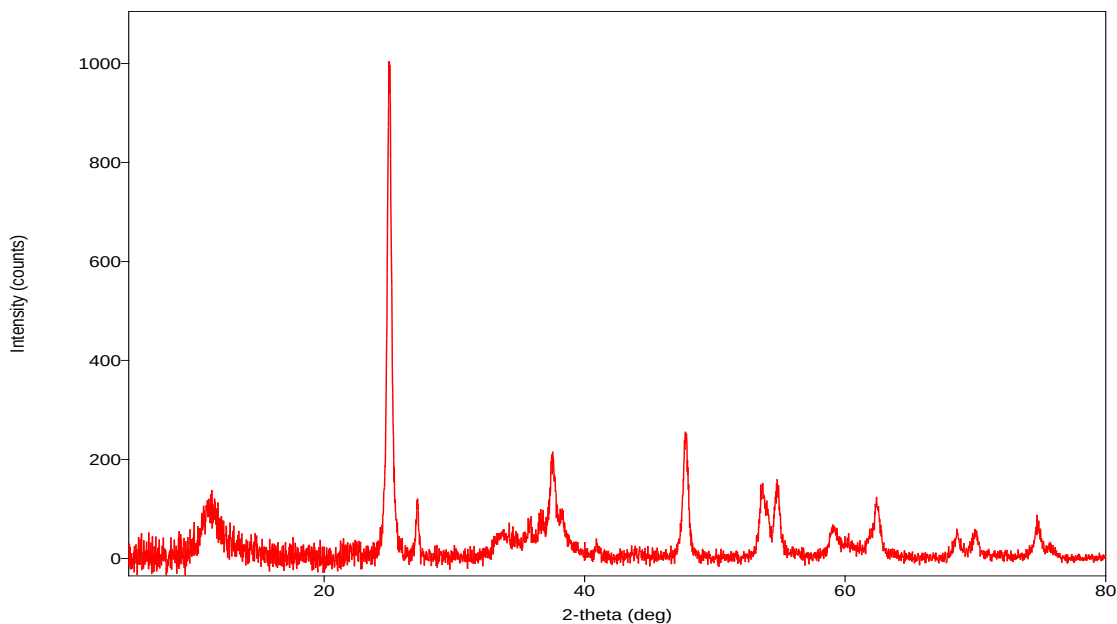


Figure 5.5 XRD of TiO<sub>2</sub>-Mg/Fe LDH calcined at 250 °C

#### 5.1.4 FESEM of calcined and uncalcined LDH

FESEM images of uncalcined Mg/Fe LDH as shown in figure 5.6, indicate that the LDH crystals are arranged in a sheet-like hexagonal structure; these images support the XRD results. The sheets are arranged such because of electrostatic attraction force generated between interlayer nitrates anions (negative charge) and metal hydroxides (positive charge) presence on the surface of LDH [67]. For LDH calcined at 250 °C as shown in figure 5.7, the crystals slightly lost the hexagonal structure with the appearance of cracks on the surface of the crystals, and the appearance of some pores resulting from the removal of water molecules and some interlayer nitrates anions. For 500 °C calcined Mg/Fe LDH as illustrated in figure 5.8, the hexagonal structure of the crystals is destroyed because of the removal of interlayers nitrates anions and water molecules which also result in the disordering shapes. The removal of interlayers means an increase in the adsorption capacity of the material.

EDX Spectrum accompanies FESEM as shown in figure 5.9, clearly illustrates the presence of magnesium and iron as the highest components. For the uncalcined LDH, LDH calcined at 250 °C, and LDH calcined at 500 °C, as shown in tables (5.1 to 5.3), the atomic percentage of magnesium was 18.65%, 20.85%, and 20.82%, respectively, and atomic percentage of iron was 6.56%, 7.63%, and 5.94%, respectively. These numbers are in agreement with the molar ratio (3:1), which was used to synthesize the LDH. Also, we can notice the reduction in oxygen percentage, which is an indicator of water molecules removal. Also, a slight increase in magnesium percentage in LDH calcined at 500 °C is an indicator of MgO formation.

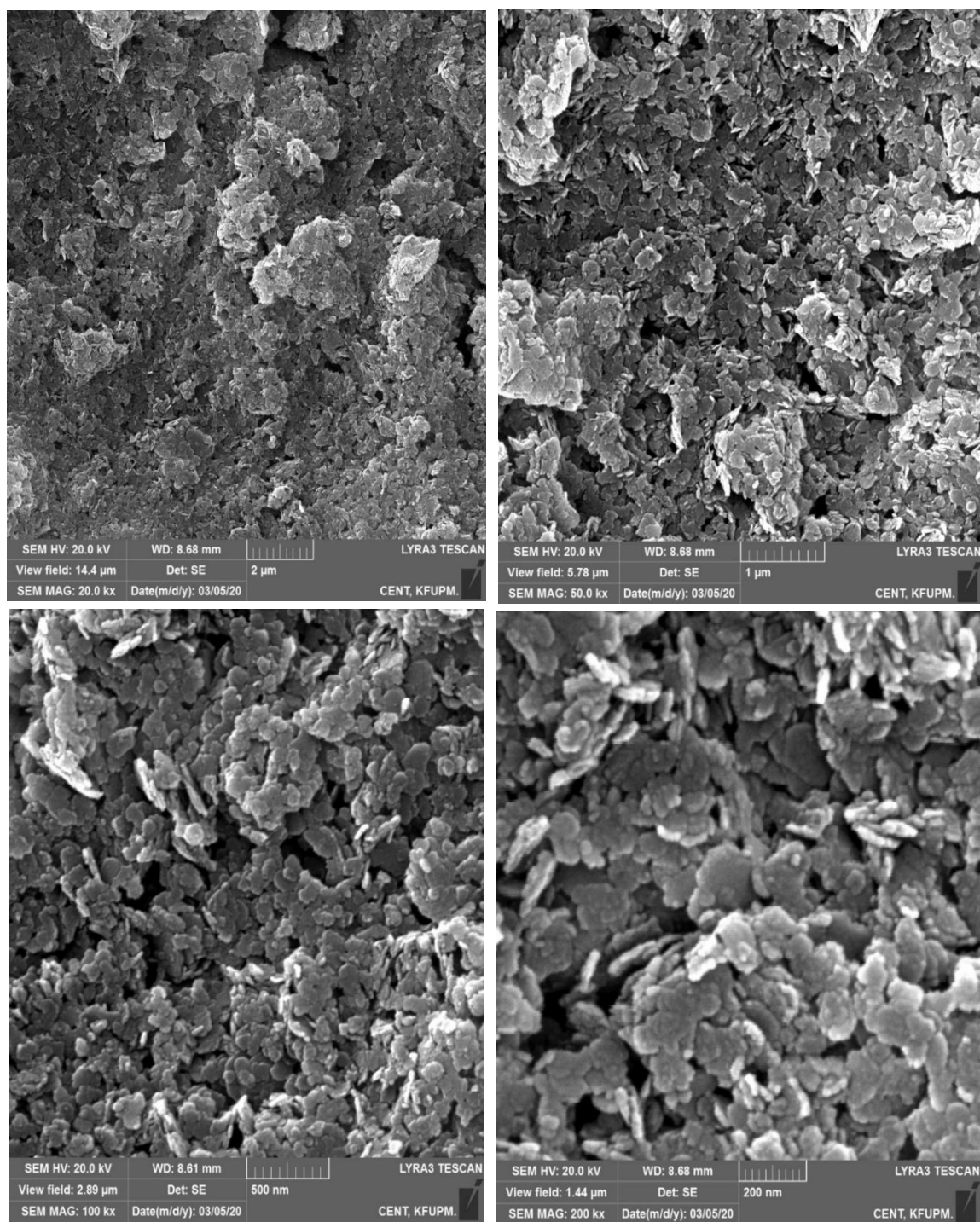


Figure 5.6 FESEM images of uncalcined Mg/Fe LDH

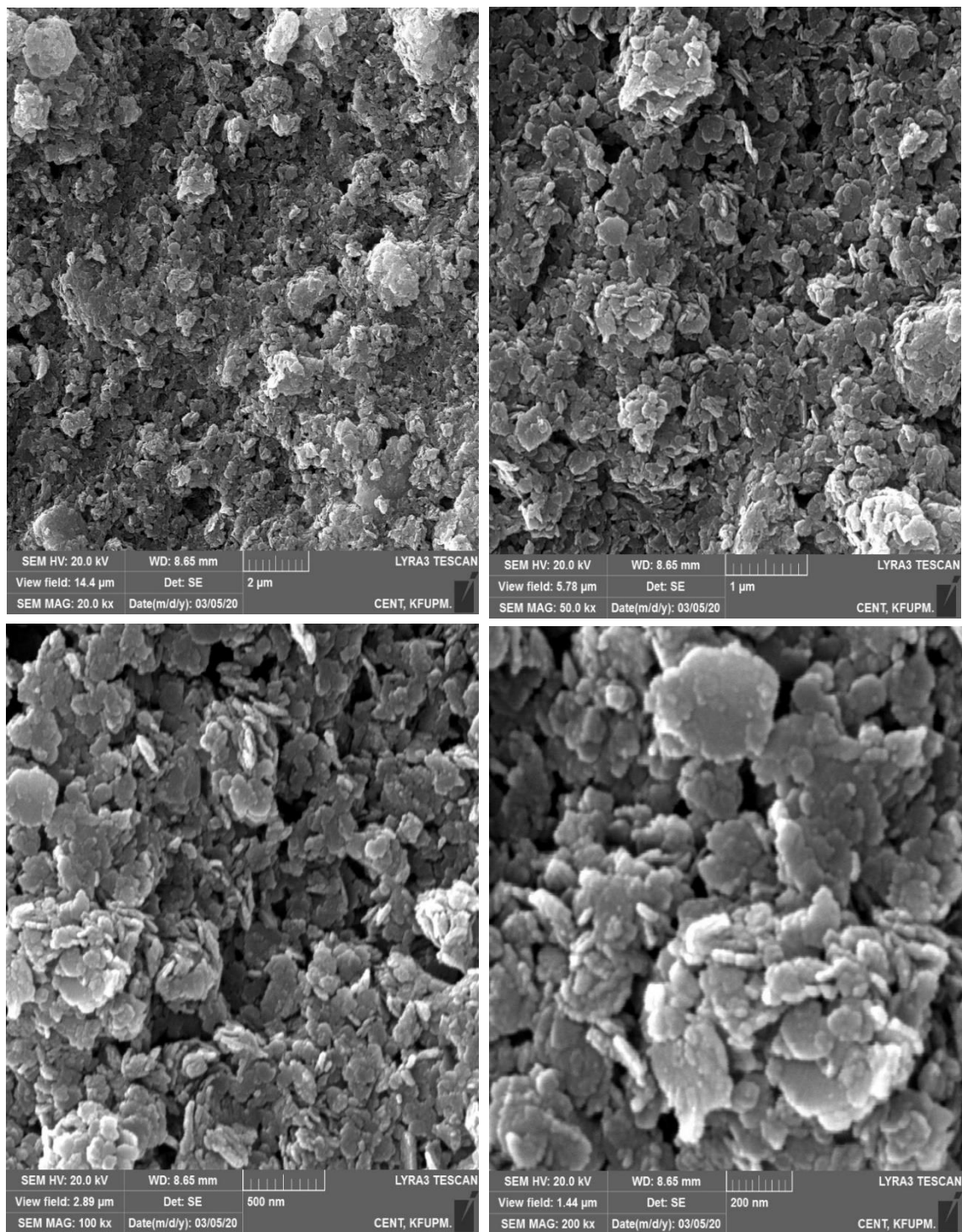


Figure 5.7 FESEM images of calcined Mg/Fe LDH (250 °C)

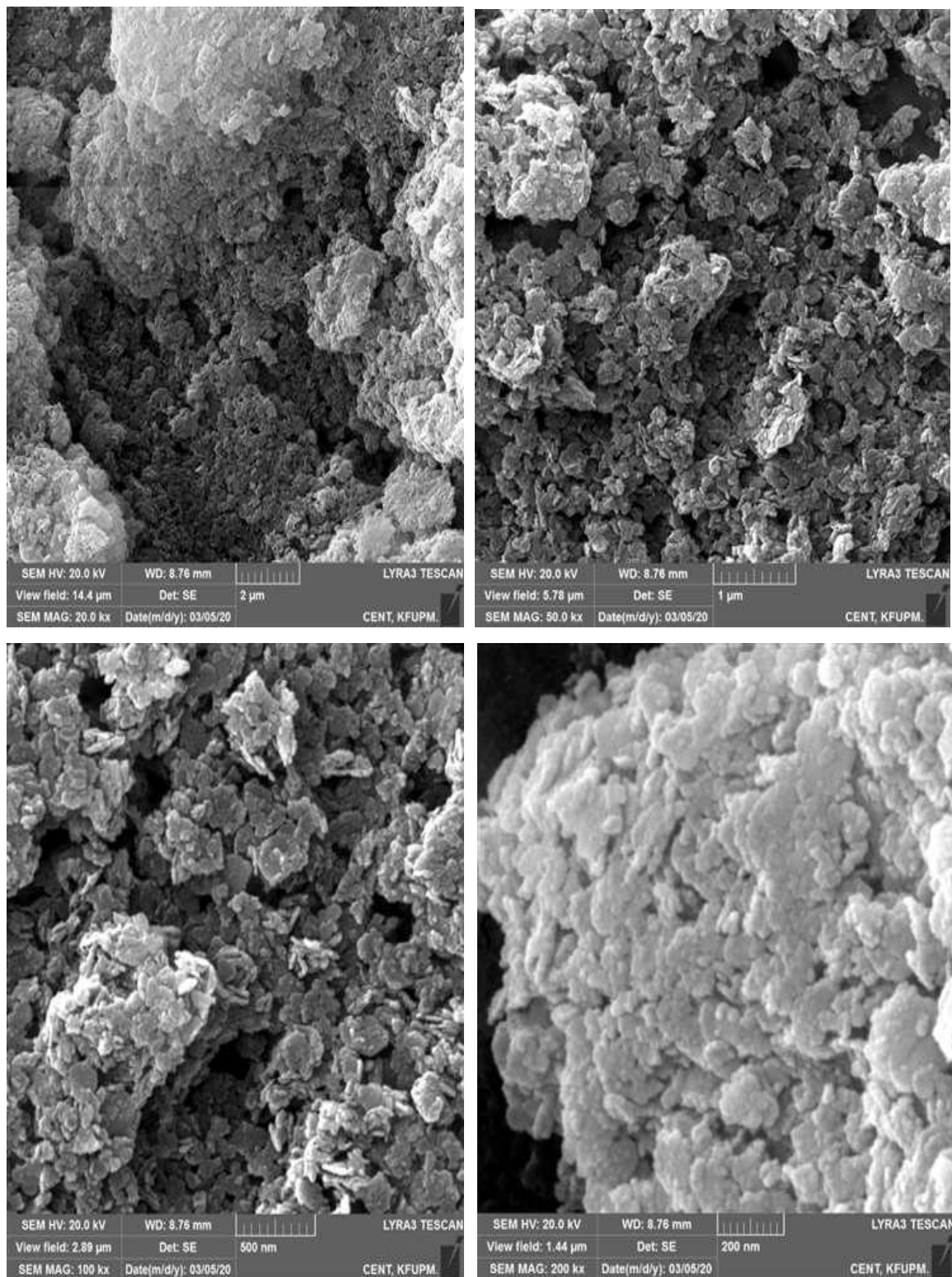


Figure 5.8 FESEM images of calcined Mg/Fe LDH (500 °C)

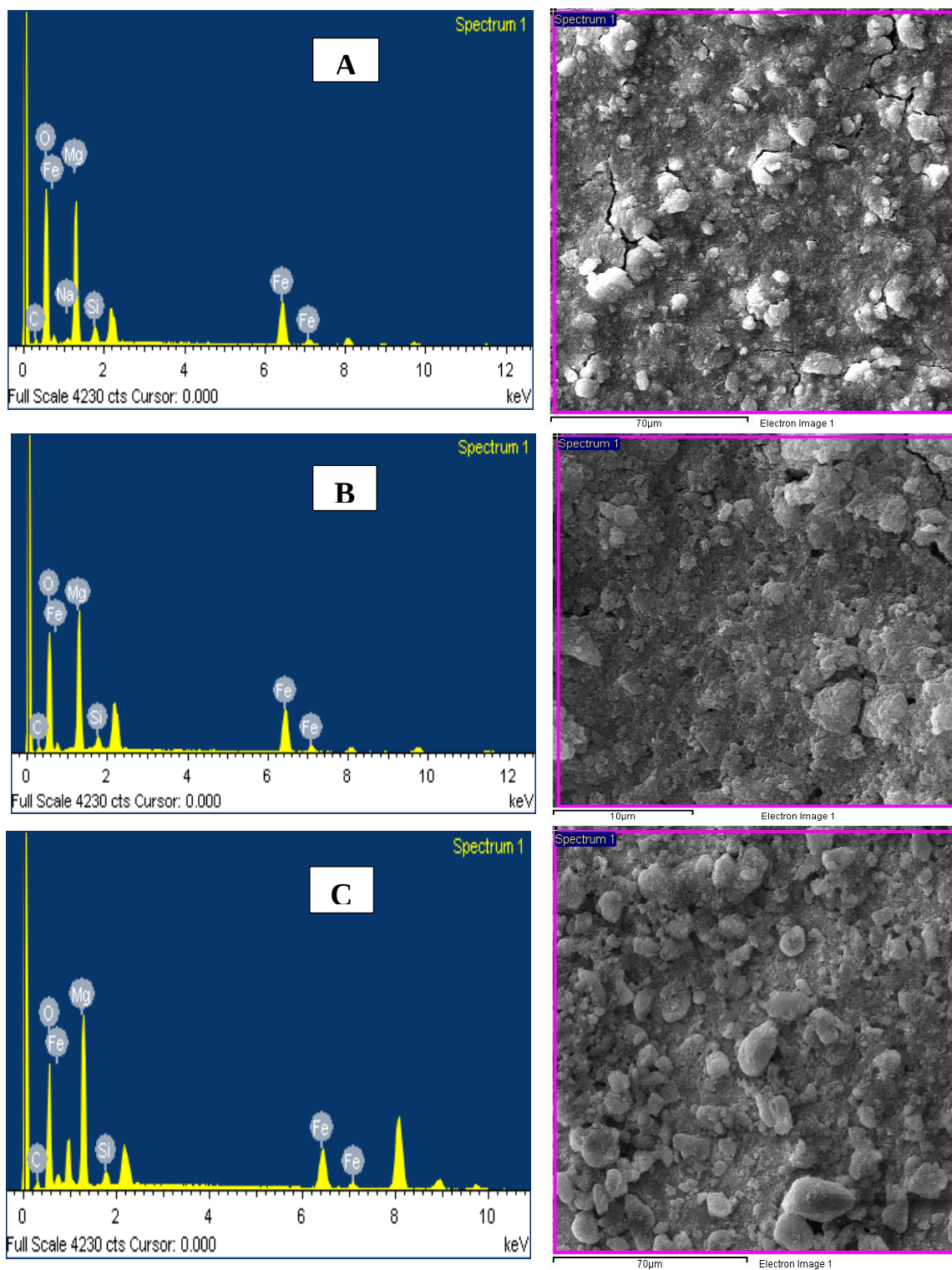


Figure 5.9 EDX spectrum of (A) uncalcined LDH (B) 250 °C calcined LDH (C) 500 °C calcined LDH

Table 5.1 EDS of uncalcined LDH components

| <b>Element</b> | <b>weight %</b> | <b>Atomic %</b> |
|----------------|-----------------|-----------------|
| <b>C k</b>     | 7.95            | 13.16           |
| <b>O k</b>     | 47.88           | 59.45           |
| <b>Na k</b>    | 0.86            | 0.75            |
| <b>Mg k</b>    | 22.83           | 18.65           |
| <b>Si k</b>    | 2.02            | 1.43            |
| <b>Fe k</b>    | 18.45           | 6.56            |
| <b>Totals</b>  | 100             |                 |

Table 5.2 EDS of calcined LDH (250 °C) components

| <b>Element</b> | <b>weight %</b> | <b>Atomic %</b> |
|----------------|-----------------|-----------------|
| <b>C k</b>     | 8.84            | 14.97           |
| <b>O k</b>     | 43.46           | 55.24           |
| <b>Mg k</b>    | 24.93           | 20.85           |
| <b>Si k</b>    | 1.81            | 1.31            |
| <b>Fe k</b>    | 20.96           | 7.63            |
| <b>Totals</b>  | 100             |                 |

Table 5.3 EDS of calcined LDH (500 °C) components

| <b>Element</b> | <b>weight %</b> | <b>Atomic %</b> |
|----------------|-----------------|-----------------|
| <b>C k</b>     | 11.27           | 18.32           |
| <b>O k</b>     | 43.93           | 53.61           |
| <b>Mg K</b>    | 25.93           | 20.82           |
| <b>Si k</b>    | 1.88            | 1.3             |
| <b>Fe k</b>    | 16.99           | 5.94            |
| <b>Totals</b>  | 100             |                 |

### 5.1.5 TGA Analysis of calcined and uncalcined LDH

TGA analysis was also performed to detect the thermal stability of the LDHs. The TGA ranged from 40 to 800 °C. For uncalcined LDH as shown in figure 5.10, the lost weight passed through three stages, at first stage the material lost approximately 12% from 40 °C to 200 °C, which is an endothermic reaction caused the removal of interlayer physisorbed water molecules. At the second stage, 14% of the weight is lost from 201 °C to 397 °C, which is corresponding to nitrates removal and de-hydroxylation process and beginning of metal oxides formation. In the third stage, about 10% of the weight is lost from 398 °C to 510 °C, which represents the continuous removal of interlayer nitrates, de-hydroxylation, and metals oxide formation such as magnesium oxide (MgO). Similar observations are reported elsewhere as well [42], [46].

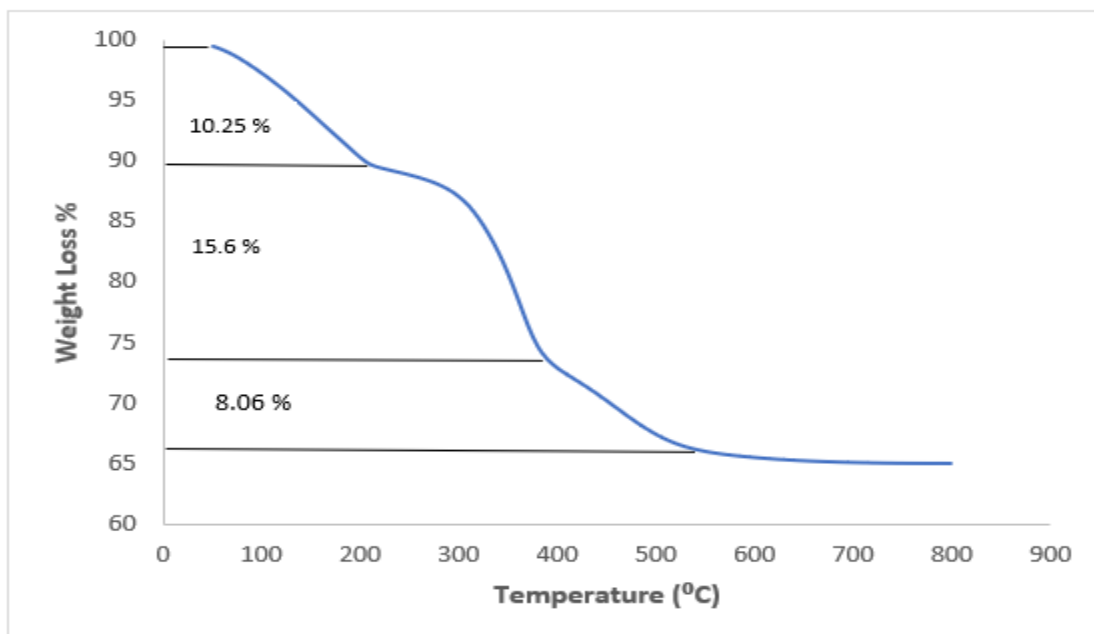


Figure 5.10 TGA curve of uncalcined LDH

In the case of 250 °C calcined LDH, as illustrated in figure 5.11, the lost weight also passed through three stages. During the first stage, about 7% of the weight was lost from 40 to 179 °C. During the second stage, the loss was 15% till 390 °C, which represents the removal of nitrates anions, de-hydroxylation, and formation of metal oxide. During the third stage, 8% weight loss, corresponds to the removal of remaining nitrates anions, de-hydroxylation, and formation of MgO.

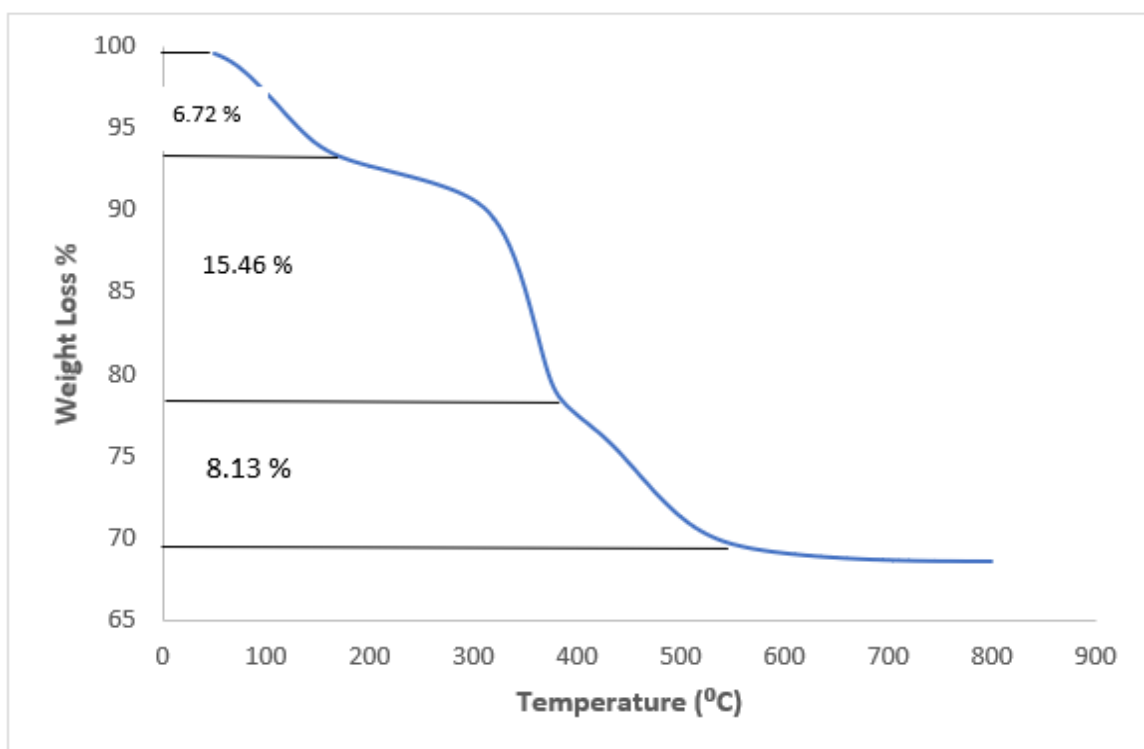


Figure 5.11 TGA curve of calcined LDH (250 °C)

For LDH calcined at 500 °C as shown in figure 5.12, the total weight loss was 11% from 40 to 700 °C. This probably results because of the removal of water molecules, [42].

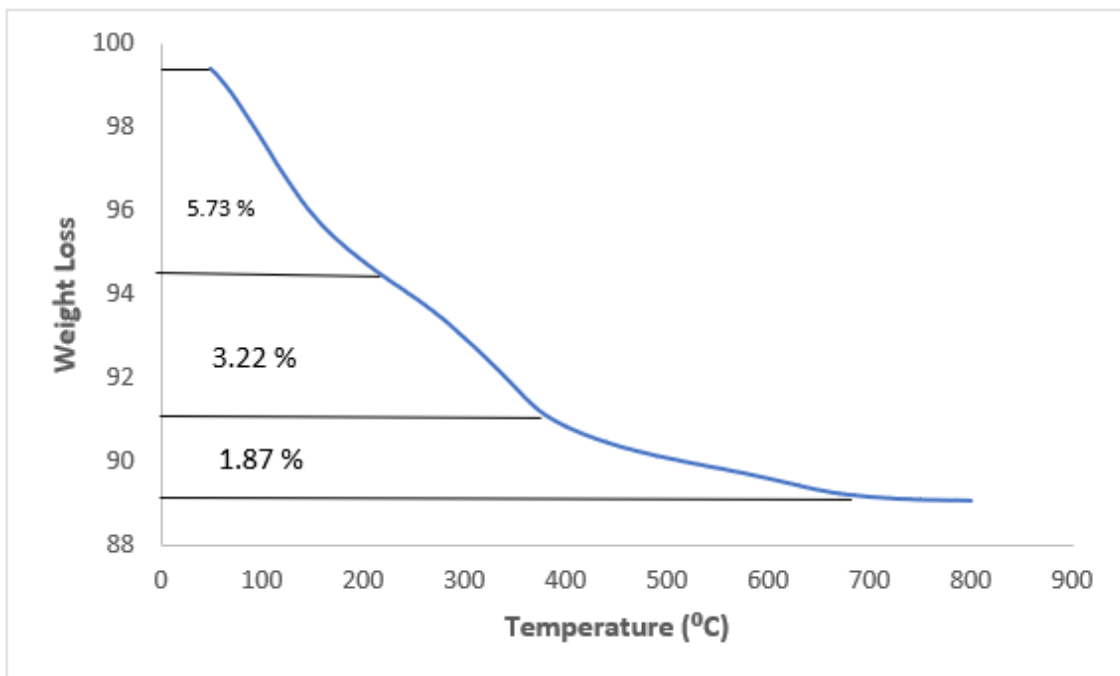


Figure 5.12 TGA curve of calcined LDH (500 °C).

## 5.2 Adsorption Results

According to the literature review, the mechanism of uncalcined LDH to adsorb the pollutant occurs by two methods. The first method is the adsorption onto the surface of LDH, where metal oxides located. These metal oxides can adsorb pollutants using physisorption through the generation of electrostatic attraction force. The adsorption of this method depends on the pH of the solution and point of zero-charge of LDH.

If the solution pH is less than the point of zero charges ( $\text{pH}_{\text{pzc}}$ ) of LDH, it is a favorable condition to adsorb pollutants with negative charge because  $\text{H}^+$  ions are dominant, which make the surface of LDH positively charged [47], [48]. If the pH of the solution is more than point of zero charges ( $\text{pH}_{\text{pzc}}$ ), the  $\text{OH}^-$  ions are dominant which make the surface negatively charged, which is favorable to adsorb the positive charge pollutants. Also, interlayers anions with a monovalent charge achieved higher removal efficiency [28], [31]. For calcined LDH, the adsorption occurs into pores resulting from the destruction of interlayer anions and water molecules. The use of calcined LDH in some studies is not affect by the pH of the solution, as noted in a previous study [46]. On the other hand, an increase in temperature increases the adsorption capacity. In some previous studies, calcination at 500 °C was noted to be the optimum temperature to adsorb different pollutants [46], [49], [50]. For both uncalcined and calcined LDH, an increase in the LDH dosage also leads to an increase in the removal efficiency of respective target pollutant [44].

In the present work, the adsorption study investigated the adsorption capacity of LDH for selenite, selenate, and selenocyanate. The parameters included calcination temperature (0, 250, and 500 °C), LDH dosage (0.5, 1.0, and 1.5 g/l) and concentrations of selenium species

(2.5, 5, and 7.5 ppm). The experiments were divided into 3 batches based on calcination; each batch included 9 bottles. The results were analyzed using Design-Expert 11 Software. The initial and final pH after 6 days was measured for each bottle as given in table 5.1.

Table 5.4 Initial and final pH of adsorption experiments

| Calcination (°C) | Dose (g/l) | SeO3 (ppm) | SeO4 (ppm) | SeCN (ppm) | initial pH | final pH |
|------------------|------------|------------|------------|------------|------------|----------|
| 500              | 1.5        | 7.5        | 2.5        | 2.5        | 7.11       | 10.62    |
| 0                | 0.5        | 2.5        | 2.5        | 7.5        | 6.61       | 8.91     |
| 500              | 0.5        | 7.5        | 7.5        | 2.5        | 7.96       | 9.61     |
| 0                | 0.5        | 2.5        | 7.5        | 2.5        | 6.3        | 9.42     |
| 250              | 1          | 5          | 5          | 7.5        | 7.15       | 9.98     |
| 250              | 1.5        | 5          | 5          | 5          | 7.01       | 10.05    |
| 0                | 0.5        | 7.5        | 7.5        | 7.5        | 6.68       | 9.41     |
| 250              | 1          | 7.5        | 5          | 5          | 7.97       | 9.98     |
| 500              | 1          | 5          | 5          | 5          | 6.6        | 9.48     |
| 500              | 0.5        | 7.5        | 2.5        | 7.5        | 7.9        | 9.4      |
| 0                | 1.5        | 7.5        | 7.5        | 2.5        | 6.6        | 9.91     |
| 250              | 1          | 5          | 5          | 5          | 7.01       | 9.95     |
| 500              | 1.5        | 2.5        | 2.5        | 7.5        | 6.46       | 10.63    |
| 0                | 1.5        | 2.5        | 2.5        | 2.5        | 6.28       | 9.88     |
| 250              | 1          | 5          | 2.5        | 5          | 7.21       | 9.98     |
| 250              | 1          | 5          | 7.5        | 5          | 7.4        | 9.58     |
| 0                | 1          | 5          | 5          | 5          | 6.4        | 9.4      |
| 0                | 1.5        | 7.5        | 2.5        | 7.5        | 6.46       | 9.88     |
| 0                | 0.5        | 7.5        | 2.5        | 2.5        | 6.53       | 9.39     |
| 0                | 1.5        | 2.5        | 7.5        | 7.5        | 6.17       | 9.88     |
| 500              | 1.5        | 7.5        | 7.5        | 7.5        | 6.56       | 10.93    |
| 250              | 1          | 5          | 5          | 2.5        | 7.07       | 9.97     |
| 500              | 0.5        | 2.5        | 2.5        | 2.5        | 6.24       | 9.16     |
| 250              | 0.5        | 5          | 5          | 5          | 7.01       | 9.35     |
| 500              | 0.5        | 2.5        | 7.5        | 7.5        | 6.38       | 9.46     |
| 250              | 1          | 2.5        | 5          | 5          | 6.76       | 9.97     |
| 500              | 1.5        | 2.5        | 7.5        | 2.5        | 6.26       | 9.73     |

### 5.2.1 RSM Result of Selenite (SeO<sub>3</sub><sup>2-</sup>) Adsorption

The obtained results were analyzed using Design – Expert 11 Software to fit the best model.

**The Quadratic Model** was the best-fitted model using  $\alpha = 0.05$  ( $\alpha$  represents a margin of error of the model). The model shows the **Predicted R<sup>2</sup>** of 0.9464 that is in reasonable agreement with the **Adjusted R<sup>2</sup>** of 0.9642; i.e. the difference is less than 0.2.

Table 5.5 Statistical analysis of Quadratic model for selenite result

|                  |       |                                |         |
|------------------|-------|--------------------------------|---------|
| <b>Std. Dev.</b> | 5.24  | <b>R<sup>2</sup></b>           | 0.9752  |
| <b>Mean</b>      | 63.26 | <b>Adjusted R<sup>2</sup></b>  | 0.9642  |
| <b>C.V. %</b>    | 8.28  | <b>Predicted R<sup>2</sup></b> | 0.9464  |
|                  |       | <b>Adeq Precision</b>          | 28.2842 |

ANOVA table of the model was also generated. The model is significant with F-value = 88.57, and p-value = < 0.0001, which is less than  $\alpha$  (p-value must be less than  $\alpha$  to be significant). Also, the ANOVA table shows that the calcination temperature, dosage of adsorbent, and selenite concentration, are significant with F-value = 551.61, 51.56, 5.31, respectively and p-value = <0.0001, <0.0001, 0.0334. That means the adsorption efficiency of selenite is affected by the calcination temperature, adsorbent dosage, and selenite concentration. Also, the ANOVA table showed that interaction terms AB, AC in addition to A<sup>2</sup> are significant terms. The other terms tested in the model showed insignificant effects such as the effect of selenate and selenocyanate ( F-values = 0.9257, 0.444 and p-value = 0.3487, 0.5136 for selenate and selenocyanate respectively).

Table 5. 6 ANOVA table of Quadratic Model for selenite removal

| Source               | Sum of Squares | df | Mean Square | F-value | p-value  |             |
|----------------------|----------------|----|-------------|---------|----------|-------------|
| <b>Model</b>         | 19417.92       | 8  | 2427.24     | 88.57   | < 0.0001 | significant |
| <b>A-Temp</b>        | 15117.71       | 1  | 15117.71    | 551.61  | < 0.0001 |             |
| <b>B-Dosage</b>      | 1413.17        | 1  | 1413.17     | 51.56   | < 0.0001 |             |
| <b>C-SeO3</b>        | 145.41         | 1  | 145.41      | 5.31    | 0.0334   |             |
| <b>D-SeO4</b>        | 25.37          | 1  | 25.37       | 0.9257  | 0.3487   |             |
| <b>E-SeCN</b>        | 12.17          | 1  | 12.17       | 0.4440  | 0.5136   |             |
| <b>AB</b>            | 244.53         | 1  | 244.53      | 8.92    | 0.0079   |             |
| <b>AC</b>            | 329.51         | 1  | 329.51      | 12.02   | 0.0027   |             |
| <b>A<sup>2</sup></b> | 2130.05        | 1  | 2130.05     | 77.72   | < 0.0001 |             |
| <b>Residual</b>      | 493.31         | 18 | 27.41       |         |          |             |
| <b>Cor Total</b>     | 19911.23       | 26 |             |         |          |             |

Further analysis was also completed to confirm the suitability of the quadratic model. Residual Analysis was fitted to check either the results are normally distributed, independent, and identical (constant variance) or not. Figure 5.13 (A) illustrates the distribution of the results around the straight line, which represents the normal distribution part, (B) illustrates the random pattern of result distribution, which represents the independent part, and (C) represents the constant variance.

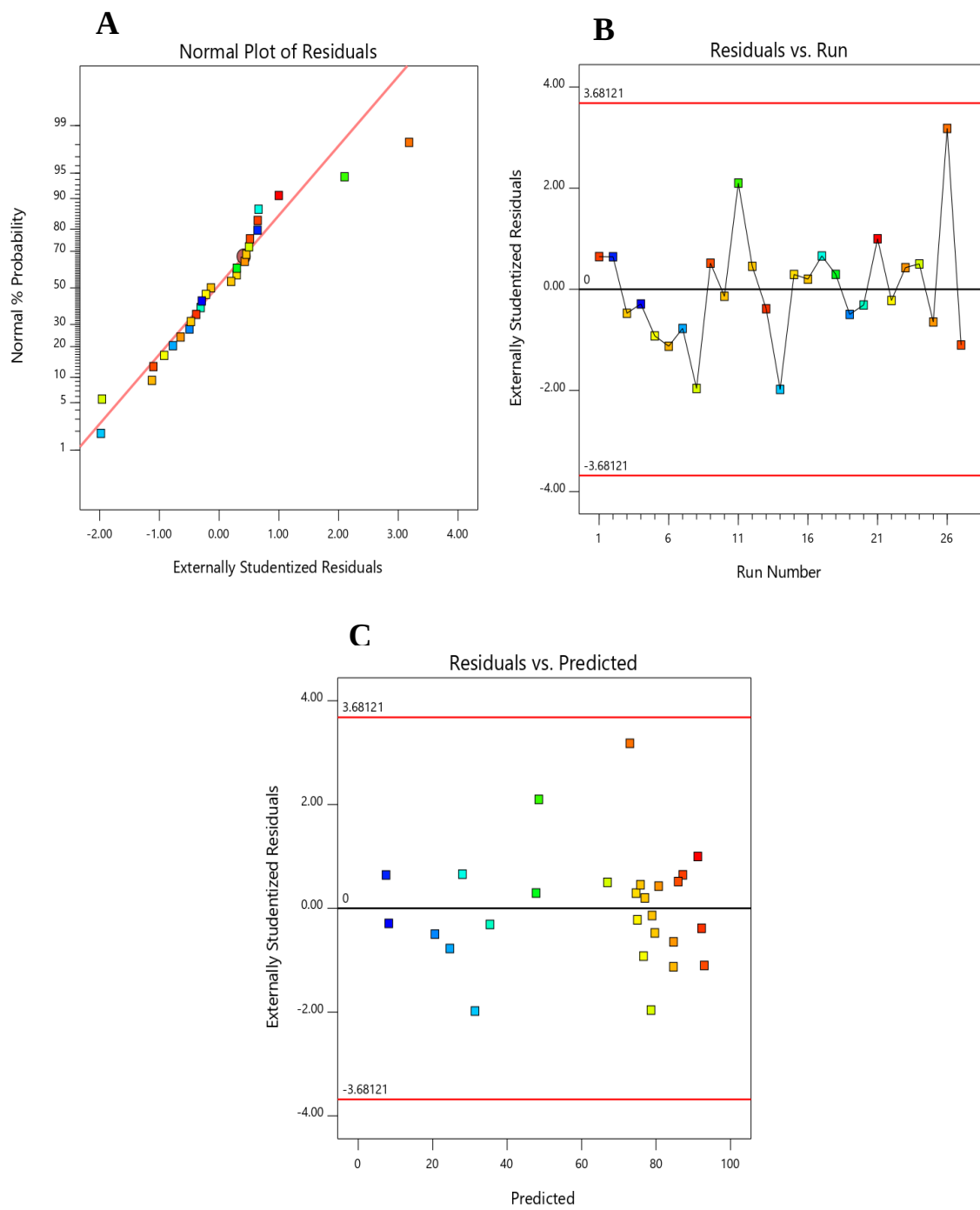


Figure 5.13 Residual Analysis of Selenite removal (A) normal distribution (B) independent (C) constant variance

### **5.2.2 Effect of Calcination, Dosage, and concentration on Removal Efficiency of Selenite ( $\text{SeO}_3^{2-}$ )**

The results showed that adsorption of selenite increased with an increase in the calcination temperature and LDH dosage as given in figure 5.14 and 5.15. LDH calcined at 500 °C and 1.5 g/l dosage show the highest removal efficiency. These results are in agreement with a previous study [25]. The highest removal was obtained at 500 °C because this high temperature caused destruction and removal of the interlayer nitrate anions and water molecules which increased the specific surface area and an increase in the adsorption capacity of LDH. On the other hand, uncalcined LDH showed the lowest removal because of high pH which made the surface of LDH negatively charged causing repulsion. Also, the optimum pH to adsorb selenite ranged from 3.8 to 8. Adsorption also was higher For LDH calcined at 250°C than uncalcined LDH. the LDH dosage also has a positive effect, increasing the dosage provides more surface and pores for adsorption also illustrates in previous work [44]. The result also showed no effects from selenate and selenocyanate on adsorption of selenite as shown in figures 5.19 and 5.20.

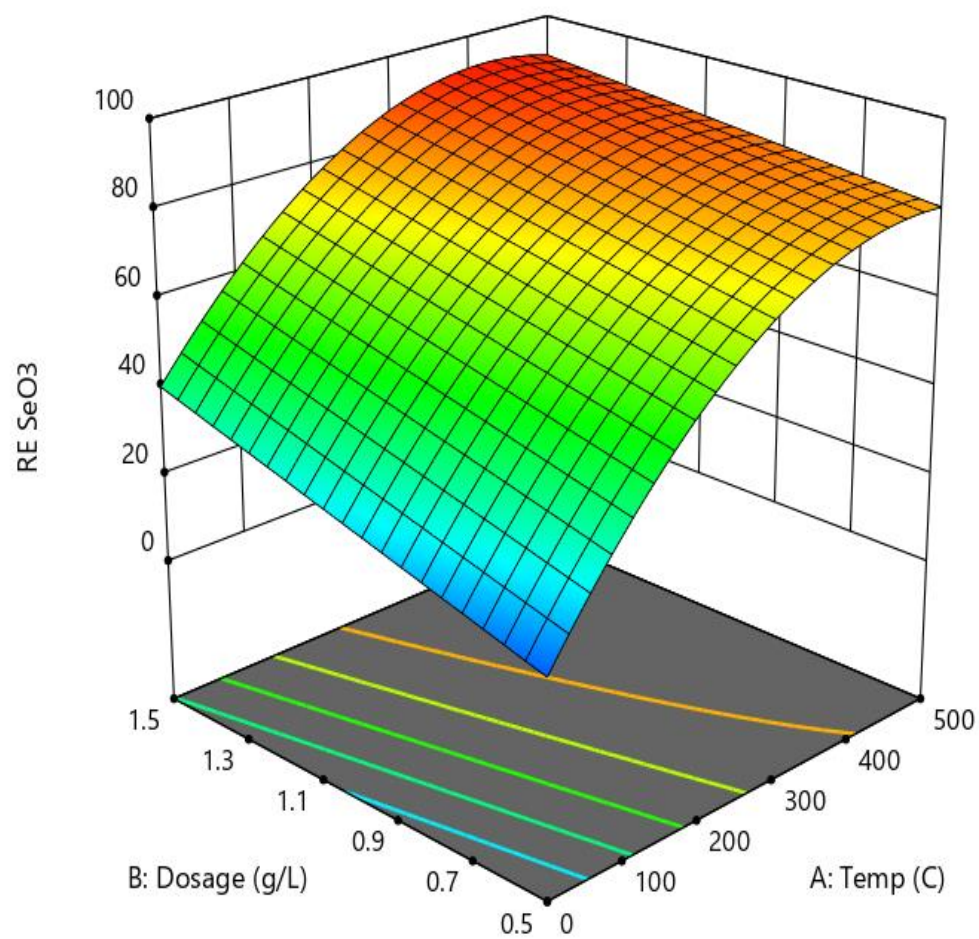


Figure 5.14 3D surface of Selenite removal efficiency as a function of Calcination temperature and Dosage

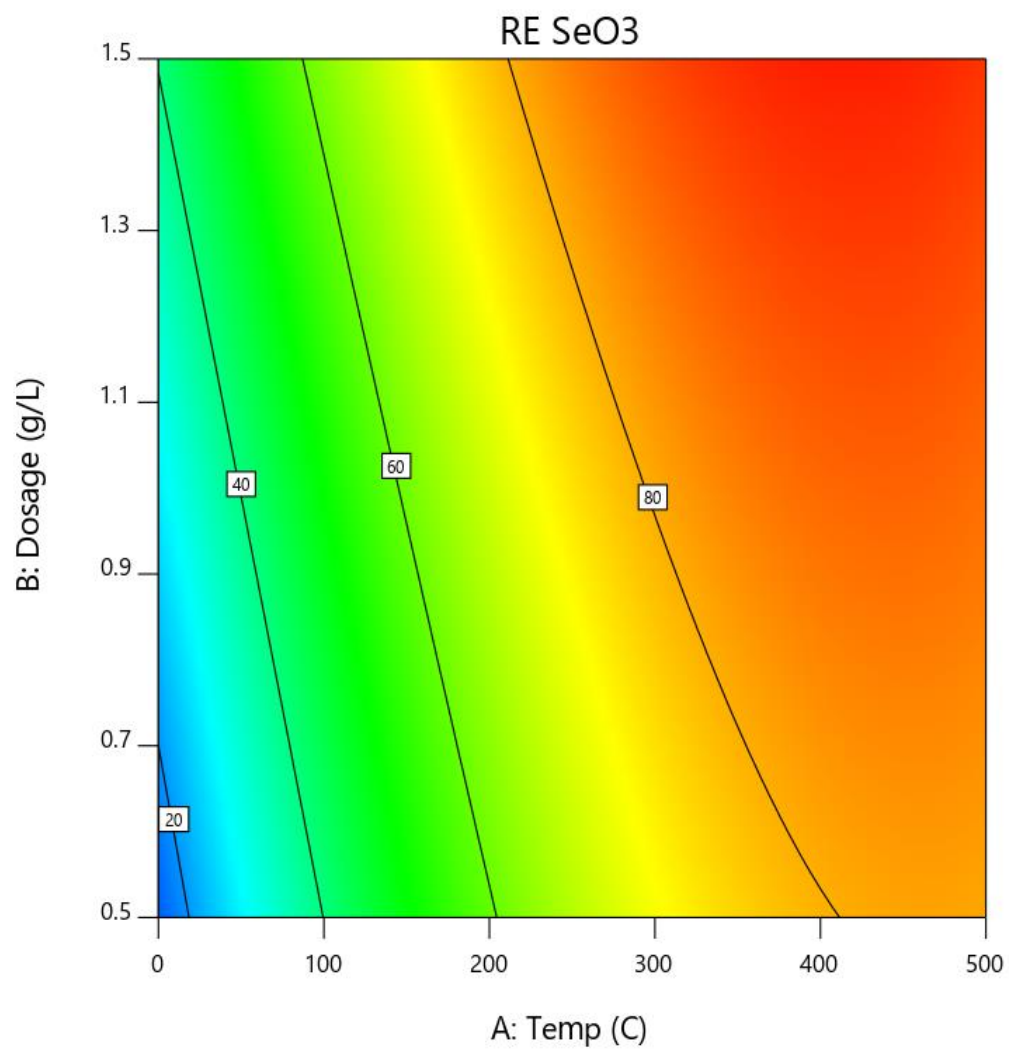


Figure 5.15 Contour map of selenite removal efficiency as a function of Calcination temperature and Dosage

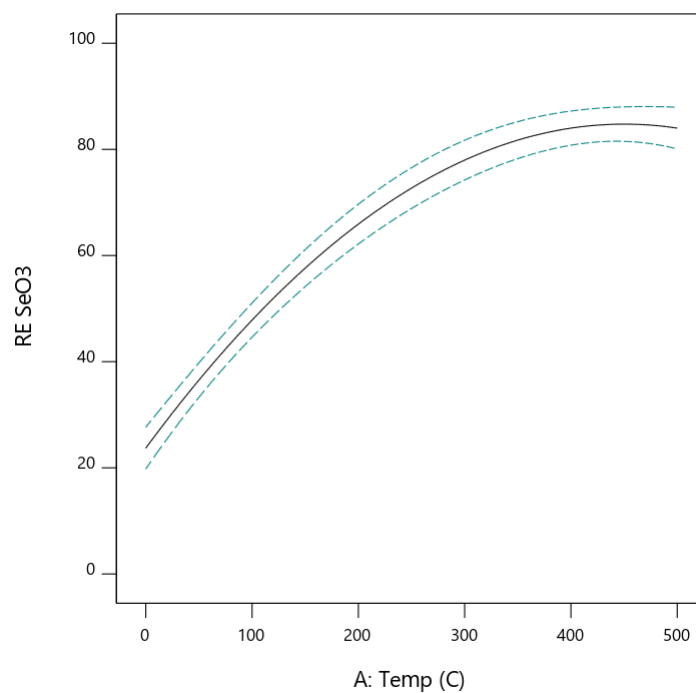


Figure 5.16 Removal efficiency of selenite as a function of Calcination Temperature

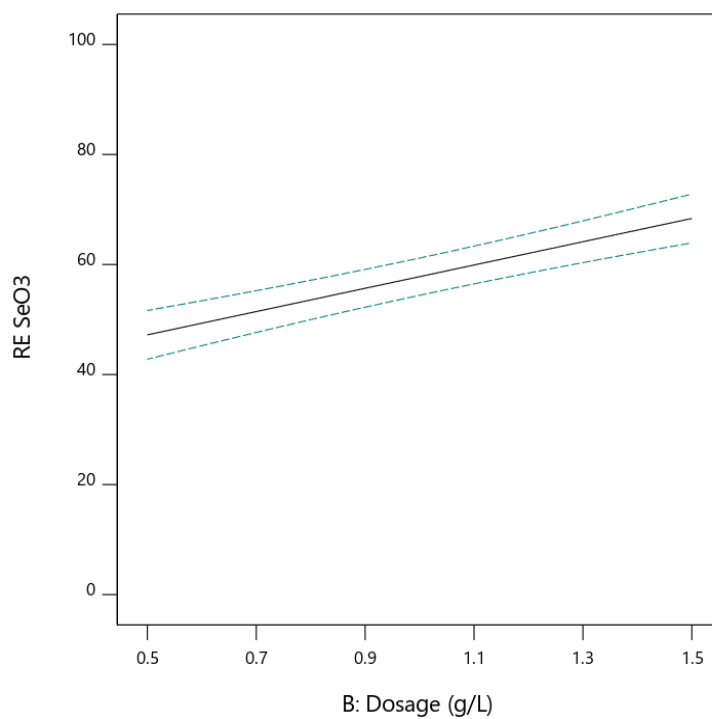


Figure 5.17 Removal efficiency of selenite as a function of Dosage

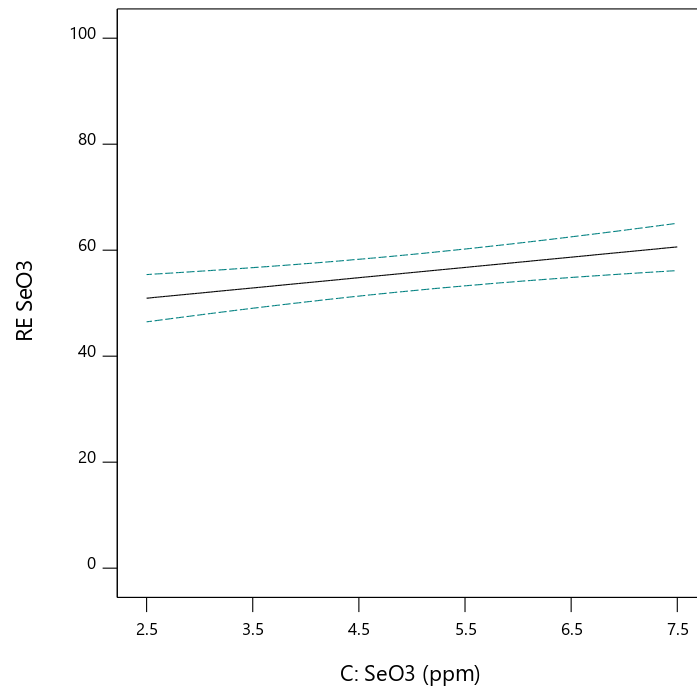


Figure 5.18 Removal of selenite as a function of selenite concentration

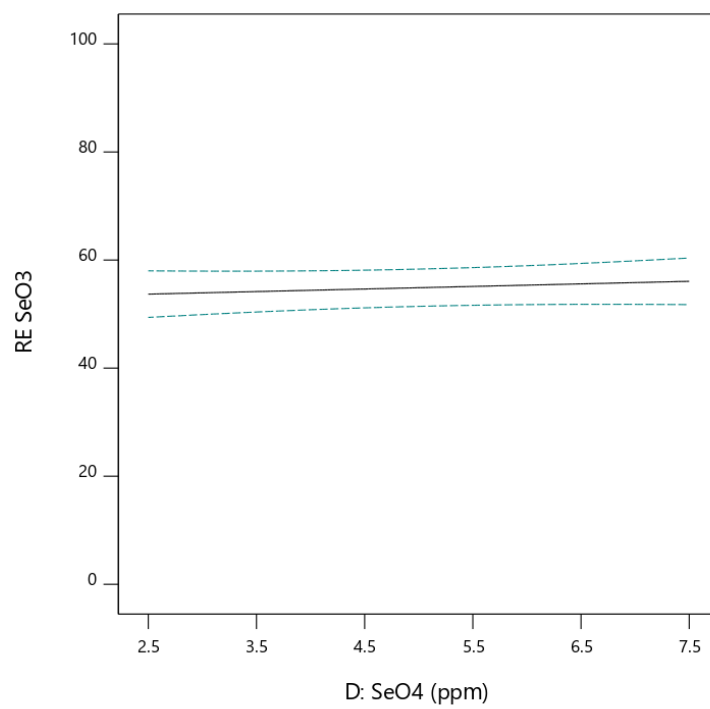


Figure 5.19 Removal of selenite as a function of selenate concentration

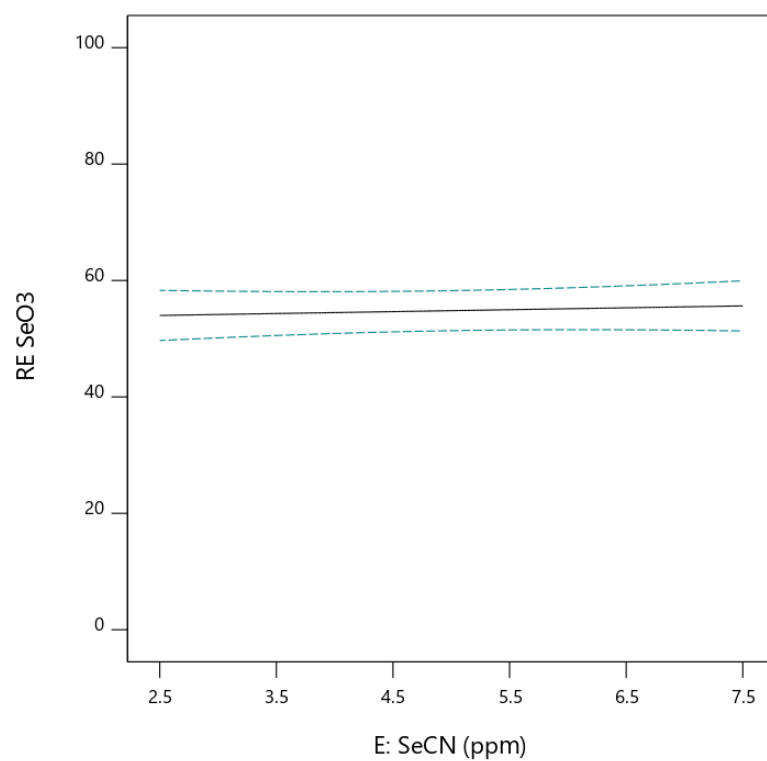


Figure 5.20 Removal of selenite as a function of selenocyanate concentration

### 5.2.3 RSM Result of Selenite ( $\text{SeO}_4^{2-}$ ) Adsorption

The results were analyzed using Design – Expert 11 software to fit the best model. The **Quadratic Model** is the best-fitted model using a margin of error  $\alpha = 0.05$ . The model showed that The **Predicted  $R^2$**  of 0.9002 is in reasonable agreement with the **Adjusted  $R^2$**  of 0.9366; i.e. the difference is less than 0.2.

Table 5.7 Statistical analysis of Quadratic model for selenate result

|                  |        |                                   |         |
|------------------|--------|-----------------------------------|---------|
| <b>Std. Dev.</b> | 0.6057 | <b><math>R^2</math></b>           | 0.9561  |
| <b>Mean</b>      | 5.92   | <b>Adjusted <math>R^2</math></b>  | 0.9366  |
| <b>C.V. %</b>    | 10.23  | <b>Predicted <math>R^2</math></b> | 0.9002  |
|                  |        | <b>Adeq Precision</b>             | 21.6400 |

ANOVA table of the fitted model was generated. The model shown significant effect (table 5.8) with **F-value** = 49.02 and **p-value** = < 0.001, which is less than margin of error  $\alpha = 0.05$ . Also, ANOVA analysis showed that Calcination temperature and LDH dosage are significant terms with F-value = 314.96, 27.17 respectively, and p-value = < 0.0001 for both. That means the removal of selenate affected directly by calcination temperature and LDH dosage. The table showed that interaction terms AB, AD, and  $A^2$  are significant terms. The ANOVA showed that effects of selenate, selenite and selenocyanate are insignificant with F-value = 0.2524, 0.4171, 1.18 respectively, and p-value = 0.6215, 0.5265, 0.2915 which are greater than  $\alpha$ .

Table 5.8 ANOVA table of Quadratic model of Selenate results

| Source               | Sum of Squares | df | Mean Square | F-value | p-value  |             |
|----------------------|----------------|----|-------------|---------|----------|-------------|
| Model                | 143.88         | 8  | 17.99       | 49.02   | < 0.0001 | significant |
| <b>A-Temp</b>        | 115.56         | 1  | 115.56      | 314.96  | < 0.0001 |             |
| <b>B-Dosage</b>      | 9.97           | 1  | 9.97        | 27.17   | < 0.0001 |             |
| <b>C-SeO3</b>        | 0.1530         | 1  | 0.1530      | 0.4171  | 0.5265   |             |
| <b>D-SeO4</b>        | 0.0926         | 1  | 0.0926      | 0.2524  | 0.6215   |             |
| <b>E-SeCN</b>        | 0.4332         | 1  | 0.4332      | 1.18    | 0.2915   |             |
| <b>AB</b>            | 1.95           | 1  | 1.95        | 5.30    | 0.0335   |             |
| <b>AD</b>            | 3.14           | 1  | 3.14        | 8.56    | 0.0090   |             |
| <b>A<sup>2</sup></b> | 12.59          | 1  | 12.59       | 34.31   | < 0.0001 |             |
| Residual             | 6.60           | 18 | 0.3669      |         |          |             |
| Cor Total            | 150.49         | 26 |             |         |          |             |

The residual analysis shows either the model follows the three assumptions (Normal distribution, independent and identical or constant variance) or not. Figure 5.21 (A) shown that the result distributed around the straight line, which represents the normality, (B) showed a random pattern of result distribution, which means the model is independent, and (C) showed a constant variance of the results.

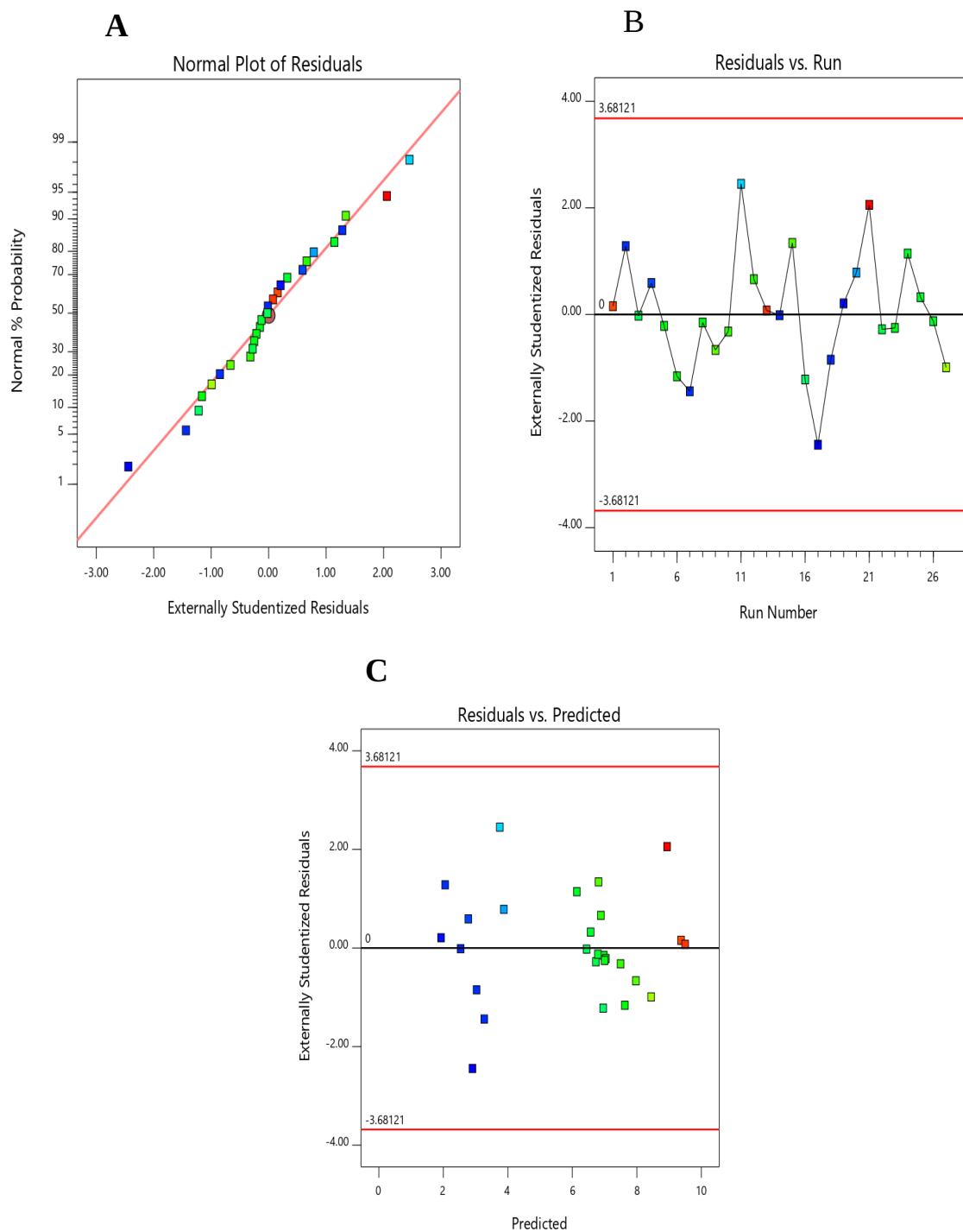


Figure 5.21 Residual Analysis of  $\text{SeO}_4$  removal (A) normal distribution (B) independent (C) constant variance

#### **5.2.4 Effect of Calcination, Dosage, and Concentration on Removal Efficiency of Selenate ( $\text{SeO}_4^{2-}$ )**

The statistical analysis of results showed that the removal efficiency of selenate increased gradually with an increase in the calcination temperature and LDH dosage as illustrates in figures 5.22 and 5.23. The highest removal efficiency was obtained for LDH calcined at 500 °C and 1.5 g/l dosage. The results showed that the removal efficiency increased with the decrease in the selenate concentration and an increase in the dosage. The adsorption of selenate depends on selenate speciation along with various pH (5.8-7.0), also depends on the surface characteristics of the adsorbent. Hereby, uncalcined LDH has achieved the lowest removal efficiency because of pH of solution, which is higher than point of zero charge of LDH causing repulsion force with selenate anions resulted in the reduction of removal efficiency [29], therefore the occurred adsorption refers probably to anion exchange. For 250 °C LDH, the removal efficiency increased more than uncalcined because selenate anions adsorbed into pores, which resulting from the removal of nitrate anions and water at high temperatures. Also, some adsorption occurred due to anion exchange between the remaining nitrate and selenate anions. At 500 °C LDH, more surface area was provided because most of the nitrate and water molecules were destroyed and removed. For LDH dosage, as illustrated in figure 5.25, increasing dosage provided more ability to adsorb through anion exchange or inside pores. Selenate concentration showed no effect on its removal efficiency as shown in figure 5.26. Furthermore, both selenocyanate and selenite showed no effect on to selenate removal efficiency, as shown in figures 5.27 and 5.28.

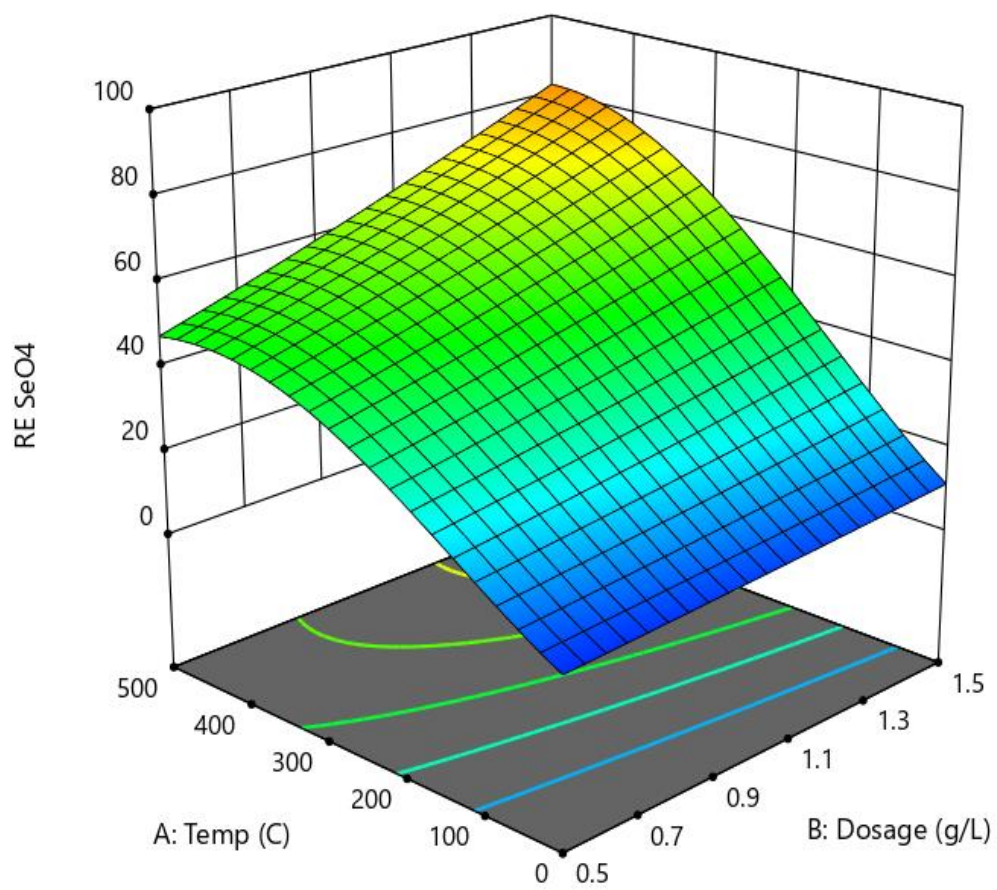


Figure 5.22 3D surface of Selenate removal efficiency as a function of Calcination temperature and Dosage

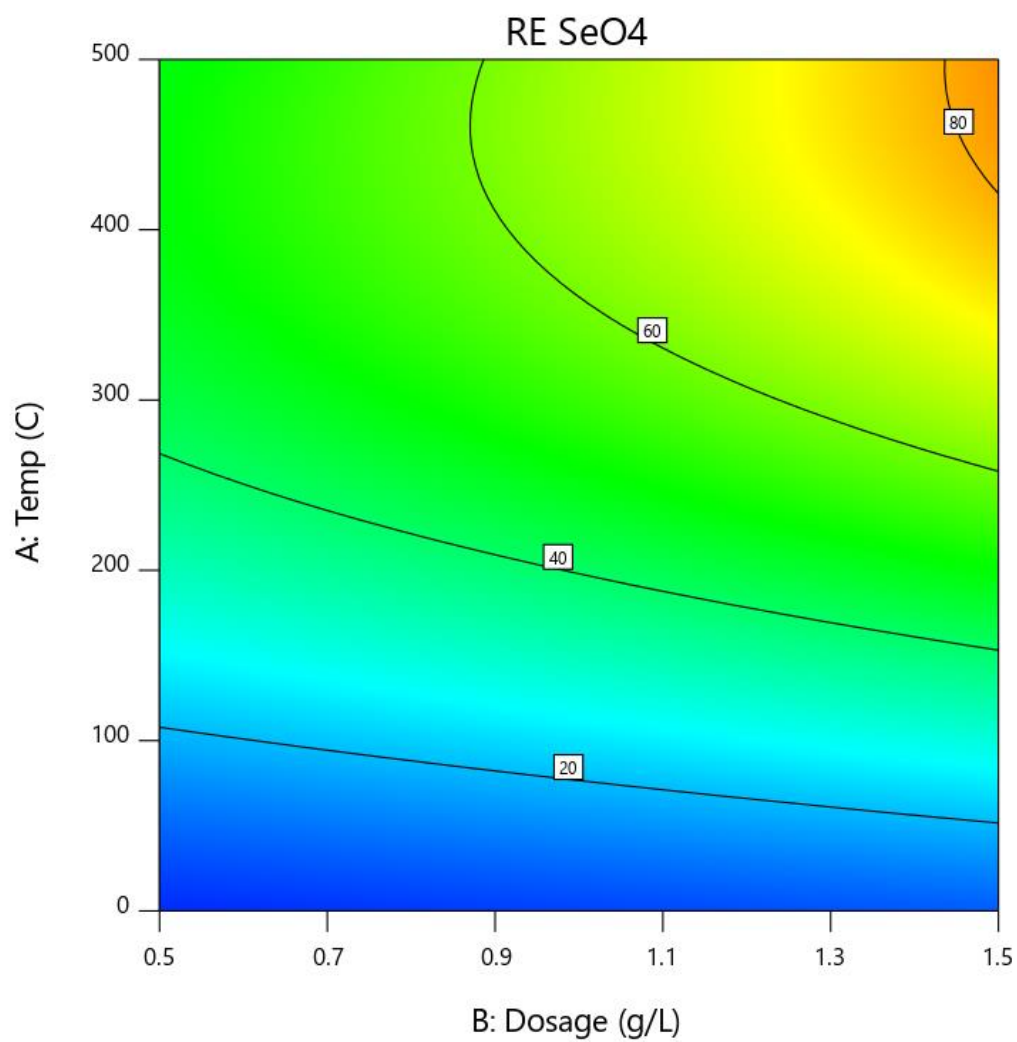


Figure 5.23 Contour map of Selenate removal efficiency as a function of Calcination temperature and Dosage

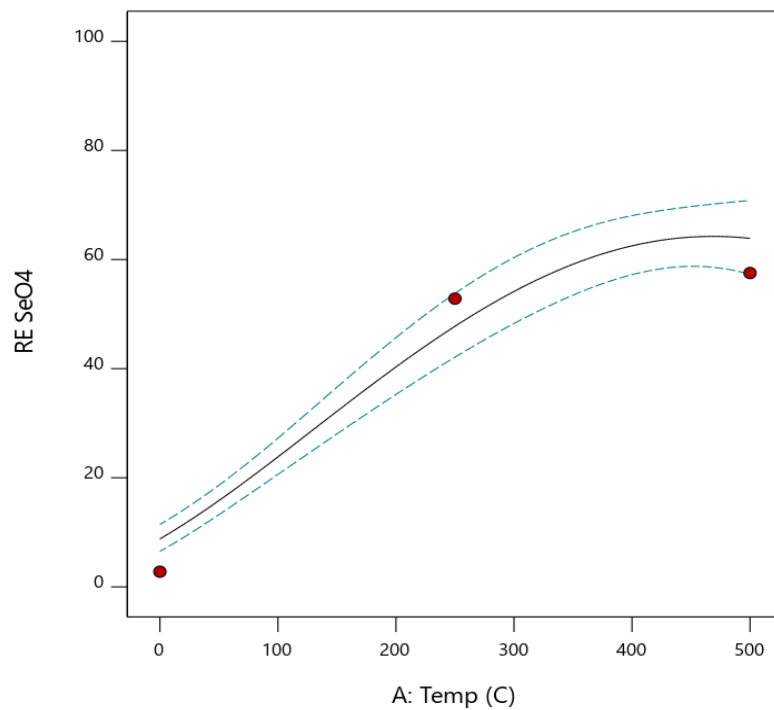


Figure 5.24 Removal Efficiency of Selenate as a function of Calcination temperature

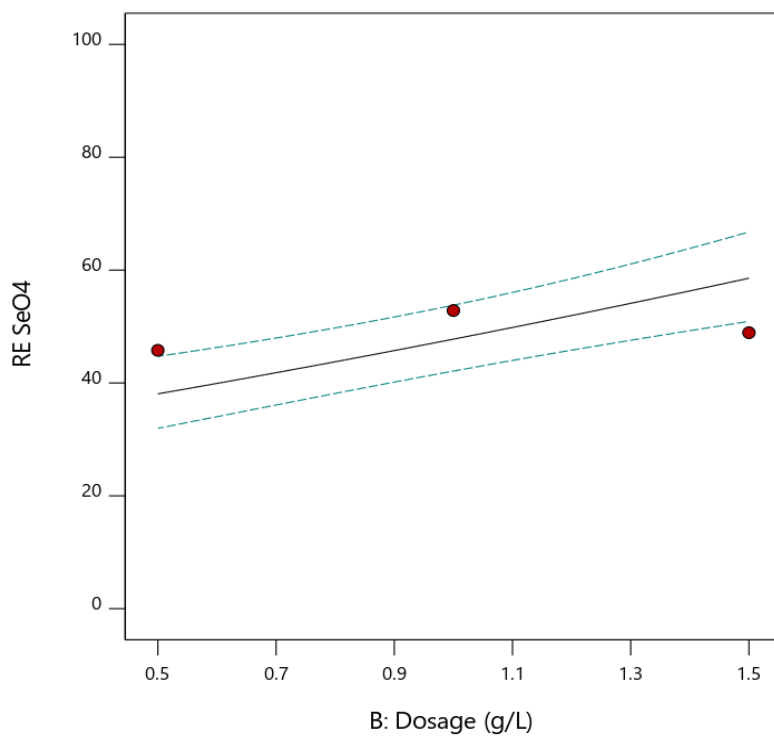


Figure 5.25 Removal Efficiency of Selenate as a function of Dosage

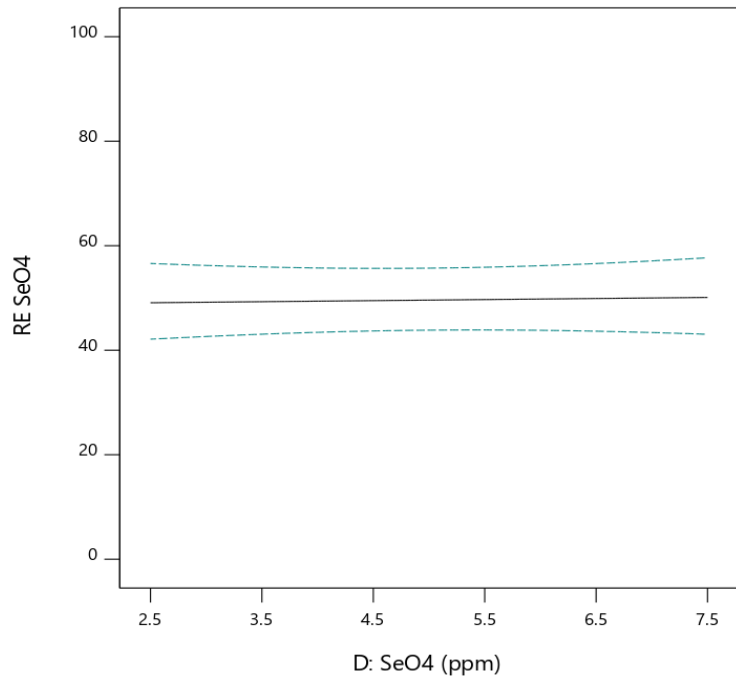


Figure 5.26 Removal Efficiency of Selenate as a function of selenate concentration

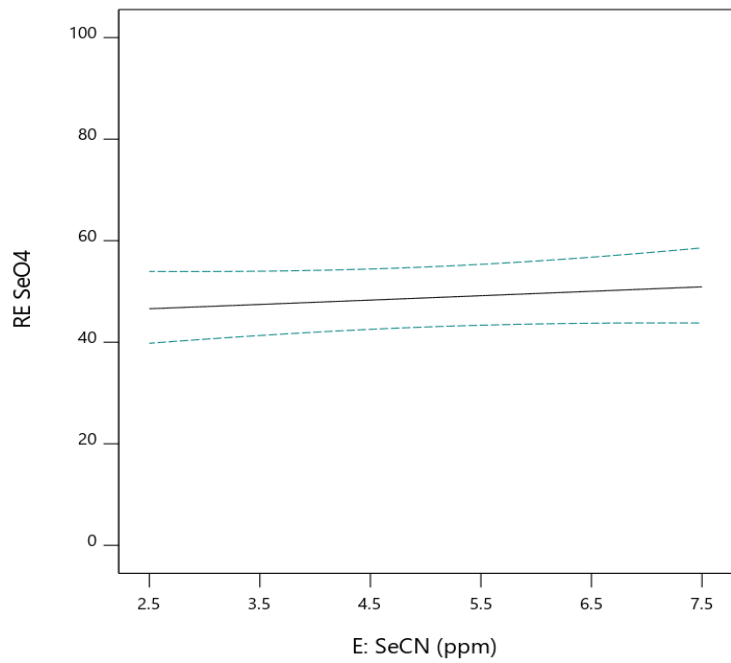


Figure 5.27 Removal Efficiency of Selenate as a function of Selenocyanate concentration

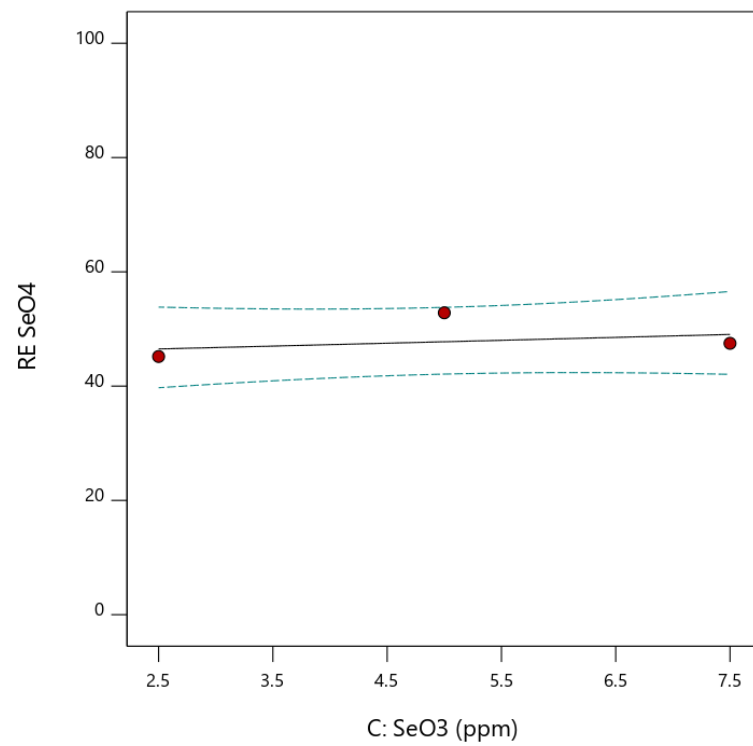


Figure 5.28 Removal Efficiency of Selenate as a function of Selenite concentration

### 5.2.5 RSM Results of Selenocyanate (SeCN<sup>-</sup>) Adsorption

The adsorption results of selenocyanate were analyzed using the Design – Expert 11 software. The quadratic Model was the best-fitted model using  $\alpha = 0.05$ . The model showed that The **Predicted R<sup>2</sup>** of 0.8225 is in reasonable agreement with the **Adjusted R<sup>2</sup>** of 0.9040; i.e. the difference is less than 0.2.

Table 5. 9 Statistical analysis of Quadratic model for selenocyanate result

|                  |               |                                |         |
|------------------|---------------|--------------------------------|---------|
| <b>Std. Dev.</b> | <b>0.5282</b> | <b>R<sup>2</sup></b>           | 0.9446  |
| <b>Mean</b>      | 3.64          | <b>Adjusted R<sup>2</sup></b>  | 0.9040  |
| <b>C.V. %</b>    | 14.51         | <b>Predicted R<sup>2</sup></b> | 0.8225  |
|                  |               | <b>Adeq Precision</b>          | 14.6798 |

ANOVA table of the model was fitted. The results showed that the model is significant with F-value = 23.26 and p-value = < 0.0001 which is less than  $\alpha$ . For the parameters of experiment, ANOVA table showed that LDH dosage and selenocyanate concentration are significant parameters with F-value = 28.07, 22.93 respectively and p-value = < 0.0001, 0.0002 respectively. Also, the terms AC, AE, BC, BD, CD, and A<sup>2</sup> are significant. ANOVA table showed there is no effect from selenite and selenate on removal of selenocyanate whereas F-value = 3.36, 0.2810 respectively and p-value = 0.0869, 0.6038 respectively.

Table 5.10 ANOVA table of Quadratic model of Selenocyanate results

| Source               | Sum of Squares | df | Mean Square | F-value | p-value  |             |
|----------------------|----------------|----|-------------|---------|----------|-------------|
| Model                | 71.39          | 11 | 6.49        | 23.26   | < 0.0001 | significant |
| <b>A-Temp</b>        | 0.8903         | 1  | 0.8903      | 3.19    | 0.0942   |             |
| <b>B-Dosage</b>      | 7.83           | 1  | 7.83        | 28.07   | < 0.0001 |             |
| <b>C-SeO3</b>        | 0.9359         | 1  | 0.9359      | 3.36    | 0.0869   |             |
| <b>D-SeO4</b>        | 0.0784         | 1  | 0.0784      | 0.2810  | 0.6038   |             |
| <b>E-SeCN</b>        | 6.40           | 1  | 6.40        | 22.93   | 0.0002   |             |
| <b>AC</b>            | 2.86           | 1  | 2.86        | 10.25   | 0.0059   |             |
| <b>AE</b>            | 4.35           | 1  | 4.35        | 15.59   | 0.0013   |             |
| <b>BC</b>            | 3.02           | 1  | 3.02        | 10.82   | 0.0050   |             |
| <b>BD</b>            | 1.74           | 1  | 1.74        | 6.25    | 0.0245   |             |
| <b>CD</b>            | 1.94           | 1  | 1.94        | 6.96    | 0.0186   |             |
| <b>A<sup>2</sup></b> | 41.34          | 1  | 41.34       | 148.21  | < 0.0001 |             |
| Residual             | 4.18           | 15 | 0.2790      |         |          |             |
| Cor Total            | 75.57          | 26 |             |         |          |             |

The residual analysis was fitted to check either this result follow probability distribution (Normal distribution, independent and identical or constant variance) or not. Figure 5.29 shows (A) the results are distributed around the straight line (normal distribution), (B) the results are distributed in a random pattern (independent), and (C) illustrates that results have a constant variance (identical).

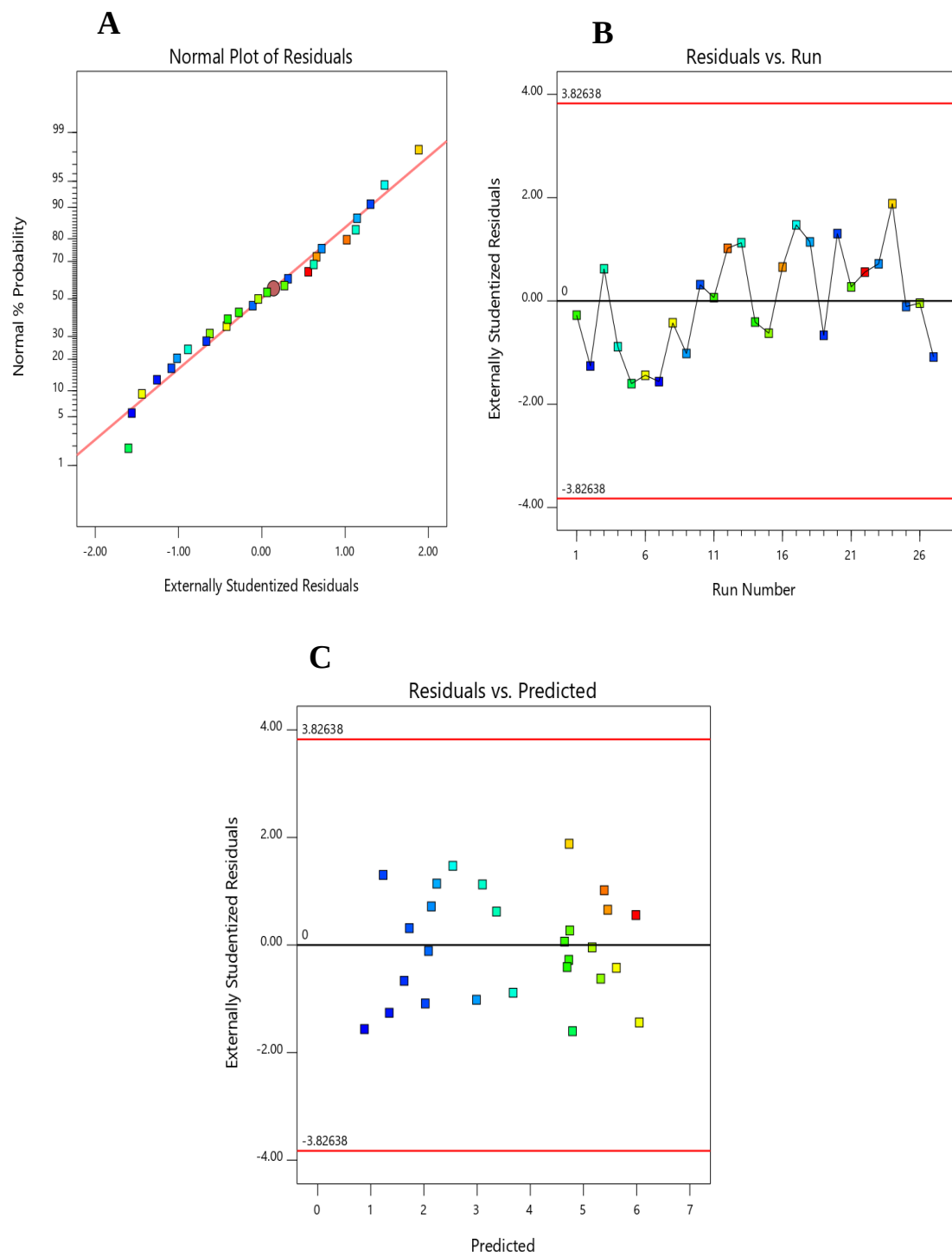


Figure 5.29 Residual Analysis of SeCN removal (A) normal distribution (B) independent (C) constant variance

### **5.2.6 Effect of Calcination, Dosage, and Concentration on Removal Efficiency of Selenocyanate ( $\text{SeCN}^-$ )**

The statistical analysis of the results showed that removal efficiency was low for uncalcined LDH and LDH calcined 500 °C however, the removal efficiency increased for 250 °C LDH. Also, the removal increased with an increase in the dosage of LDH as shown in figures 5.30 and 5.31. The highest removal efficiency achieved for 250 °C LDH with 1.5 g/l of LDH dosage. For uncalcined LDH, the low adsorption transpired because of two reasons; the first reason is high suspension pH, which made  $\text{OH}^-$  ions dominant on the surface of LDH causing a competition between the  $\text{OH}^-$  ions and  $\text{SeCN}^-$  species, which led to a decrease the removal efficiency. The second reason is the reduction in the influence of anion exchange because nitrate anions and selenocyanate anions both hold monovalent charge, which led to repulsion causing a decrease in the removal efficiency, as concluded in some previous studies [31], [32]. For LDH calcined at 250 °C, most of the adsorption probably occurred into free spaces which resulted from the destruction of nitrate anions and water, therefore the effect of anion exchange almost very low. For LDH calcined at 500 °C, the decrease in removal efficiency might result from high suspension pH that exceeds 10 in most cases. The removal efficiency also decreased with an increase in selenocyanate concentration and increased when selenocyanate concentration decreased, as shown in figure 5.31. Furthermore, the selenocyanate removal was lower for uncalcined LDH, which increased for the 250 °C calcined LDH and reduced for the 500 °C calcined LDH as shown in figure 5.32. Furthermore, selenite and selenate do not affect the removal efficiency of selenocyanate as illustrated in figures 5.36 and 5.37.

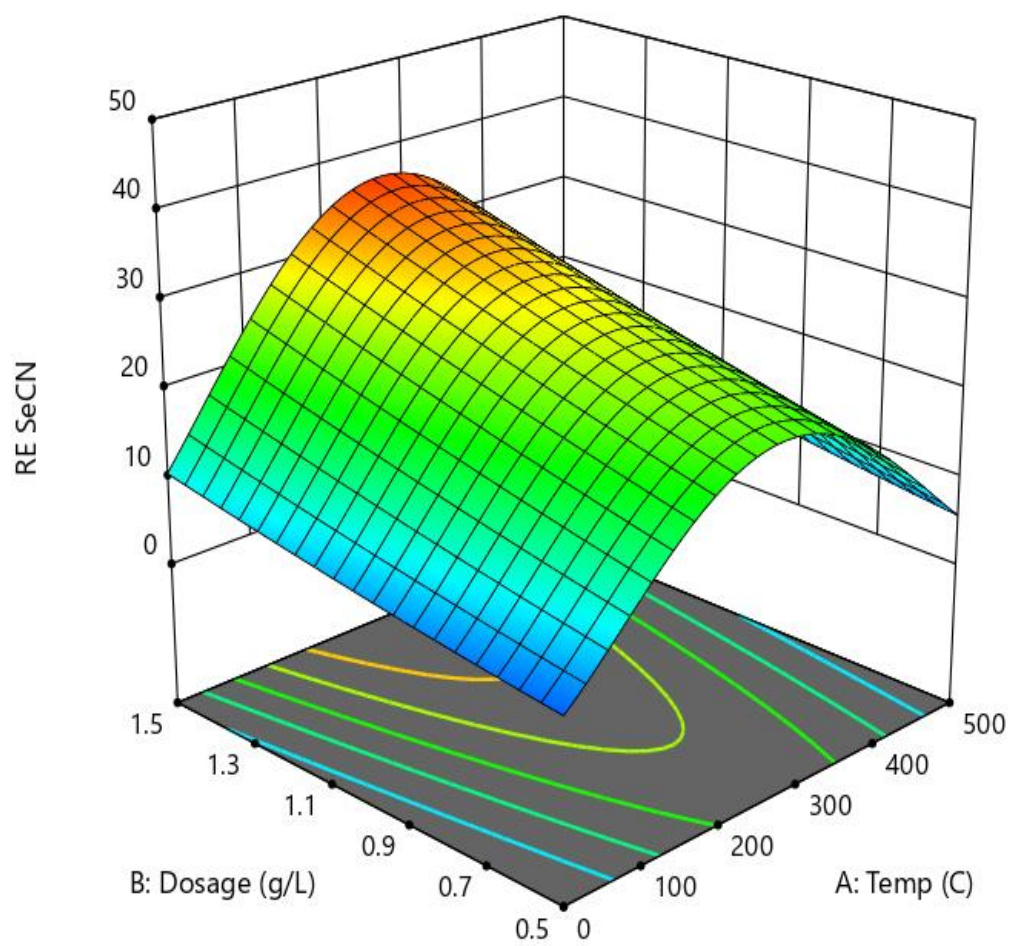


Figure 5.30 3D surface of Selenocyanate removal efficiency as a function of Calcination temperature and Dosage

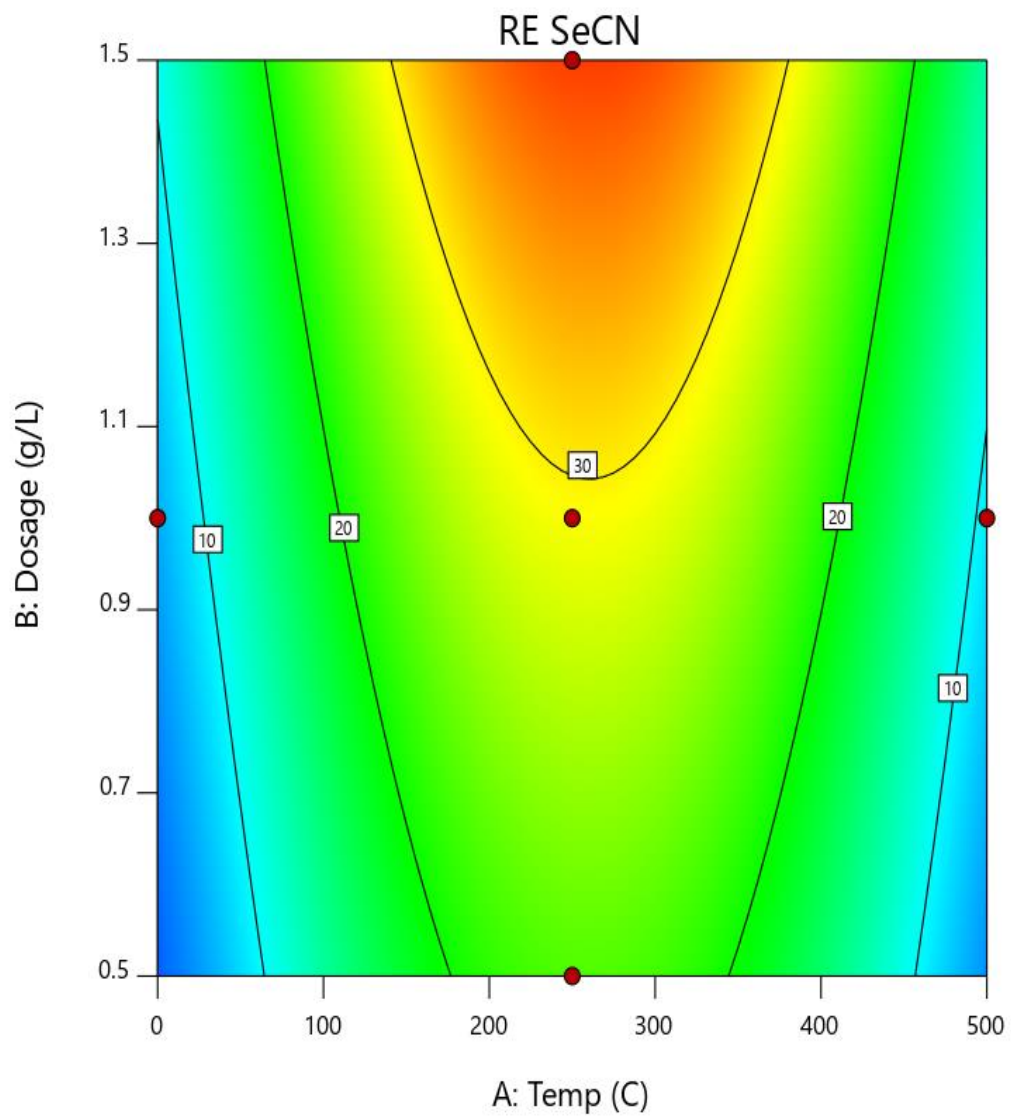


Figure 5.31 Contour map of Selenocyanate removal efficiency as a function of Calcination temperature and Dosage

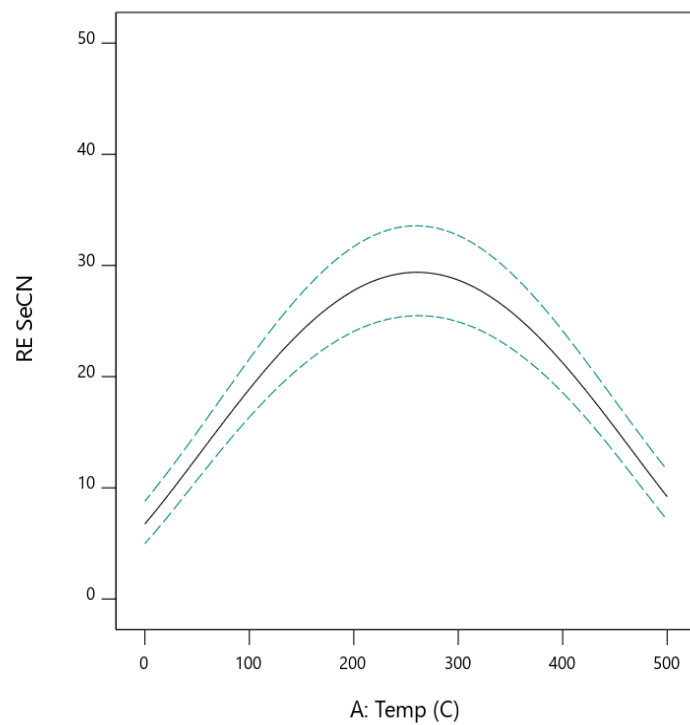


Figure 5.32 Removal Efficiency of Selenocyanate as a function of Calcination Temperature

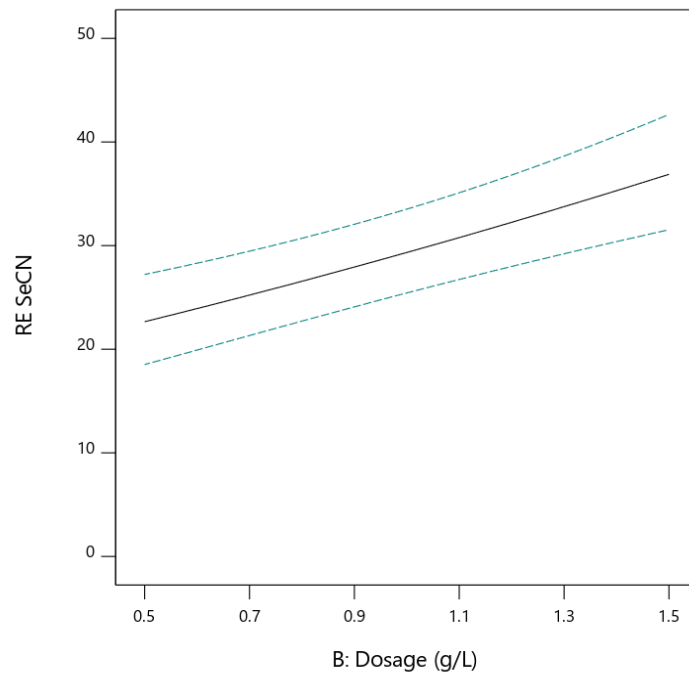


Figure 5.33 Removal Efficiency of Selenocyanate as a function of Dosage

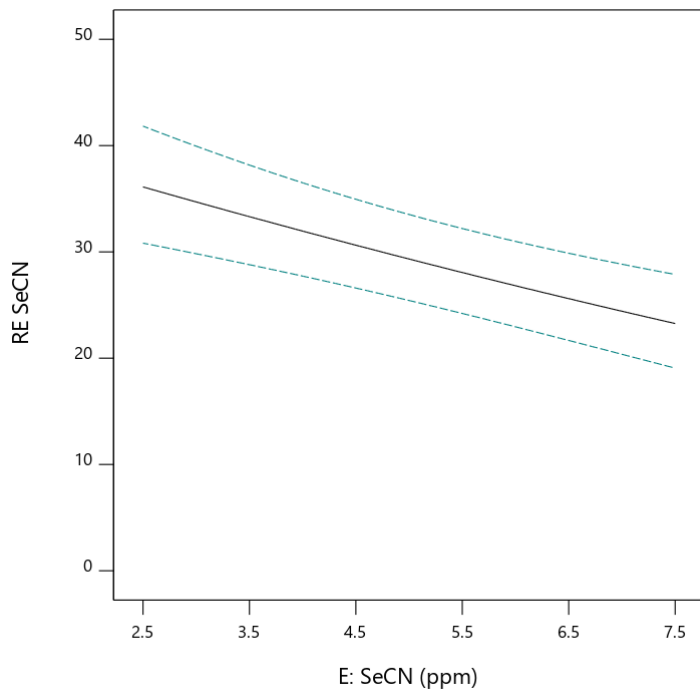


Figure 5.34 Removal Efficiency of Selenocyanate as a function of Selenocyanate concentration

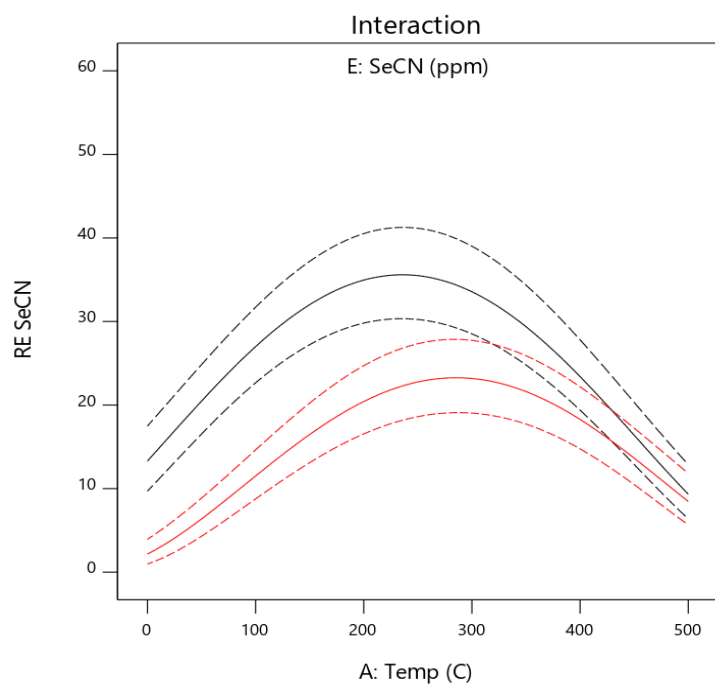


Figure 5.35 Removal Efficiency of Selenocyanate as a function of Calcination temperature and selenocyanate concentration

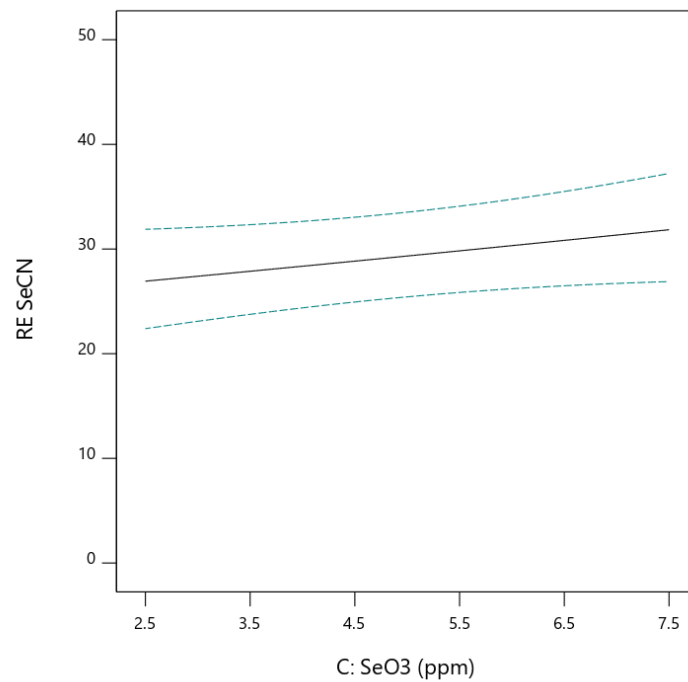


Figure 5.36 Removal Efficiency of Selenocyanate as a function of Selenite concentration

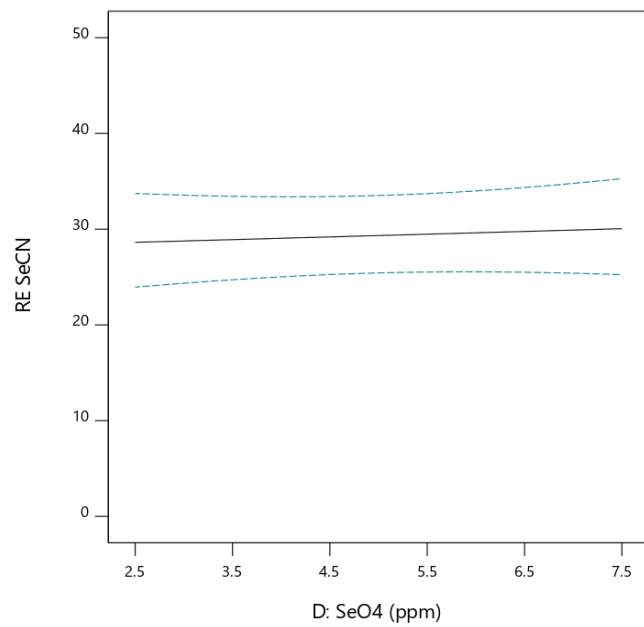


Figure 5.37 Removal Efficiency of Selenocyanate as a function of Selenate

### 5.3 Adsorption Isotherm

The adsorption isotherm describes the amount of an adsorbate that can be adsorbed onto an adsorbent at equilibrium and at a constant temperature. The adsorption equilibrium of selenium species (selenite, selenate, and selenocyanate) onto calcined LDH (250 °C) was modeled using the Langmuir and Freundlich models.

The Langmuir model's linear form is given by equation 5-1:

$$\frac{C_A}{q_A} = \frac{1}{b_A Q_M} + \frac{C_A}{Q_M} \quad (5-1)$$

Where  $C_A$  is the equilibrium concentration of adsorbate (mg/l),  $q_A$  is mg adsorbate/g adsorbent,  $Q_M$  is the maximum adsorption (mg adsorbate/g adsorbent),  $b_A$  is Langmuir adsorption constant (L/mg).

Furthermore the Freundlich model which is typically used for heterogeneous adsorbents is given by equation 5-2:

$$\log(q_A) = \log(K_A) + \left(\frac{1}{n}\right) \log(C_A) \quad (5-2)$$

Where  $K_A$  represents the Freundlich adsorption capacity parameter (mg/g) (L/mg)<sup>1/n</sup>, and 1/n represents Freundlich adsorption intensity parameter.

Also the adsorption equilibrium capacity is calculated using equation 5-3:

$$q_A = \frac{V}{M} (C_0 - C_A) \quad (5-3)$$

Where  $C_0$  represents the initial aqueous-phase concentration of adsorbate (mg/l),  $V$  represents the volume of aqueous-phase (L), and  $M$  represents the mass of adsorbent (g).

### 5.3.1 Adsorption Equilibrium of Selenite

The adsorption equilibrium of selenite onto calcined LDH (250 °C) was modeled using the Langmuir and Freundlich models. The respective values for Freundlich and Langmuir parameters are given in Table 5.11 and Figure 5.38. The respective  $R^2$  value for the Freundlich isotherm is 0.9245, and for the Langmuir isotherm is 0.928. This indicates that for selenite adsorption the Langmuir model is somewhat better. Also, the maximum adsorption capacity is 4.7 mg/g.

Table 5.11 Freundlich and Langmuir isotherm findings for selenite adsorption

| Selenium Species | Freundlich Model |           |               | Langmuir Model |                   |              |
|------------------|------------------|-----------|---------------|----------------|-------------------|--------------|
|                  | 1/n              | Log $K_A$ | $R^2$         | $b_A$ (l/mg)   | $Q_{\max}$ (mg/g) | $R^2$        |
| <b>Selenite</b>  | 0.3951           | 0.4795    | <b>0.9245</b> | 0.68           | 4.7               | <b>0.928</b> |

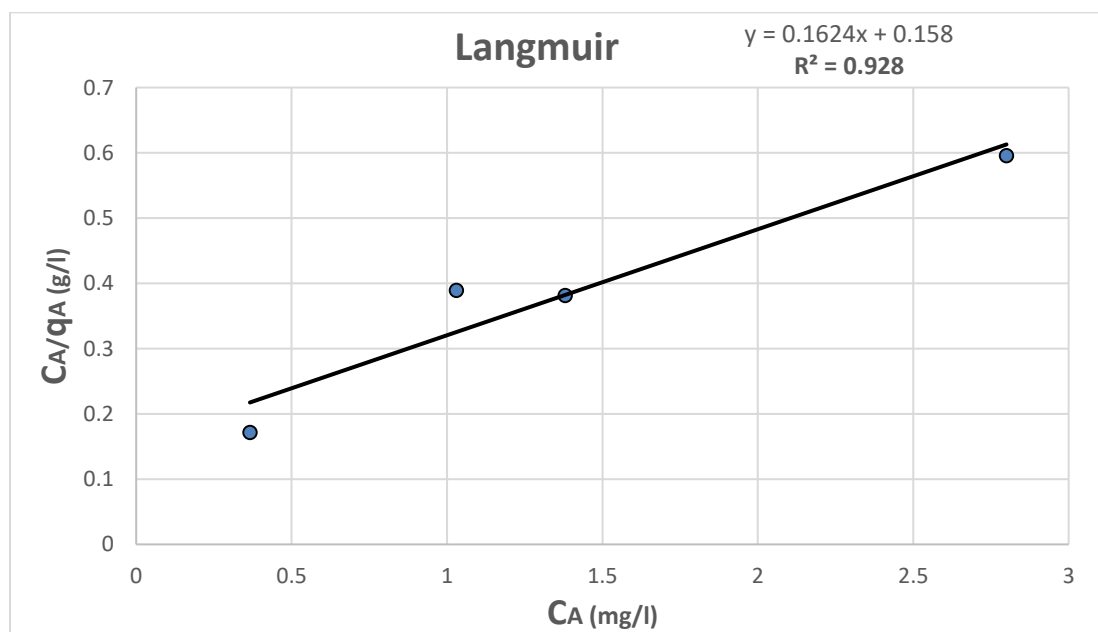


Figure 5.38 Langmuir isotherm for selenite adsorption

### 5.3.2 Adsorption Equilibrium of Selenate

The values of Freundlich and Langmuir's parameters for selenate adsorption are given in table 5.12 and figure 5.39. The coefficient of correlation  $R^2$  value for the Freundlich isotherm is 0.9282, and for the Langmuir isotherm is 0.8762, which means that the Freundlich model fits well for selenate adsorption. Also, the maximum selenate adsorption capacity is 2.969 mg/g.

Table 5.12 Freundlich and Langmuir isotherm findings for selenate adsorption

| Selenium Species | Freundlich Model |           |               | Langmuir Model |                   |               |
|------------------|------------------|-----------|---------------|----------------|-------------------|---------------|
|                  | 1/n              | Log $K_A$ | $R^2$         | $b_A$ (l/mg)   | $Q_{\max}$ (mg/g) | $R^2$         |
| <b>Selenate</b>  | 0.5241           | 0.125     | <b>0.9282</b> | 0.346          | 2.969             | <b>0.8762</b> |

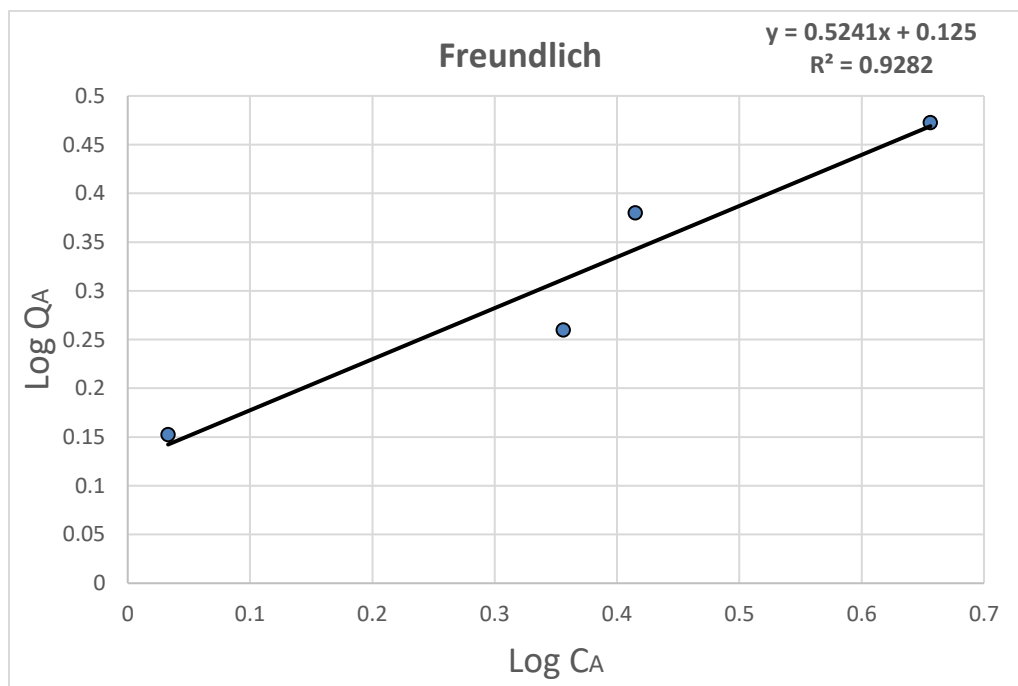


Figure 5.39 Freundlich isotherm for selenate adsorption

### 5.3.3 Adsorption Equilibrium of Selenocyanate

The values of the Freundlich and Langmuir's parameters for selenocyanate adsorption are given in table 5.13 and figure 5.39. The coefficient of correlation  $R^2$  value for the Freundlich model is 0.3553, and for the Langmuir model is 0.9366, which means that the Langmuir model fits well for selenocyanate adsorption. The maximum adsorption capacity is 1.47 mg/g.

Table 5.13 Freundlich and Langmuir isotherm findings for selenocyanate adsorption

| Selenium Species | Freundlich Model |           |        | Langmuir Model |                  |        |
|------------------|------------------|-----------|--------|----------------|------------------|--------|
|                  | 1/n              | Log $K_A$ | $R^2$  | $b_A$ (l/mg)   | $Q_{max}$ (mg/g) | $R^2$  |
| Selenocyanate    | 0.1822           | - 0.0241  | 0.3553 | 2.35           | 1.47             | 0.9366 |

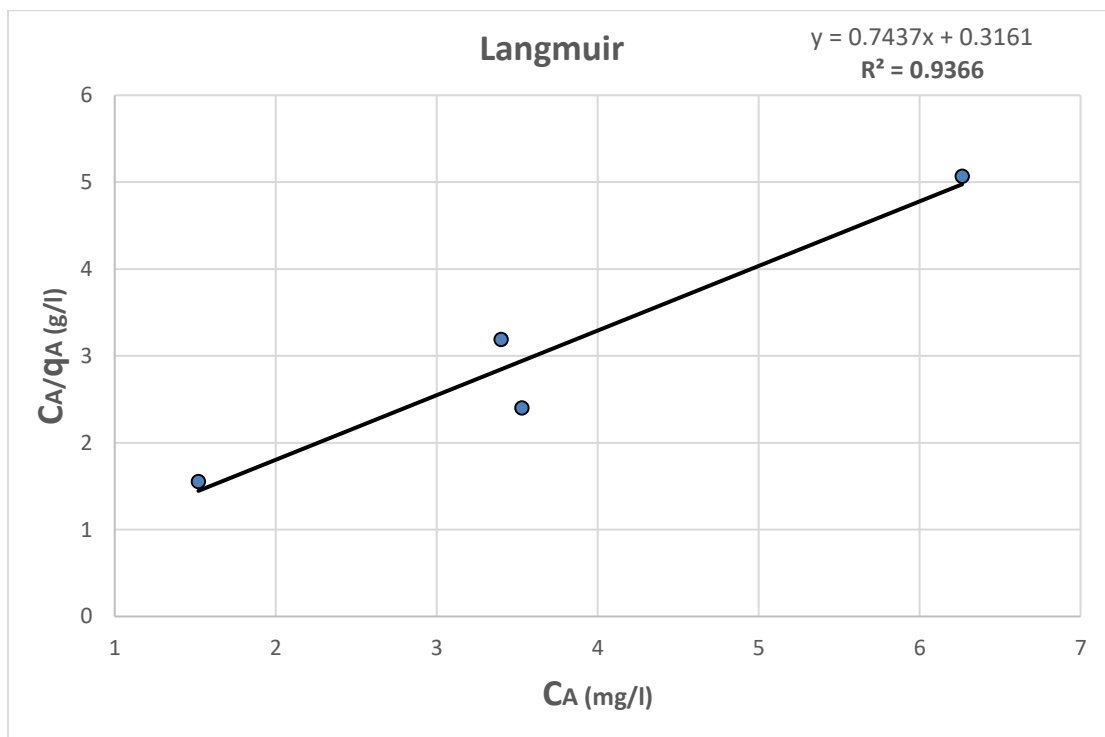


Figure 5.40 Langmuir isotherm of selenocyanate adsorption

## 5.4 Adsorption Kinetics

There are several models that describe the adsorption kinetics. In this work, the pseudo-first-order and pseudo-second-order models have been used with details given below.

### 5.4.1 Pseudo-first-order model (PFO)

Equation 5-4 shows the pseudo first-order kinetic model:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5-4)$$

Where  $q_t$  is the amount adsorbed at time  $t$  (mg/g),  $q_e$  represents the equilibrium adsorption capacity (mg/g), and  $k_1$  is the rate constant (per min).

The equation 5-4 can be rearranged as given in equation 5-5:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5-5)$$

### 5.4.2 Pseudo-second-order model (PFO)

Equation 5-6 shows the pseudo second-order kinetic model:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (5-6)$$

Where  $k_2$  represents the rate constant of the PSO model (g/mg min).

The equation 5-6 can be rearranged as given in equation 5-7:

$$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1} \quad (5-7)$$

Figure 5.41 shows that selenocyanate adsorption increased gradually for 30 min, then after 60 min the desorption took place and it decreased the selenocyanate concentration to 6.483 ppm. From 120 min to 1440 min, the concentrations were 6.138 ppm, and 6.033 ppm,

respectively. These results indicate that the adsorption starts to reach the equilibrium. On day 6, another sample was analyzed and showed 6.012 ppm, which means the adsorption reached the equilibrium.

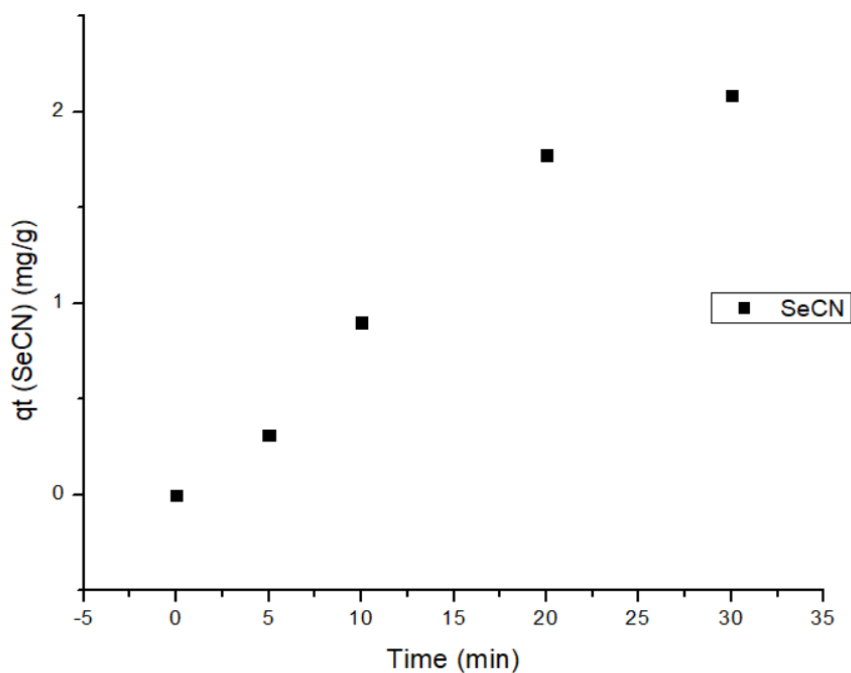


Figure 5.41 Kinetics of selenocyanate adsorption onto calcined Mg/Fe LDH (250°C)

Figure 5.42 illustrates the kinetics of selenite, selenate, and selenocyanate adsorption during competitive removal. For selenite, the adsorption increased gradually for 120 min. After 1440 min, the adsorption decreased slightly because of the desorption and kept almost constant till it reached equilibrium after six days. For selenate, the adsorption increased gradually for 30 min, then after 60 min decreased slightly due to the desorption. After 120 min, the adsorption increased slightly till 1440 min, then the adsorption kept constant until it reached equilibrium after six days. For selenocyanate, the adsorption increased at a constant rate for 1440 min then stayed constant till it reached equilibrium at

day 6. The result obtained after six days for respective selenium species almost agreed with the result obtained in the adsorption experiment.

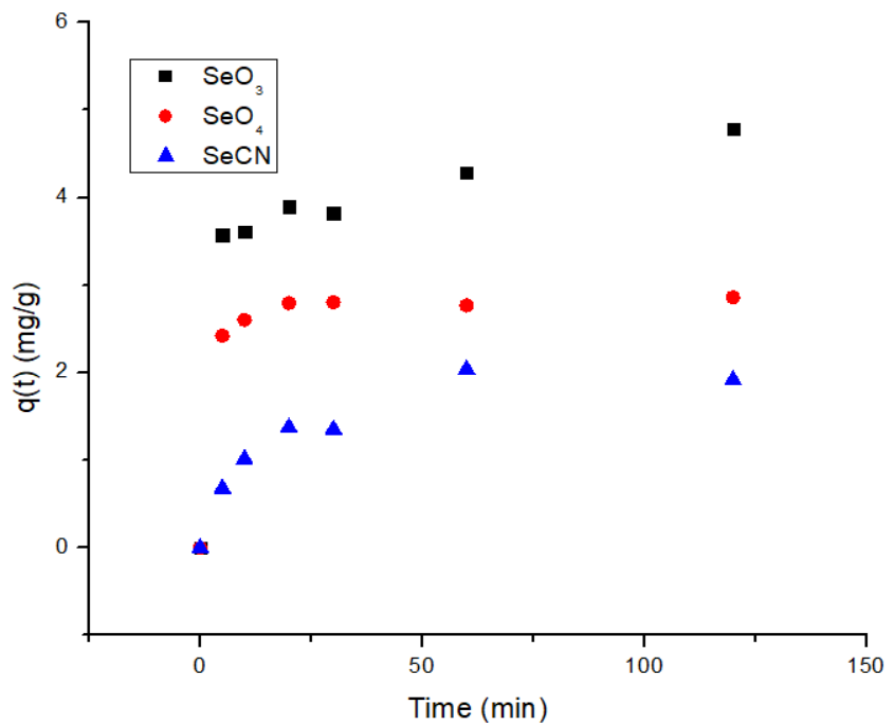


Figure 5.42 Kinetics of selenite, selenate, and selenocyanate adsorption onto Calcined Mg/Fe LDH (250°C)

The parameters of pseudo-first-order and pseudo-second-order, and the correlation coefficient of selenium species (selenite, selenate, and selenocyanate) were fitted using the nonlinear equations described earlier and the respective results are as shown in table 5.14.

Table 5.14 Parameters of pseudo-first-order and pseudo-second-order finding for selenite, selenate, and selenocyanate

| Selenium Species     | Pseudo first order         |                   |            | Pseudo second order |                   |            |
|----------------------|----------------------------|-------------------|------------|---------------------|-------------------|------------|
|                      | $k_1$ (min <sup>-1</sup> ) | $Q_{\max}$ (mg/g) | Adj. $R^2$ | $k_2$ (g/mg min)    | $Q_{\max}$ (mg/g) | Adj. $R^2$ |
| <b>Selenite</b>      | 18.32                      | 3.995             | 0.912      | 0.145               | 4.38              | 0.964      |
| <b>Selenate</b>      | 10.232                     | 2.71              | 0.975      | 0.378               | 2.867             | 0.998      |
| <b>Selenocyanate</b> | 0.0644                     | 1.915             | 0.943      | 0.037               | 2.19              | 0.961      |

From the above table, it is obvious that the coefficients of determination and estimated adsorption capacity for the pseudo-second-order model are higher than the pseudo-first-order model so, the adsorption of selenite, selenate, and selenocyanate onto LDH followed the pseudo-second-order model.

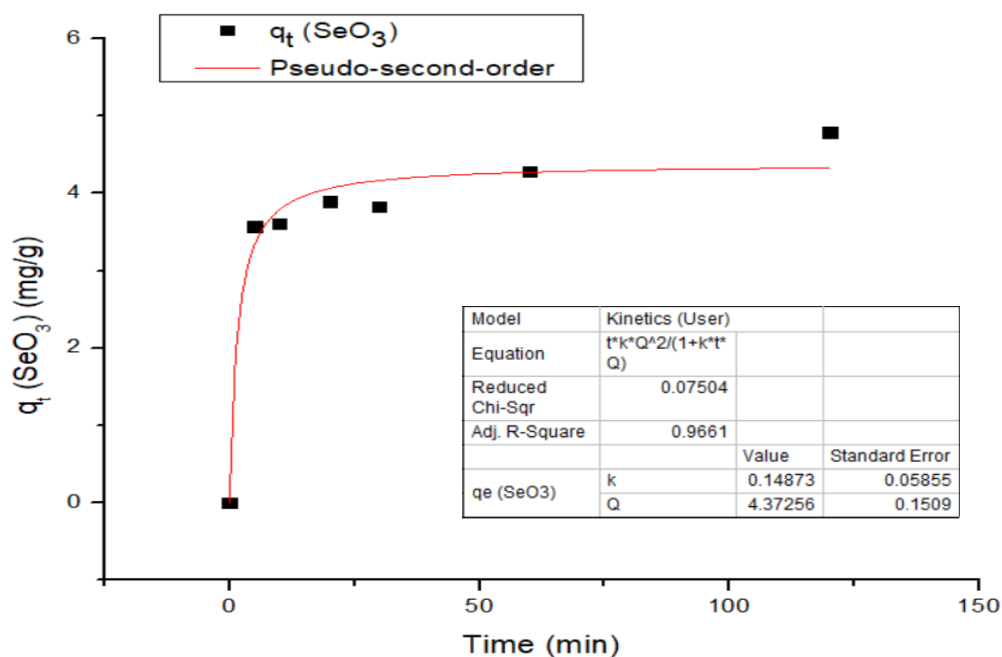


Figure 5.43 Pseudo-second-order kinetics for adsorption of selenite onto calcined Mg/Fe LDH (250°C)

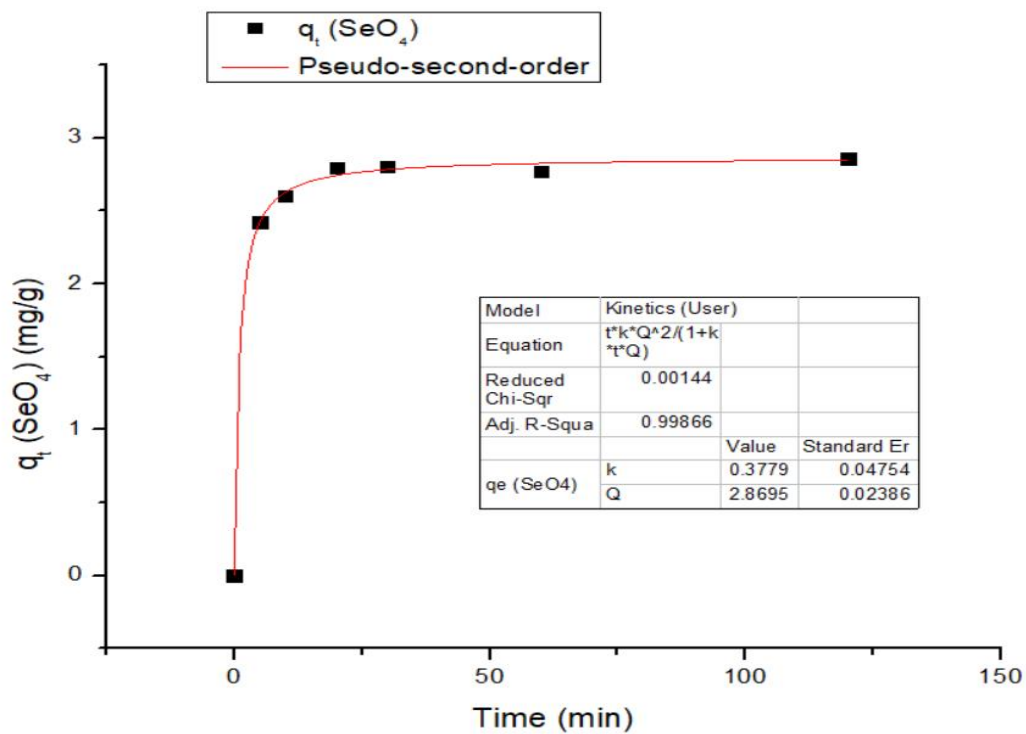


Figure 5.44 Pseudo-second-order kinetics for adsorption of selenate onto calcined Mg/Fe LDH (250°C)

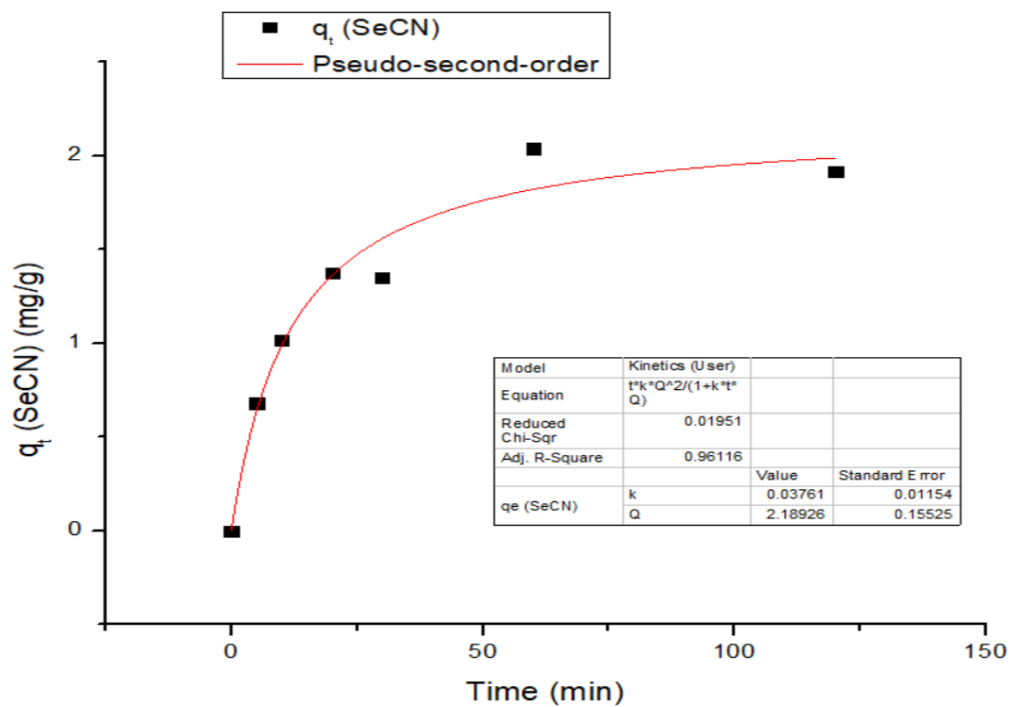
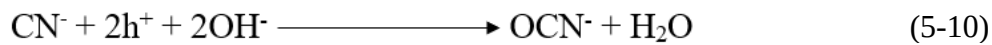
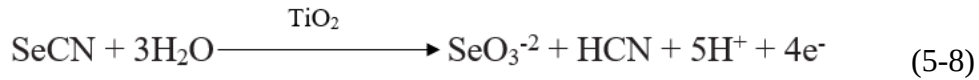


Figure 5.45 Pseudo-second-order kinetics for adsorption of selenocyanate onto calcined Mg/Fe LDH (250°C)

## 5.5 Photocatalytic Degradation (PCD) Results

Photocatalytic degradation using TiO<sub>2</sub> has shown efficient removal of selenocyanate in previous studies [54], [68]. This study further investigated the removal of selenocyanate using combined Photocatalytic Degradation and Adsorption employing TiO<sub>2</sub>-Mg/Fe LDH. The mechanism of this technology is briefly discussed here for clarification. The TiO<sub>2</sub> semiconductor material when exposed to UV light initiates positive hole (h<sup>+</sup>) generation in the valence band. The respective holes react with the hydroxylated surface and produce hydroxyl radicals (OH•)[22]. The generated hydroxyl radicals are powerful oxidizing agents that convert selenocyanate to selenite and then to selenate [54]. After this step, the LDH adsorbs the respective selenite and selenate species. Furthermore, the released cyanide (CN<sup>-</sup>) is oxidized to cyanate (OCN<sup>-</sup>). These reactions are given below:



Based on adsorption experiments, the highest removal of selenocyanate was noted for LDH calcined at 250 °C, and thus it was also used during the PCD experiments. The PCD studies investigated the effect of the three parameters, i.e., the Weight Ratio of (TiO<sub>2</sub>: LDH w/w) (1:0.5, 1:1 and 1:1.5), dosage of adsorbent (1 g/l, 1.5 g/l and 2 g/l) and selenocyanate concentration (2.5, 5, 7.5 ) ppm. The respective results were then analyzed using the Design – Expert 11 software, and the respective details are given in the next section.

### 5.5.1 RSM Results of Photocatalytic Degradation of Selenocyanate (SeCN<sup>-</sup>)

Design – Expert 11 software was used to fit the best statistical model. **2 FI model** (Sequential sum of squares for the two-factor interaction (AB, BC, etc.) terms) is the best-fitted model to analyze the obtained results using  $\alpha = 0.05$ . The model showed that The **Predicted R<sup>2</sup> of 0.8642** is in reasonable agreement with the **Adjusted R<sup>2</sup> of 0.9420**; i.e. the difference is less than 0.2.

Table 5.15 Statistical analysis of Linear model for PCD result

|                  |       |                                |         |
|------------------|-------|--------------------------------|---------|
| <b>Std. Dev.</b> | 3.31  | <b>R<sup>2</sup></b>           | 0.9627  |
| <b>Mean</b>      | 47.01 | <b>Adjusted R<sup>2</sup></b>  | 0.9420  |
| <b>C.V. %</b>    | 7.03  | <b>Predicted R<sup>2</sup></b> | 0.8642  |
|                  |       | <b>Adeq Precision</b>          | 23.2217 |

ANOVA table was fitted to provide the significant and insignificant terms. The model is significant with F- value = 46.48 and p-value = < 0.0001. The main terms; Ratio, Dose, and Selenocyanate concentration are significant terms with F-value = 116.44, 38.21, 39.06, and p- value = < 0.0001, 0.0002, 0.0001 respectively.

Table 5.16 ANOVA table of 2 FI model of PCD results

| Source         | Sum of Squares | df | Mean Square | F-value | p-value  |             |
|----------------|----------------|----|-------------|---------|----------|-------------|
| Model          | 2540.17        | 5  | 508.03      | 46.48   | < 0.0001 | significant |
| <b>A-Ratio</b> | 1272.80        | 1  | 1272.80     | 116.44  | < 0.0001 |             |
| <b>B-Dose</b>  | 417.67         | 1  | 417.67      | 38.21   | 0.0002   |             |
| <b>C-SeCN</b>  | 426.97         | 1  | 426.97      | 39.06   | 0.0001   |             |
| <b>AB</b>      | 170.04         | 1  | 170.04      | 15.56   | 0.0034   |             |
| <b>AC</b>      | 252.68         | 1  | 252.68      | 23.12   | 0.0010   |             |
| Residual       | 98.38          | 9  | 10.93       |         |          |             |
| Cor Total      | 2638.55        | 14 |             |         |          |             |

The Residual Analysis was fitted to check either the values corresponding to the three assumptions (normal distribution, independent and identical) of a probability distribution or not. In figure 5.46, (A) the values distributed around the straight line, which means they are normally distributed. (B) the values followed a random pattern that corresponding to independently and (C) represents the constant variance (identical).

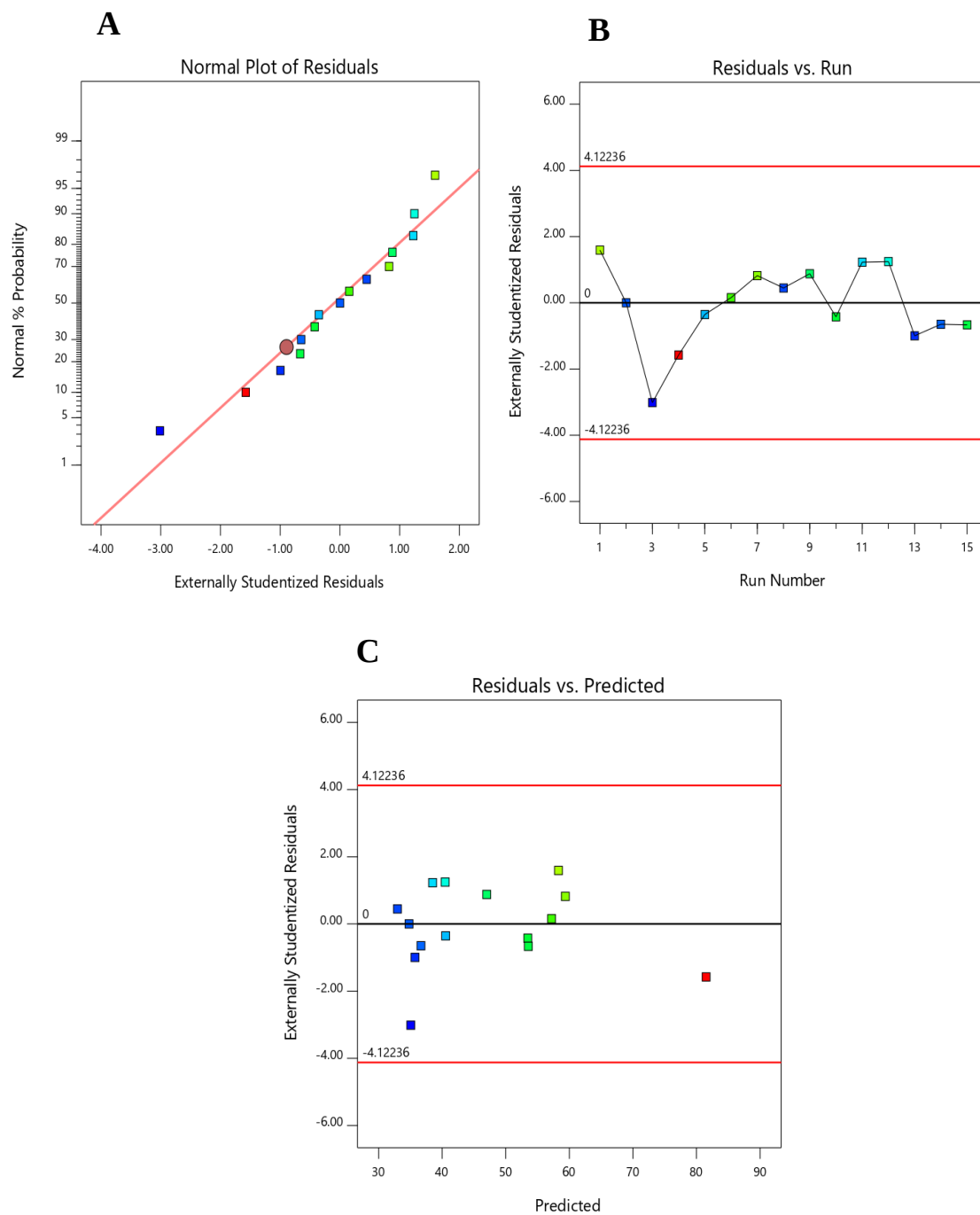


Figure 5.46 Residual Analysis of PCD of SeCN removal (A) normal distribution (B) independent (C) constant variance

### **5.5.2 Effect of Ratio, Concentration of Selenocyanate and Dosage on Removal Efficiency of Selenocyanate in Photocatalytic Degradation (PCD)**

The analysis of obtained results showed that the removal efficiency of selenocyanate increased with an increase in the weight ratio (figure 5.47), and an increase in the dosage (figure 5.48). However, the removal efficiency decreased with an increase in the selenocyanate concentration (figure 5.49). The highest removal of selenocyanate was 2.5 ppm and 1.5 in concentration and weight ratio, respectively. The adsorption capacity of LDH to adsorb selenate was low at high concentration and increased with low concentration. The variation in the removal efficiency of selenate is the same variation obtained in the removal efficiency of selenate in adsorption experiments, taking into consideration the conditions of pH for both experiments which are almost the same. Hereby, we can conclude that low adsorption of selenate was unrelated to the presence of  $\text{TiO}_2$  but because of the low adsorption capacity, resulted from the high pH of solution that caused repulsion force which led to decrease adsorption through the surface of LDH and anion exchange. Also, this temperature did not destroy or remove large amounts of nitrates and water molecules, hence it generated a little space area. For weight ratio, an increase in removal efficiency with an increase in weight ratio can be explained as; an increase in LDH amounts provided more particles caused an increase in the adsorption surface. At 0.5 ratio, the LDH amount is half of  $\text{TiO}_2$  which means fewer particles, hence low removal efficiency. At 1.5 ratio, the amount of LDH was more than  $\text{TiO}_2$  which increased the removal efficiency. For dosage, an increase in the adsorbent amount provided more  $\text{TiO}_2$  for degradation of selenocyanate and more LDH to adsorb anions generated from the photocatalytic degradation process. The removal efficiency decreased with an increase in

the selenocyanate concentrations which refers to the low capability of adsorbent to degrade and remove the higher concentrations of selenocyanate.

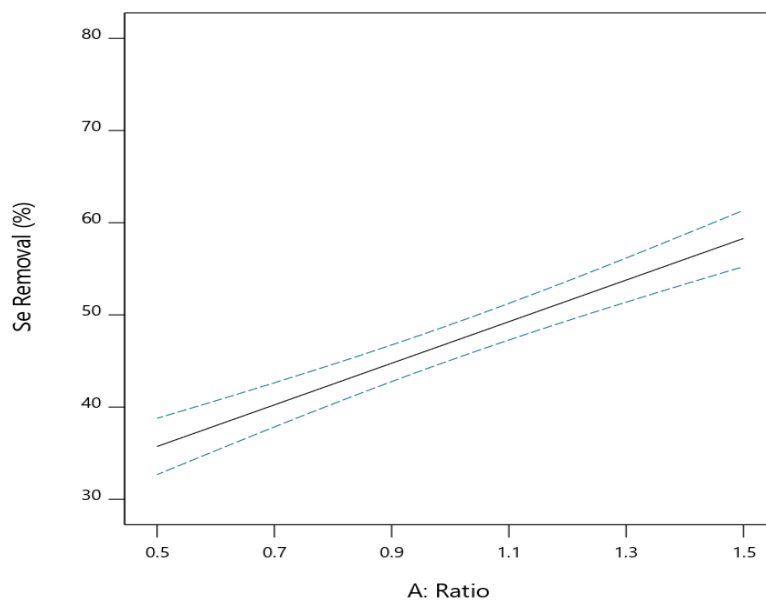


Figure 5.47 Removal Efficiency of total selenium as a function of the weight ratio

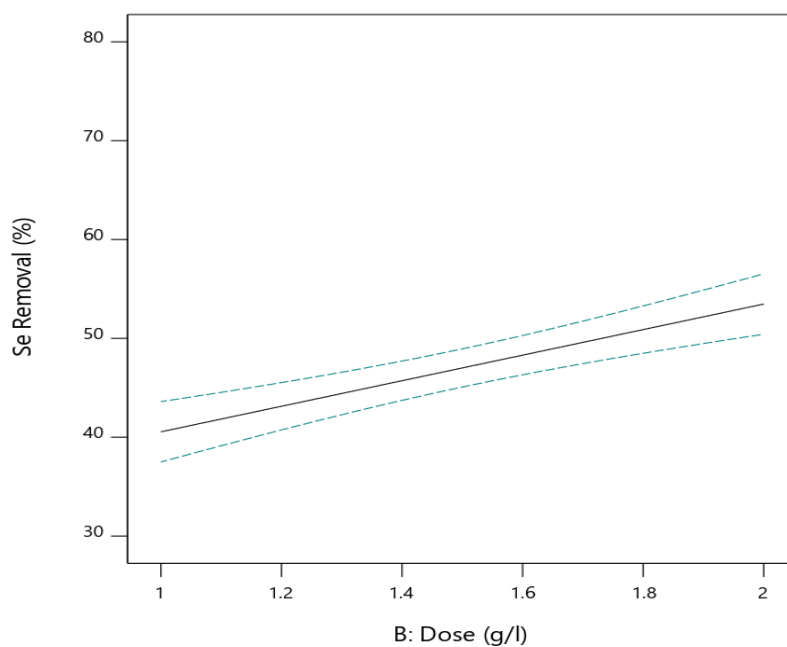


Figure 5.48 Removal Efficiency of total selenium as a function of adsorbent Dose

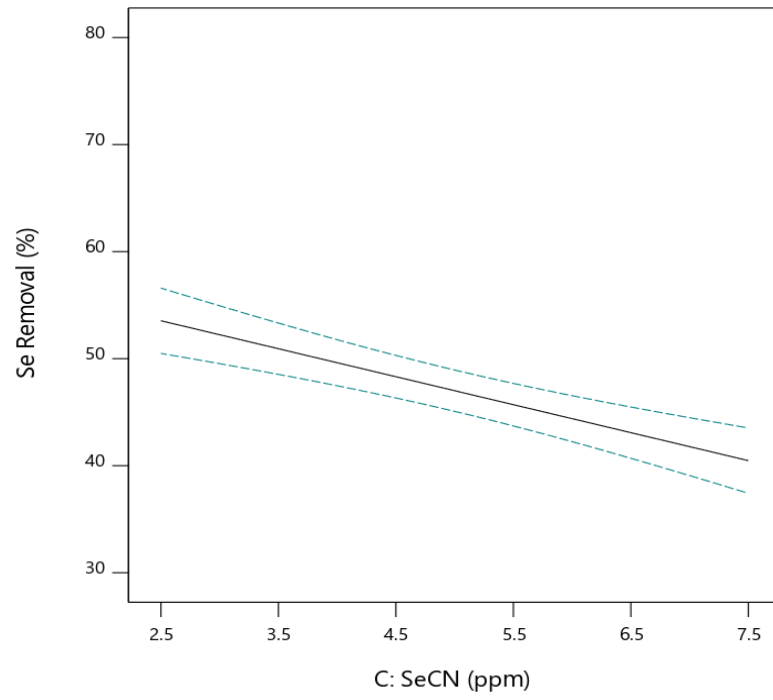


Figure 5.49 Removal Efficiency of Selenate as a function of selenocyanate concentration

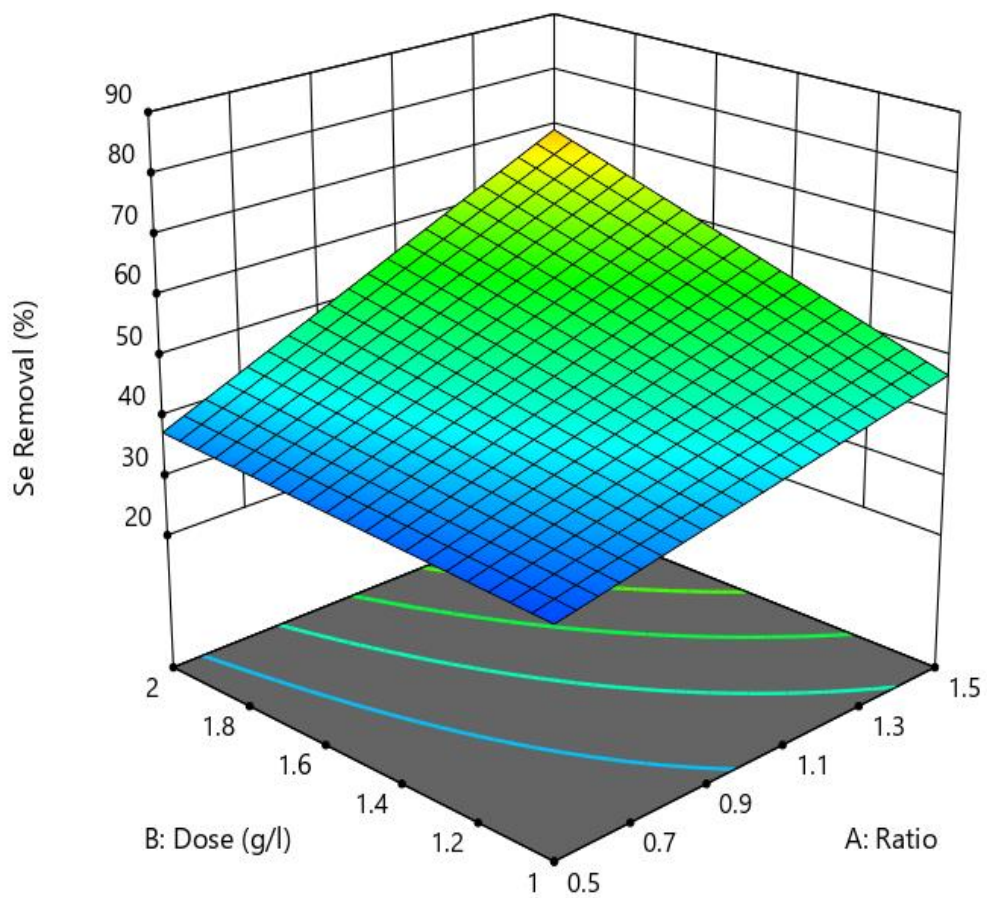


Figure 5.50 3D surface of Selenate removal efficiency as a function of the Adsorbent dosage and Weight ratio

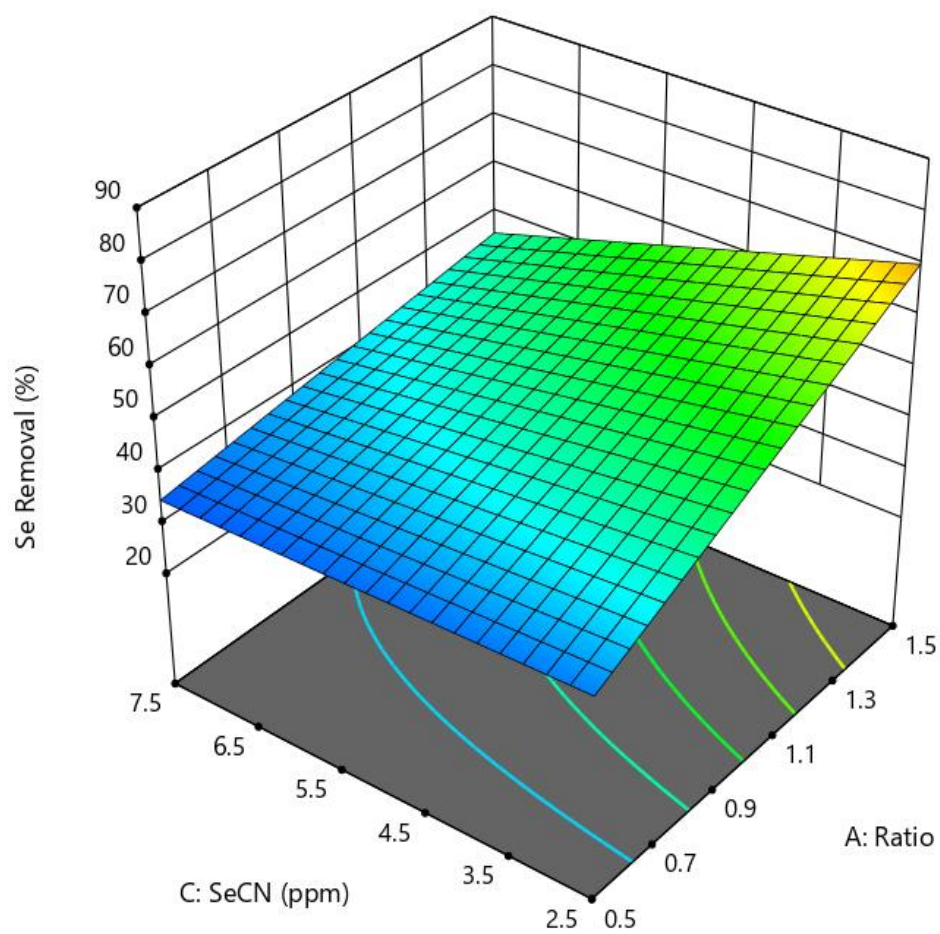


Figure 5.51 3D surface of Selenoate removal efficiency as a function of Weight ratio and selenocyanate concentration

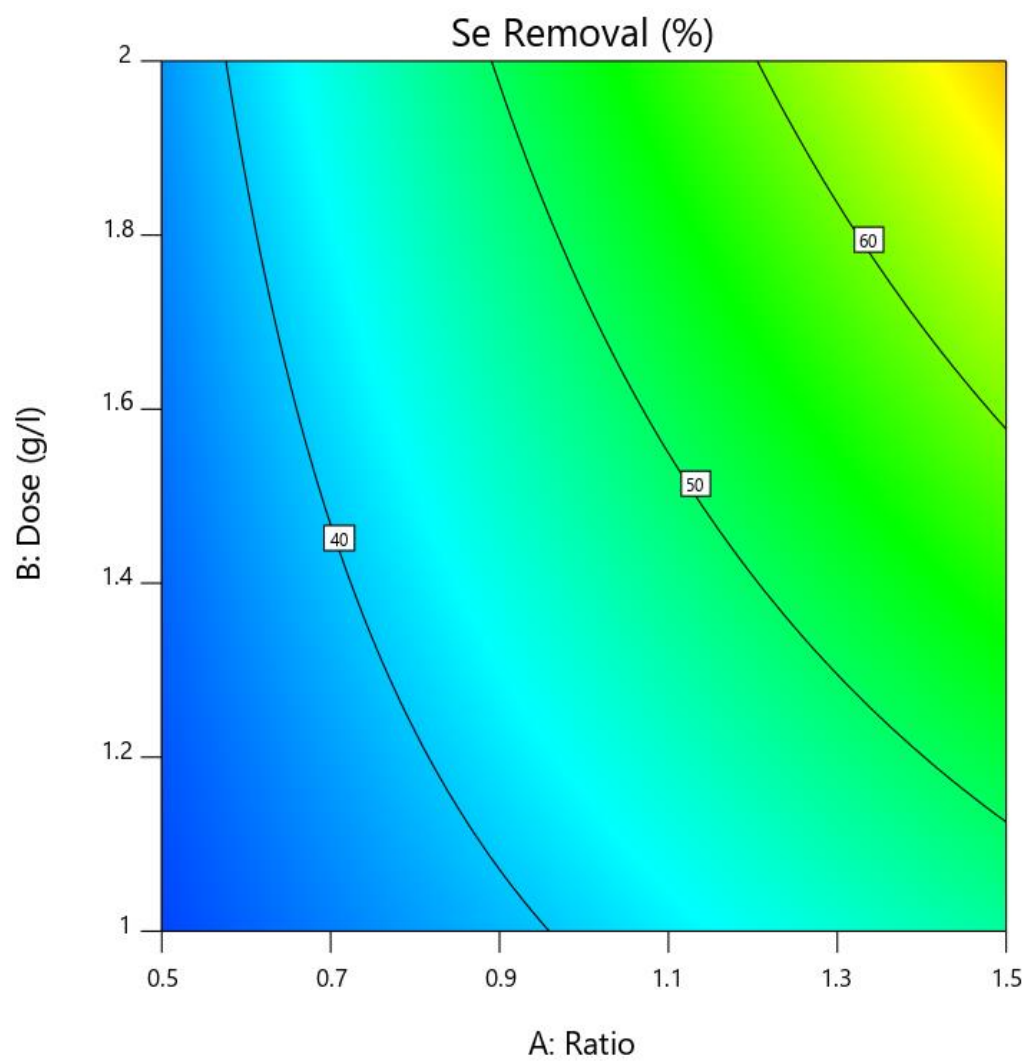


Figure 5.52 Contour map of selenium removal efficiency as a function of the Adsorbent dosage and Weight ratio

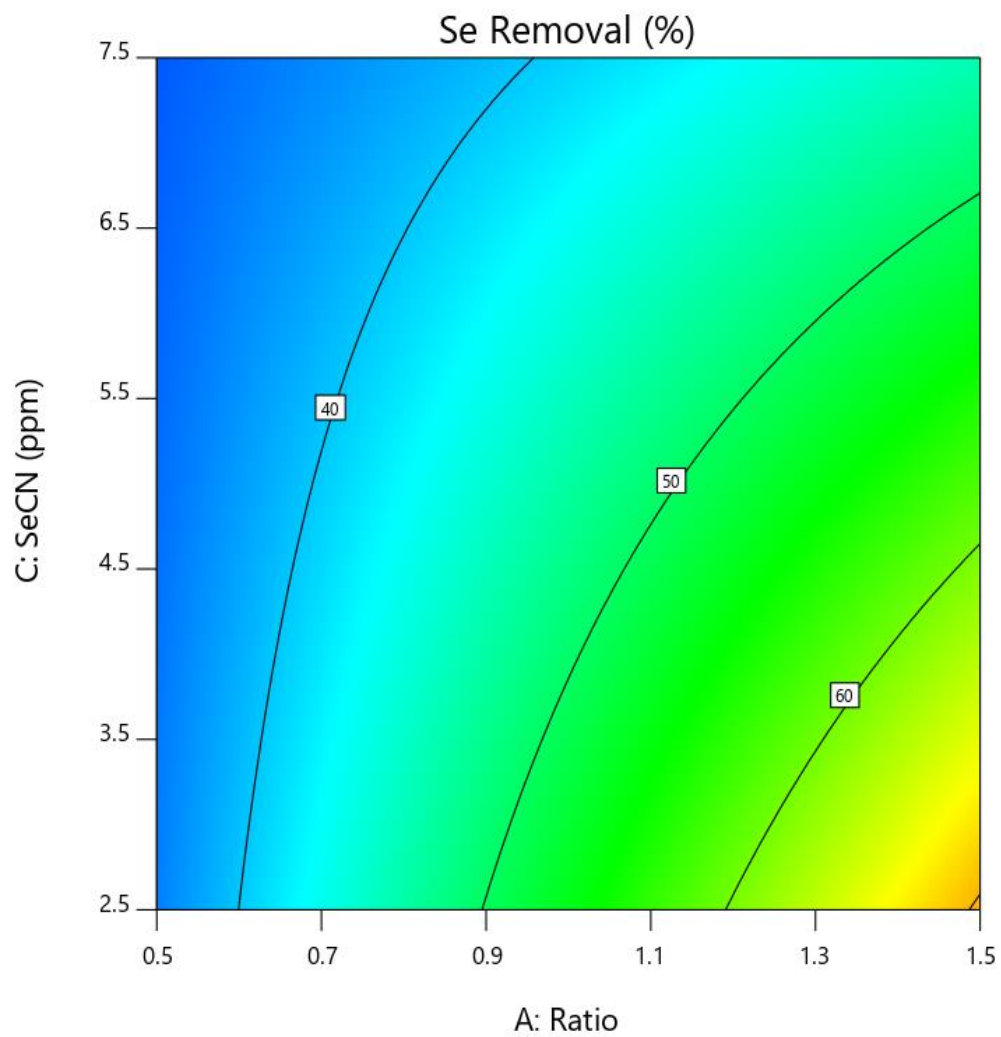


Figure 5.53 Contour map of Selenate removal efficiency as a function of weight ratio and selenocyanate concentration

### 5.5.3 Experimental Results of Photocatalytic Degradation of Selenocyanate (SeCN<sup>-</sup>)

For all PCD experiments, the initial pH was measured twice, one before adding the TiO<sub>2</sub>/LDH and the second 30 min after adding TiO<sub>2</sub>/LDH (but before exposure to the UV light source). Samples were taken between 5 and 360 min. For each experiment, SeCN<sup>-</sup>, SeO<sub>3</sub><sup>2-</sup>, SeO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, OCN<sup>-</sup>, and CN<sup>-</sup> were measured to explore the selenocyanate removal process.

For all experiments, it was noted that the selenocyanate species degraded rapidly, and converted to selenite in a short period ranging from 5 to 20 min. This quick degradation supports that LDH improves and accelerates the photocatalytic degradation process, and that the presence of Fe<sup>3+</sup> in the structure of LDH enhances photocatalytic degradation due to its good photo-responsive property [14]. Nitrate showed an increase (because of ion exchange resulting in release nitrate anions in the water) whereas cyanide from degradation of selenocyanate converted to cyanate.

The initial pH, & pH after 30 min of stirring in the absence of UV light, and the final pH after 6 hours, were measured, as shown in table 5.17. After 30 min of mixing, the suspension pH increased. It was also noted that the final pH was reduced, which is probably due to the consumption of hydroxide ions to degrade selenocyanate.

The change in pH after adding the adsorbent over 30 min, showed that the pH increased gradually with time and stabilized after 15 min, as shown in figure 5.54.

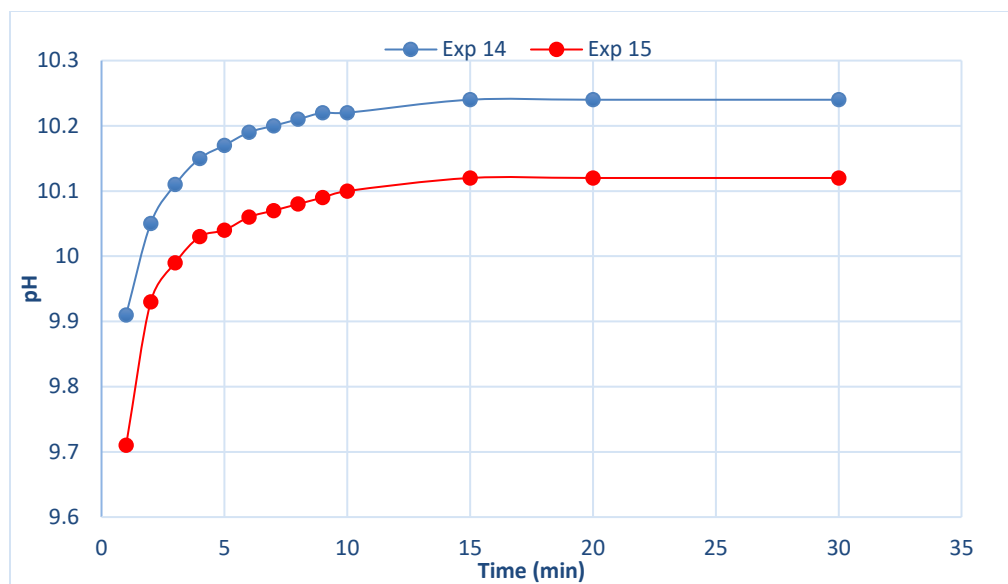


Figure 5.54 The change in pH as a function of time

Table 5.17 pH of photocatalytic degradation experiments

| Ratio | Dose | SeCN | Initial pH | pH after 30 min without UV | Final pH |
|-------|------|------|------------|----------------------------|----------|
| 1.5   | 1    | 7.5  | 6.68       | 10.02                      | 9.4      |
| 1     | 2    | 5    | 6.62       | 10.28                      | 9.36     |
| 0.5   | 2    | 2.5  | 6.46       | 10.15                      | 9.6      |
| 1     | 1.5  | 7.5  | 6.64       | 10.24                      | 9.67     |
| 1     | 1.5  | 2.5  | 6.26       | 10.18                      | 9.63     |
| 0.5   | 2    | 7.5  | 6.61       | 10.24                      | 9.69     |
| 1     | 1.5  | 5    | 6.42       | 10.17                      | 9.56     |
| 1.5   | 2    | 7.5  | 6.64       | 10.28                      | 9.67     |
| 0.5   | 1    | 2.5  | 6.38       | 10.08                      | 9.58     |
| 0.5   | 1.5  | 5    | 6.51       | 10.13                      | 9.61     |
| 1.5   | 2    | 2.5  | 6.32       | 10.25                      | 9.67     |
| 1.5   | 1.5  | 5    | 6.61       | 10.24                      | 9.64     |
| 1     | 1    | 5    | 6.62       | 10.2                       | 9.63     |
| 0.5   | 1    | 7.5  | 6.66       | 10.1                       | 9.52     |
| 1.5   | 1    | 2.5  | 6.32       | 10.09                      | 9.62     |

#### 5.5.4 Effect of weight ratio and dosage on removal of 2.5 ppm selenocyanate

Figure 5.55 illustrates PCD experimental results for  $\text{SeCN}^-$  2.5 ppm, Ratio 1 and Dose 1.5 g/l. In the absence of UV light, a sample was collected immediately after adding the adsorbent and showed 1.9 ppm of selenocyanate. This noted removal may occur due to the low concentration of  $\text{SeCN}^-$  and comparatively high dose of adsorbent. Also, the low suspension pH provided optimum conditions to achieve enough selenium removal. Another sample collected after 30 min showed 2.34 ppm of selenocyanate. The noted change is probably caused by desorption of selenocyanate. Using the UV light, selenocyanate degraded and disappeared after 10 min. Selenite species also increased for 10 min, then reduced and disappeared after 45 min. Selenate formation started after 5 min and kept increasing until 60 min, and reached to 2.38 ppm near 5 hours. Then, the pH of was adjusted to 4 for further removal. After 5 min a sample was collected and showed 1.067 ppm of selenate.  $\text{NO}_3^-$  increased during the first 5 min and reached to 4.89 ppm at near 5 hours and increased again after adjusting pH.  $\text{OCN}^-$  started to form after 5 min and continued to increase till near 5 hours and disappeared after adjusting the pH.

Figure 5.56 illustrates results for  $\text{SeCN}^-$  2.5 ppm, Ratio = 1.5 and Dose = 1 g/l. The sample collected after adding adsorbent showed 2.153 ppm selenocyanate, and after 30 min of stirring showed 2.083 ppm of selenocyanate. In the presence of UV light, selenocyanate disappeared after 20 min due to low concentration. Selenite appeared within 5 min and disappeared after 45 min. Selenate started to form within 5 min and increased reaching 1.404 ppm after 1 hour, then stayed almost constant and reached 1.323 ppm after 6 hours. The pH was adjusted to 4 for more removal, and after 5 min selenate was only 0.769 ppm,

due to high amount of LDH.  $\text{OCN}^-$  increased till 6 hours and then reduced slightly after adjusting pH.

Figure 5.57 illustrates the experimental results for  $\text{SeCN}^-$  2.5 ppm, Ratio 0.5 and Dose 2 g/l. A sample was collected immediately after adding the adsorbent and showed 2.46 ppm of selenocyanate. After 30 min 2.055 ppm of Selenocyanate was noted, which is low because of low LDH amount. After starting the photocatalysis, selenocyanate disappeared after 10 min. Selenite reached 1.5 ppm after 5 min, then disappeared after 45 min. Selenate appeared quickly and reached 0.677 ppm within 5 min, then passed through adsorption and desorption and reached 2 ppm after 6 hours. After 6 hours, the pH of the solution was adjusted to 4. After 5 min, a sample was collected and showed 0.977 ppm of selenate, and after 10 min, another sample was collected that showed further increase. Cyanate increased gradually till it reached 1.304 ppm after 6 hours, and disappeared after decreasing the pH.

Figure 5.58 illustrates results for  $\text{SeCN}^-$  2.5 ppm, Ratio 0.5, and Dose 1 g/l. The 5 min sample showed 2.412 ppm of Selenocyanate, and after 30 min 2.15 ppm Selenocyanate was noted. The low removal of selenocyanate refers to the low dosage and low LDH amount. In the presence of UV light, selenocyanate degraded totally after 5 min. Selenite, after 5 min was 1.654 ppm and it declined gradually and disappeared after 1 hour. Selenate started appearing within 5 min and increased gradually till it reached 2.217 ppm after 6 hours. Then the pH was decreased to 4, and after 5 min, a sample was collected and showed 1.484 ppm selenate. This removal compared with the removal from the previous experiments is considered slightly low because of the low amount of the adsorbent. Cyanate increased gradually along the time and reached 2.175 ppm after 6 hours, then disappeared at the acidic condition.

Figure 5.59 illustrates results for  $\text{SeCN}^-$  2.5 ppm, Ratio 1.5, and Dose 2 g/l. The 5 min sample showed 2.033 ppm of selenocyanate, and 30 min of stirring without UV light, showed selenocyanate concentration to be 2.033 ppm. In the presence of UV light, selenocyanate degraded and disappeared after 10 min. Selenite after 5 min was 1.316 ppm, then declined gradually and disappeared within 30 min. Selenate after 5 min was 0.375 ppm, which increased slightly and passed through adsorption and desorption till it reached 0.73 ppm after 6 hours, which is the highest removal efficiency because of highest dosage and ratio. For further investigation, the pH of the solution was declined to 4. After 5 min, a sample was collected and showed 0.53 ppm selenate. Cyanate concentration built up gradually till it reached 2.199 ppm after 3 hours, then declined and reached 1.776 ppm after 6 hours.

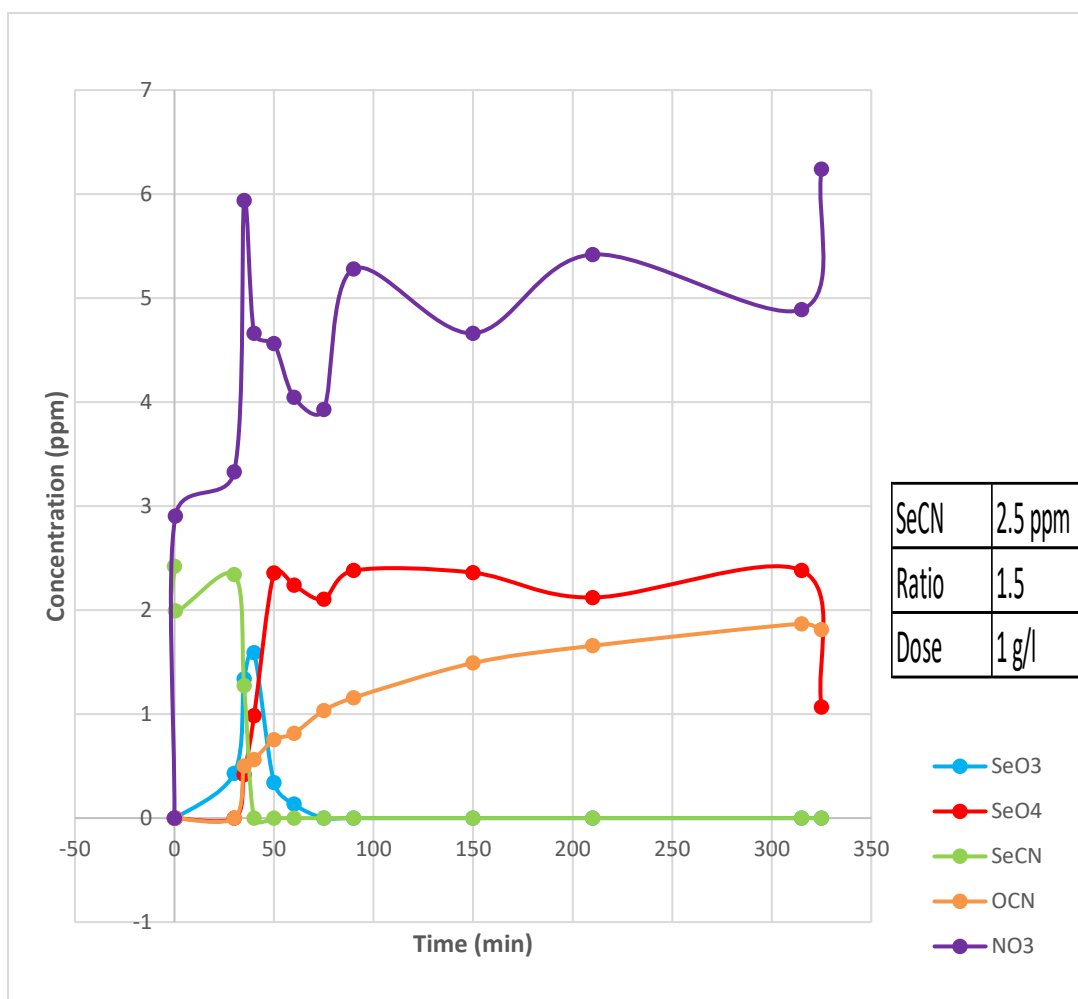


Figure 5.55 Photocatalytic Degradation of 2.5 ppm SeCN with ratio 1.5 and dose 1 g/l

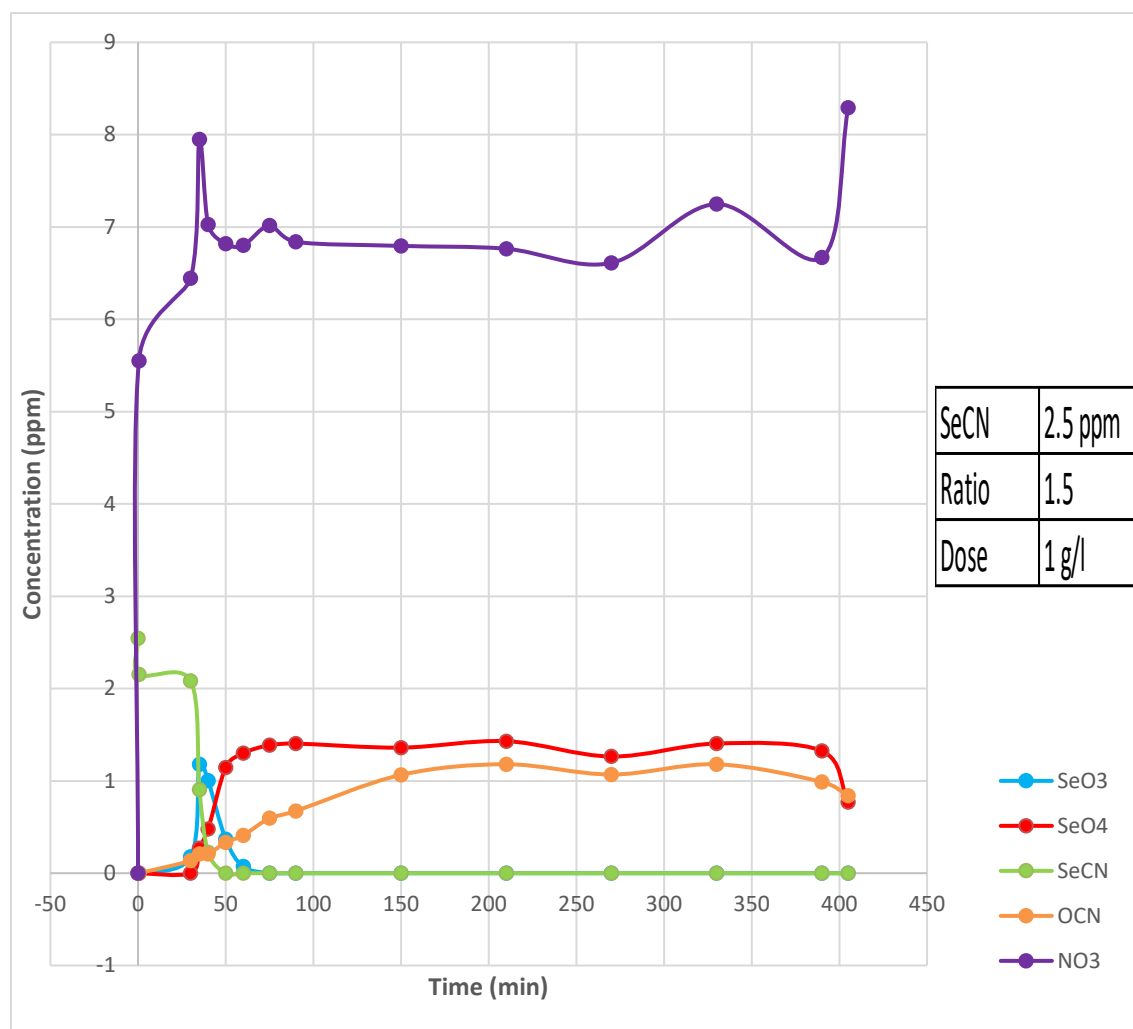


Figure 5.56 Photocatalytic Degradation of 2.5 ppm of SeCN, Ratio = 1.5 and Dose = 1g/l

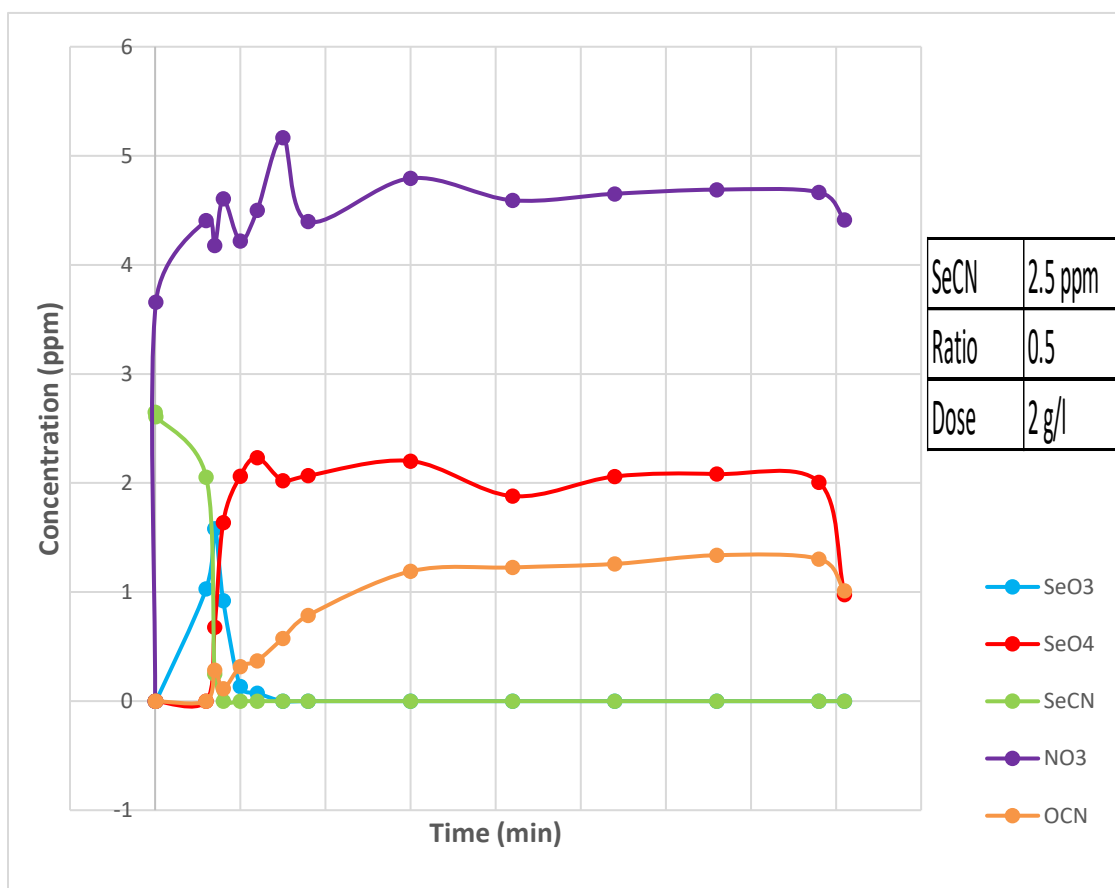


Figure 5.57 Photocatalytic Degradation of 2.5 ppm of SeCN, Ratio = 0.5 and Dose = 2g/l

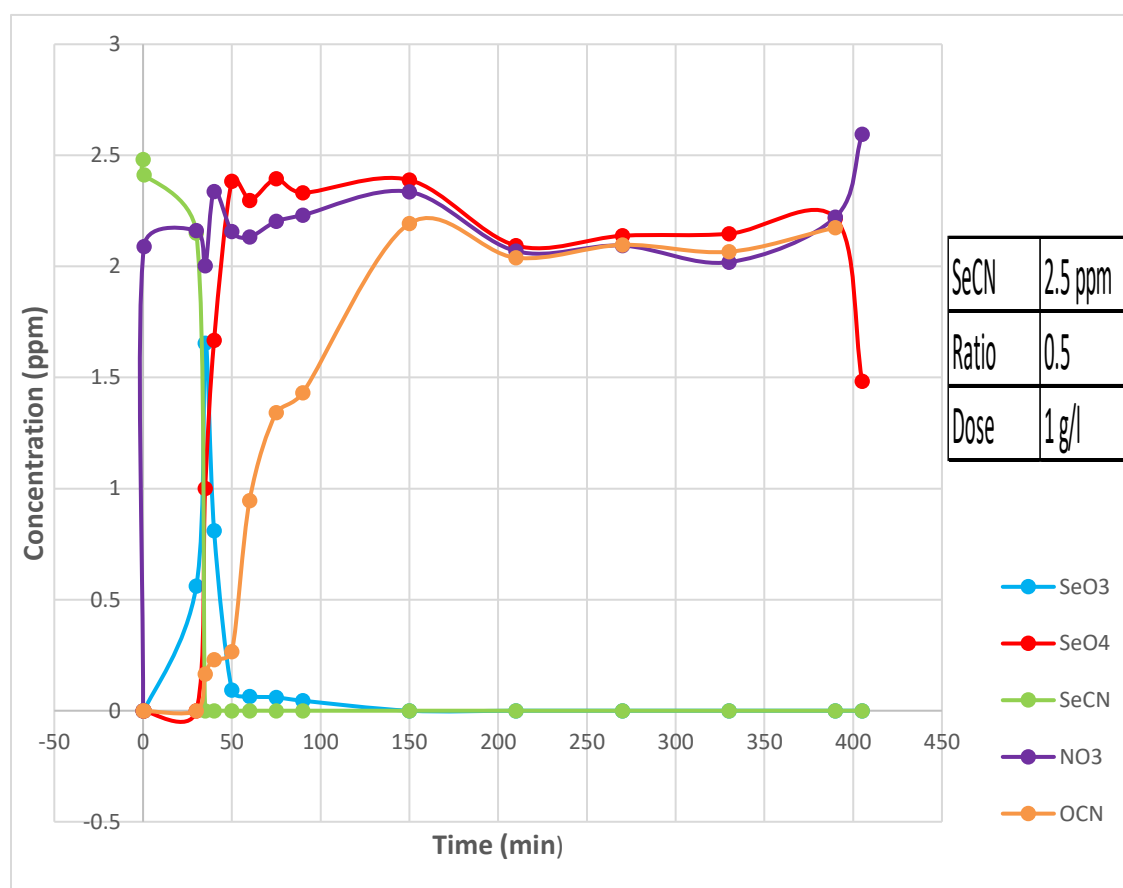


Figure 5.58 Photocatalytic Degradation of 2.5 ppm of SeCN, Ratio = 0.5 and Dose = 1 g/l

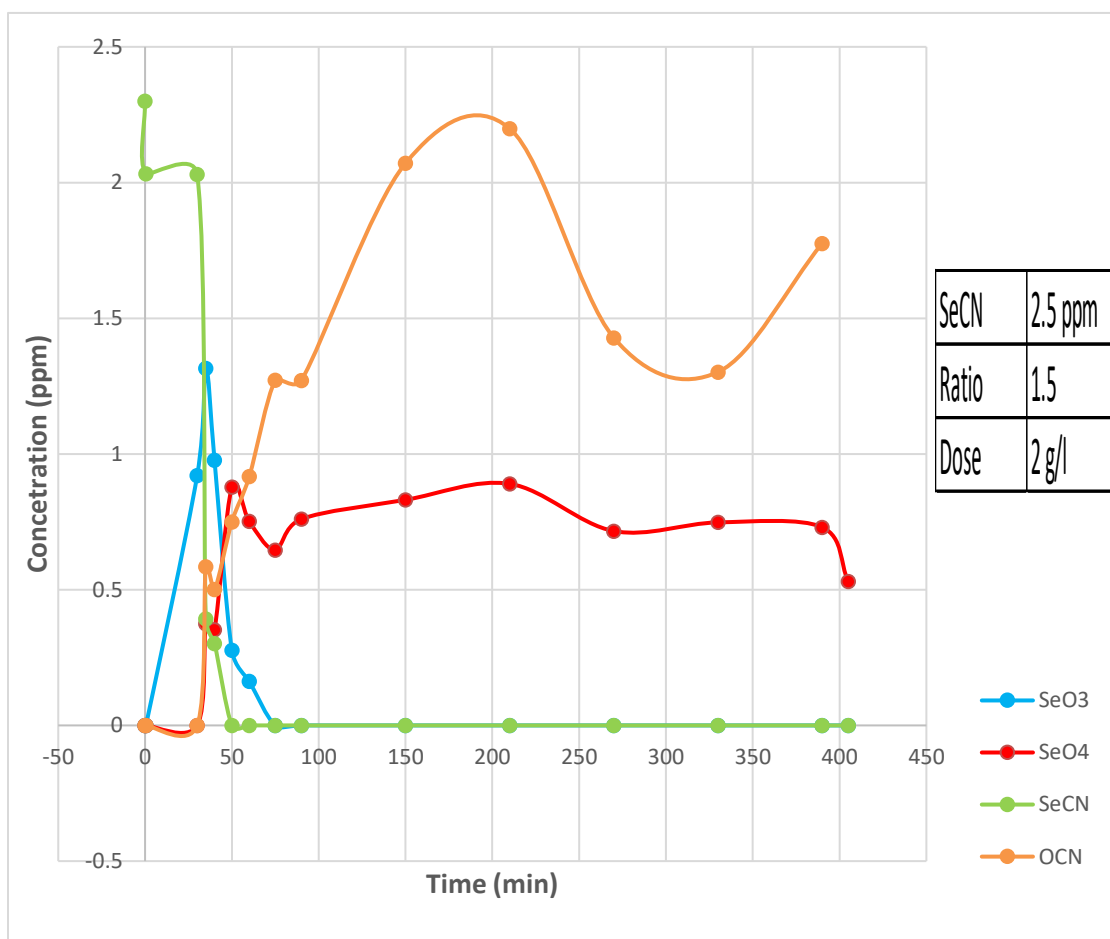


Figure 5. 59 Photocatalytic Degradation of 2.5 ppm of SeCN, Ratio = 1.5 and Dose = 2 g/l

### 5.5.5 Effect of weight ratio and dosage on removal of 5 ppm selenocyanate

Figure 5.60 illustrates PCD experimental results for  $\text{SeCN}^-$  5 ppm, Ratio 1 and Dose 1.5 g/l. In the presence of UV light, selenocyanate disappeared after 30 min. Selenite appeared within 5 min and converted quickly to selenate till it disappeared after 45 min. Selenate formation started after 5 min and continued to increase till it reached 4.74 ppm after 45 min, then it passed through adsorption and desorption till it reached 3.4088 ppm after 6 hours. The obtained removal efficiency was considered at the same ranges obtained in the removal of selenate in adsorption experiments for LDH calcined at 250 °C.  $\text{CN}^-$  appeared at low concentration, which might be because of the rapid conversion to  $\text{OCN}^-$ . Nitrate presented at low concentrations.

Figure 5.61 illustrates results for  $\text{SeCN}^-$  5 ppm, Ratio 1 and Dose 2 g/l. The 30 min sample showed 4.64 ppm of selenocyanate. After starting the photocatalysis, selenocyanate disappeared after 30 min. Selenite species increased for 20 min then decreased and disappeared after 30 min. Selenate formation started after 5 min and increased till it reached the maximum removal 60 min then kept constant till it reached 3.255 ppm after 6 hours. More investigation was done by reducing pH of the solution to 6. After 5 min a sample was collected and showed 2.798 ppm of selenate. For nitrate, the concentration increased after reducing the pH, which means the adsorption of selenate because of the anion exchange. Cyanide appeared at low concentration and disappeared after 5 hours. Cyanate concentration increased with time during the PCD and disappeared after reducing pH.

Figure 5.62 illustrates the experimental results for  $\text{SeCN}^-$  5 ppm, Ratio 0.5 and dose 1.5 g/l. After 30 min of stirring without UV light, selenocyanate concentration was 4.711 ppm. In the presence of UV light, selenocyanate disappeared after 5 min. Selenite formation was

rapid during the first 10 min, then declined till it disappeared after 45 min. Selenate started appearing within 5 min and increased for 30 min then stayed almost constant till it reached 4.575 ppm after 6 hours. Then the pH was adjusted to 6 for more removal. After 5 min, a sample was collected and showed 4.008 ppm of selenate. Nitrate stayed in constant range even after reducing pH.  $\text{CN}^-$  showed low concentrations during the removal process until disappearing after 5 hours.  $\text{OCN}^-$  increased gradually, then stayed constant from 2 to 6 hours.

Figure 5.63 illustrates results for  $\text{SeCN}^-$  5 ppm, Ratio 1.5 and Dose 1.5 g/l. After adding the adsorbent, a sample was collected immediately and showed 4.34 ppm of  $\text{SeCN}^-$ . After 30 min 4.53 ppm of selenocyanate was noted. This result can be explained as; the immediate sample was collected at pH of solution, and another sample was collected when pH of solution gained pH of adsorbent, which caused the decrease in the removal efficiency. In the presence of UV light, selenocyanate disappeared after 20 min. Selenite initially increased, then decreased and disappeared after 30 min. Selenate built up till it reached 2.751 ppm after 45 min and stayed almost constant till it reached 2.534 ppm after 6 hours. For more removal, the pH of the solution was reduced to 4. After 5 min a sample was collected and showed 1.749 ppm of selenate. Nitrate concentrations were high along the PCD period.  $\text{OCN}^-$  increased till it reached 1.808 ppm after 3 hours, then stayed constant during the remaining time.

Figure 5.64 illustrates results for  $\text{SeCN}^-$  5 ppm, Ratio 1 and Dose 1 g/l. After adding adsorbent, a sample was collected immediately and showed no removal. Also, the same result obtained for the sample collected after 30 min, which can refer to the low adsorbent dosage. In the presence of UV light, selenocyanate disappeared after 10 min. Selenite

formation started after 5 min and disappeared after 60 min. Selenate appeared after 5 min then passed through adsorption and desorption till it reached 4.199 ppm after 6 hours. The pH was adjusted to 4 for more removal. After 5 min, a sample was collected and showed 3.034 ppm. Nitrate was almost constant along the PCD period and reduced slightly after adjusting pH.  $\text{OCN}^-$  after 6 hours was 2.478 ppm.

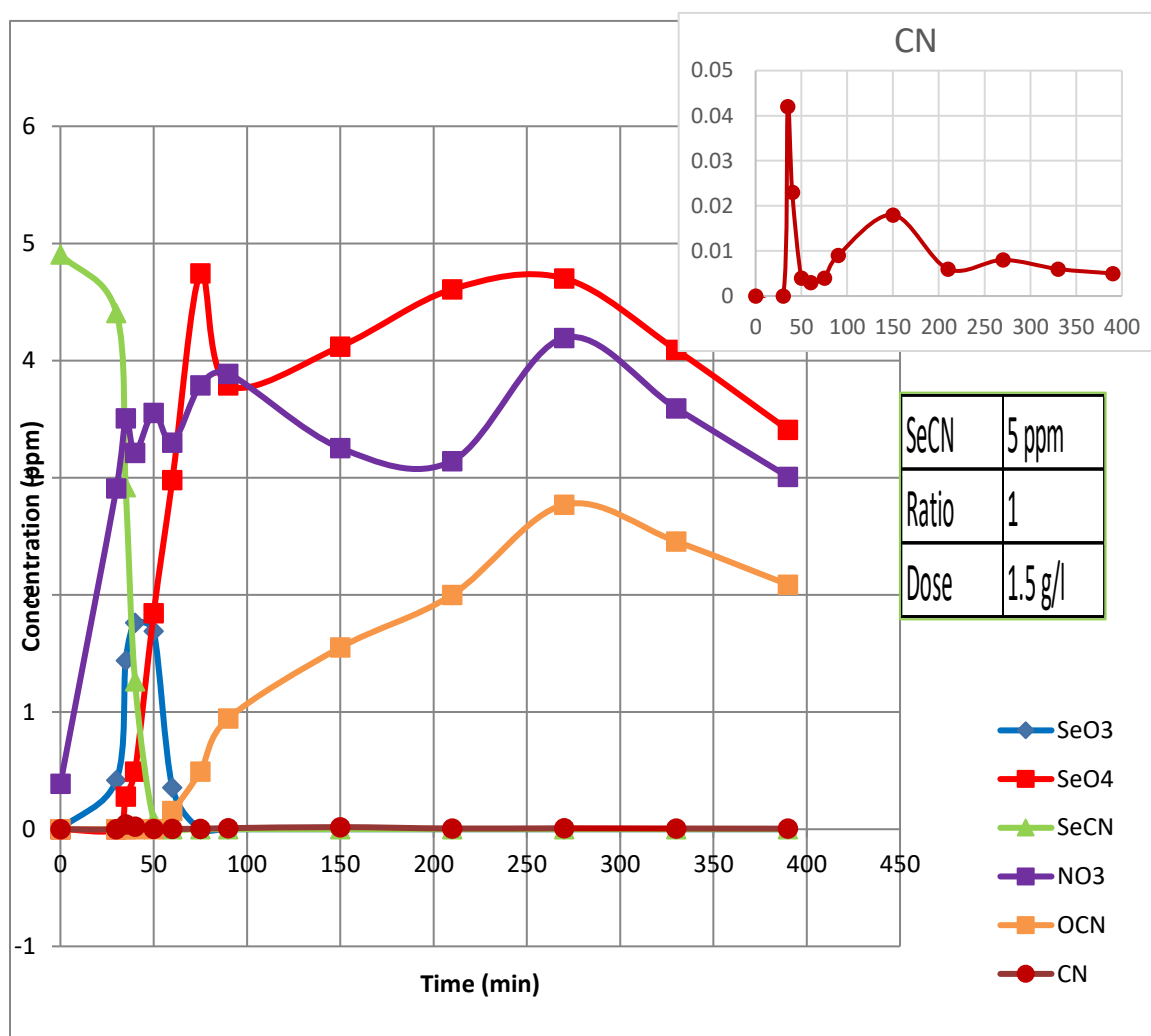


Figure 5.60 Photocatalytic Degradation of 5 ppm of SeCN with Ratio = 1 and Dose = 1.5g/l

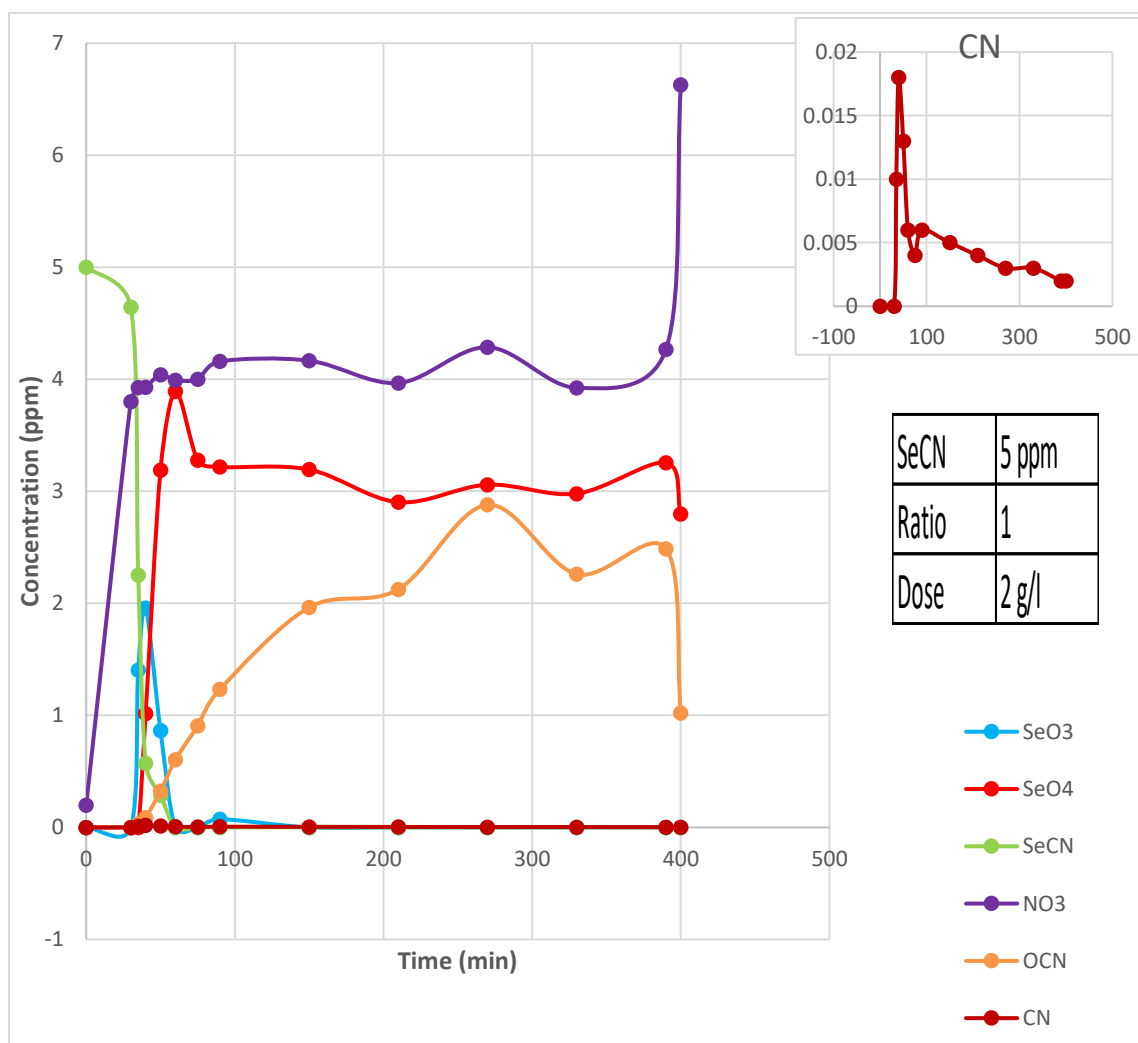


Figure 5.61 Photocatalytic Degradation of 5 ppm of SeCN with Ratio = 1 and Dose = 2 g/l

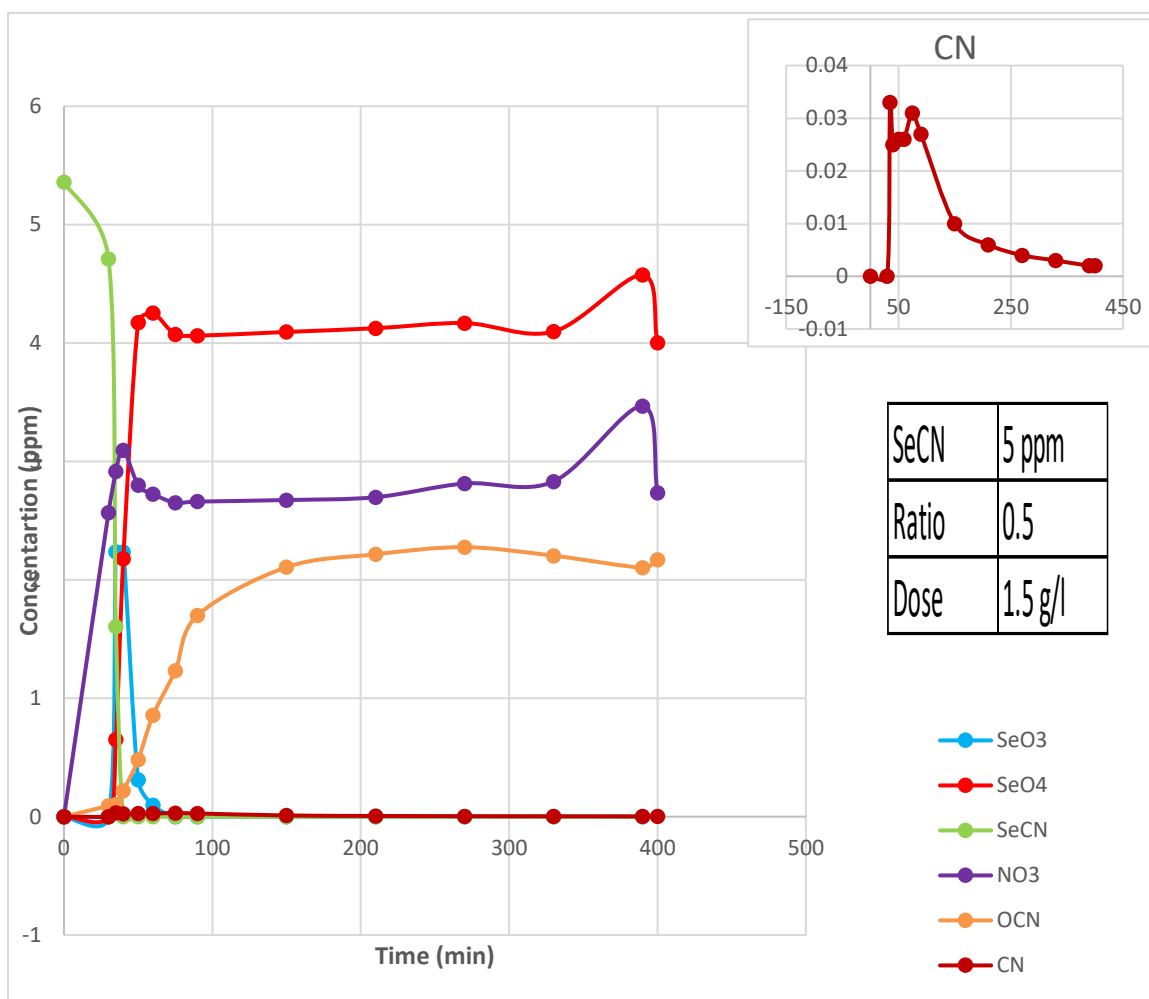


Figure 5.62 Photocatalytic Degradation of 5 ppm of SeCN with Ratio = 0.5 and Dose = 1.5 g/l

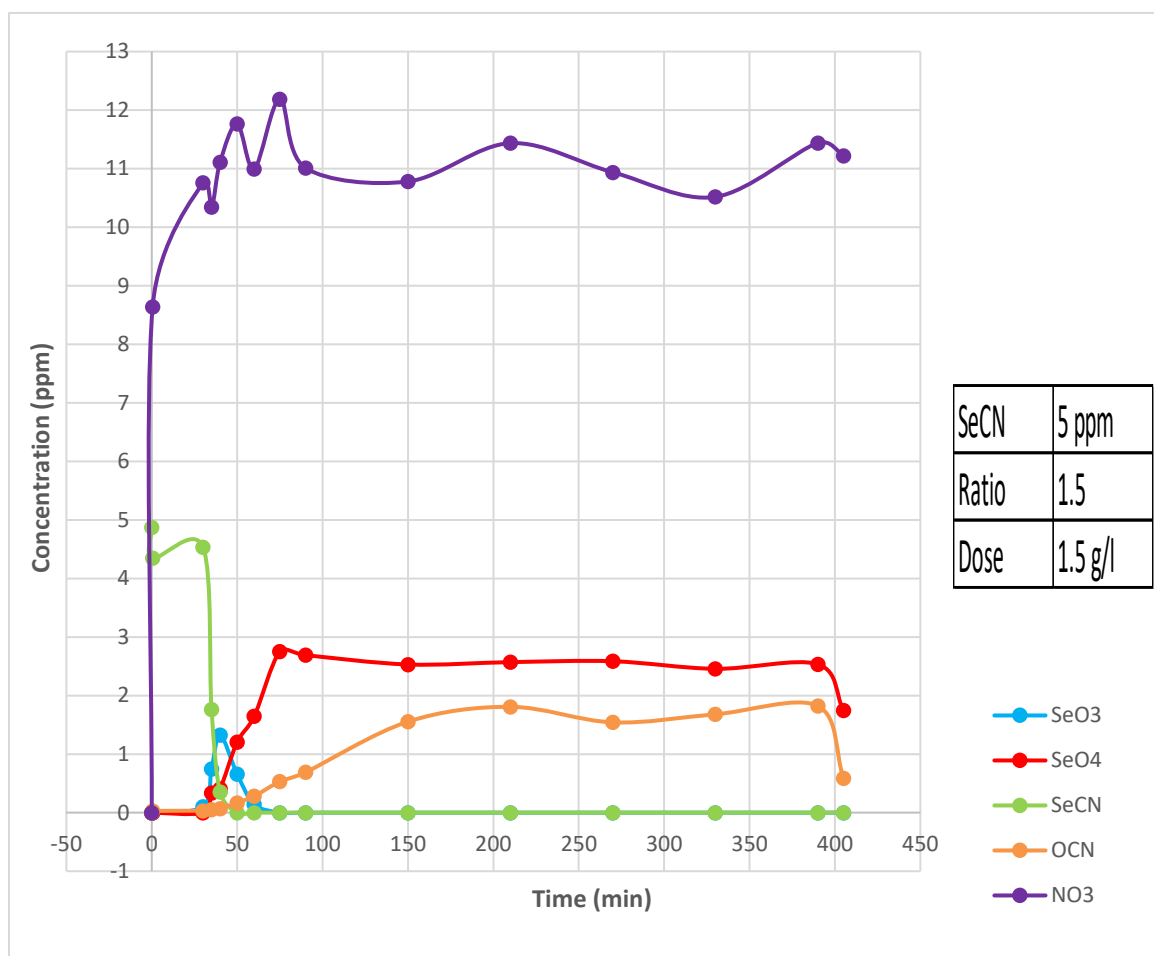


Figure 5.63 Photocatalytic Degradation of 5 ppm of SeCN with Ratio = 1.5 and Dose = 1.5 g/l

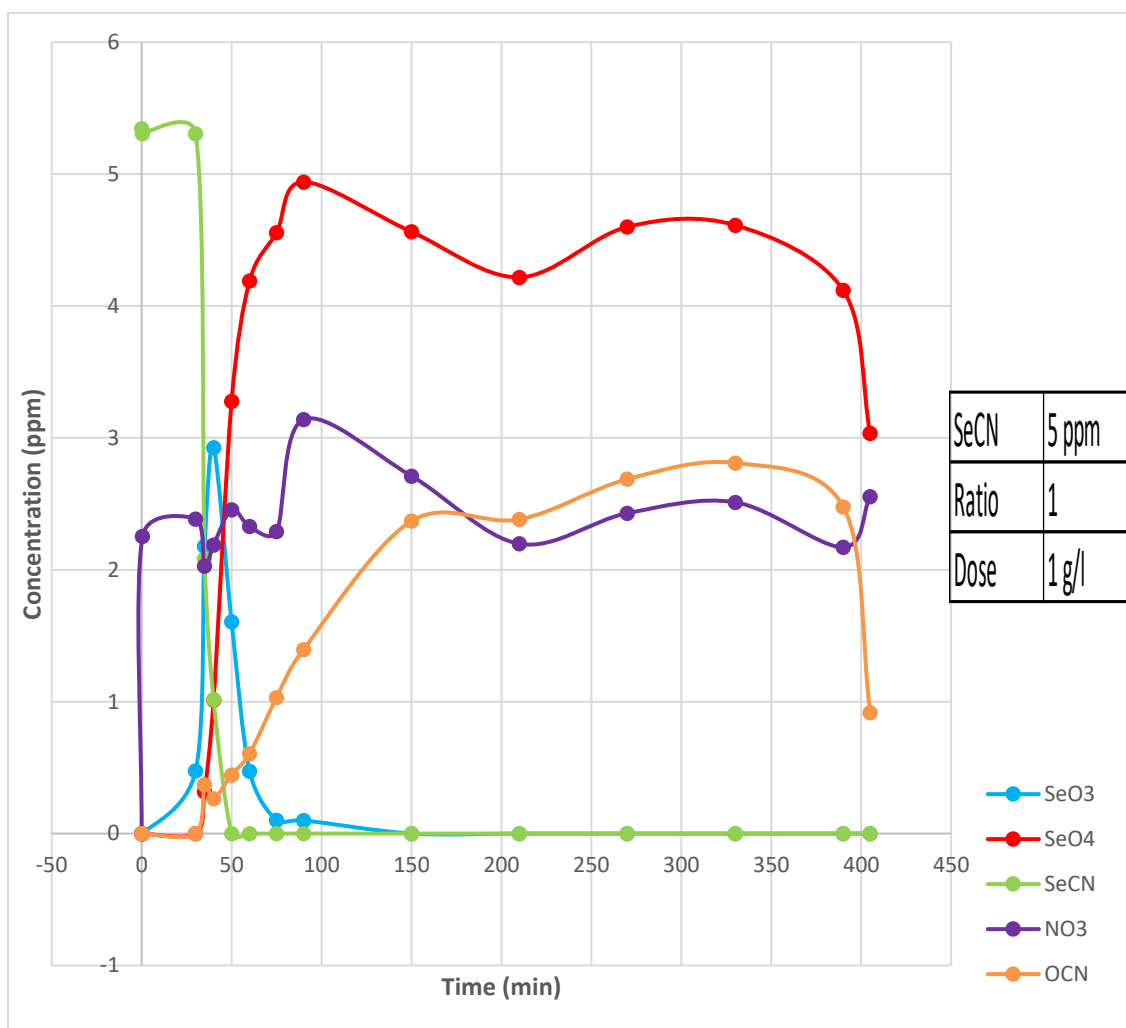


Figure 5.64 Photocatalytic Degradation of 5 ppm of SeCN with Ratio = 1 and Dose = 1 g/l.

### 5.5.6 Effect of weight ratio and dosage on removal of 7.5 ppm selenocyanate

Figure 5.65 illustrates PCD experimental results for  $\text{SeCN}^-$  7.5 ppm, Ratio 1.5, and Dose 1 g/l. The 30 min sample showed that selenocyanate concentration was 6.96 ppm. In the presence of UV, selenocyanate disappeared after 20 min. Selenite increased rapidly for 20 min and reduced till it disappeared after 45 min. Selenate increased for 60 min then stayed constant from 2 to 6 hours. pH was adjusted to 6 for more removal and after 5 min a sample was collected and showed selenate concentration = 6.502 ppm. This low removal was probably due to the high concentration of selenate, which is higher than adsorption capacity.  $\text{CN}^-$  showed low concentration for 3 hours then disappeared after 4 hours.  $\text{OCN}^-$  increased during PCD time and disappeared after decreasing the pH. Nitrate was almost constant along the PCD and increased after adjusting pH.

Figure 5.66 illustrates results for  $\text{SeCN}^-$  7.5 ppm, Ratio 0.5 and Dose 1 g/l. The 30 min sample showed that selenocyanate concentration did not reduce because of low amount of LDH in adsorbent and high concentration of selenocyanate. In the presence of UV light, selenocyanate disappeared after 10 min. Selenite appeared within 5 min and disappeared after 30 min. Selenate increased and reached 7.12 ppm after 20 min then stayed almost constant till it reached 6.75 ppm after 6 hours. The pH was adjusted to 5 for more removal, and after 5 min a sample was collected and showed 5.85 ppm of selenate. Nitrate stayed constant during the PCD and increased slightly after reducing pH.  $\text{CN}^-$  concentrations were low during the PCD and disappeared after 4 hr.  $\text{OCN}^-$  increased till it reached 3.48 ppm after 6 hours.

Figure 5.67 illustrates the experimental results for  $\text{SeCN}^-$  7.5 ppm, Ratio 1.5 and Dose = 2 g/l. A sample was collected immediately and showed 7.11 ppm of selenocyanate. After 30

min 7.35 ppm of selenocyanate was noted. After starting the photocatalysis, selenocyanate degraded after 20 min. Selenite reached 2.812 ppm after 10 min, then declined gradually till it disappeared after 60 min. Selenate reached 4.978 ppm after 3 hours. Then declined till it reached 4.33 ppm after 6 hours as the highest removal efficiency achieved for 7.5 ppm concentration of selenocyanate. Nitrate concentration was high during the photocatalytic degradation. Cyanate increased for 4 hours, then declined till it reached 3.2 ppm after 6 hours.

Figure 5.68 illustrates results for  $\text{SeCN}^-$  7.5 ppm, Ratio 0.5 and Dose 2 g/l. The 5 min sample showed 6.393 ppm of selenocyanate, and after 30 min 7.433 ppm of selenocyanate was noted. In the presence of UV light, selenocyanate disappeared after 20 min. Selenite reached 4.073 ppm after 10 min, then disappeared after 60 min. Selenate started appearing within 5 min and increased gradually till 60 min, then passed through adsorption and desorption till it reached 6.6 ppm after 6 hours. The pH of the solution was decreased to 4 for more removal, and after 5 min a sample was collected and showed 4.731 ppm of selenate. Nitrate concentrations stayed almost constant during the photocatalytic degradation. The cyanate formation started within 5 min and built up gradually for 5 hours, then declined to 4.692 ppm after 6 hours.

Figure 5.69 illustrates results for  $\text{SeCN}^-$  7.5 ppm, Ratio 1 and Dose 1.5 g/l. The 5 min sample showed 6.152 ppm of selenocyanate, and 30 min of stirring without UV light, showed selenocyanate concentration to be 7.018 ppm. In the presence of UV light, the remaining of selenocyanate degraded and disappeared after 20 min. Selenite was 3 ppm after 5 min then declined till it disappeared after 60 min. Selenate started the formation within 5 min and increased gradually for 45 min, then passed through adsorption and

desorption in the remaining time till it reached 5.699 ppm after 6 hours. For more removal, pH of solution was decreased to 4. After 5 min, a sample was collected and showed 3.28 ppm of selenate. Nitrate concentration was almost constant for 60 min, then declined slightly for a short time and increased again till it reached 3.858 ppm after 6 hours. The cyanate concentration increased gradually for 6 hours.

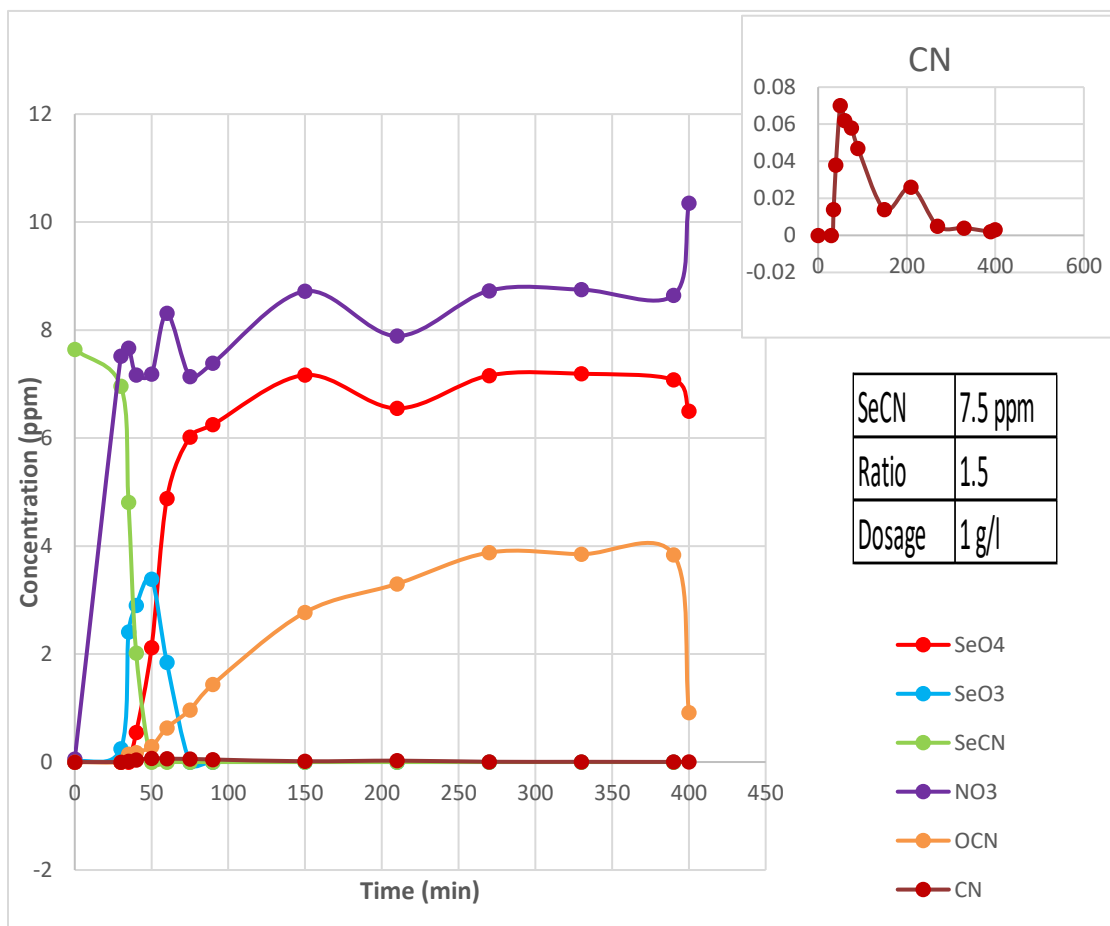


Figure 5.65 Photocatalytic Degradation of 7.5 ppm of SeCN with Ratio = 1.5 and Dose = 1 g/l

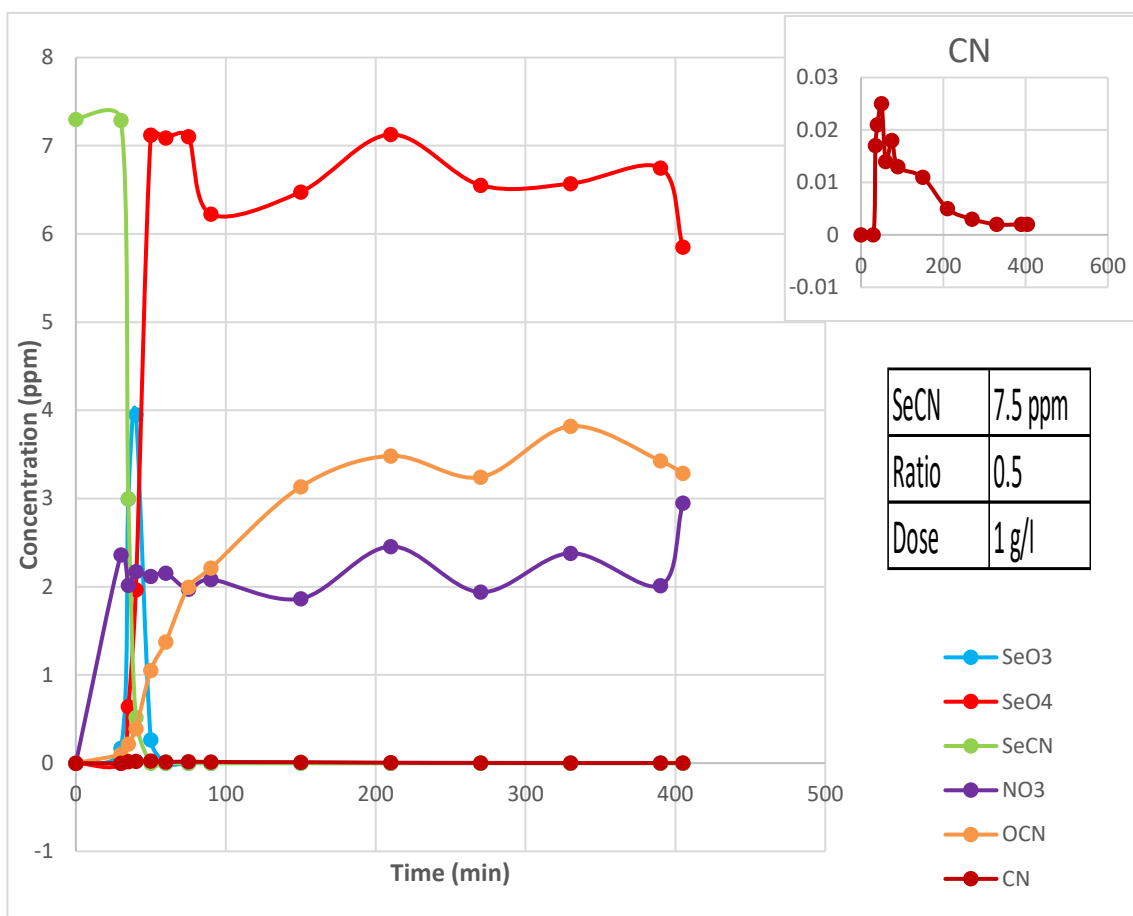


Figure 5.66 Photocatalytic Degradation of 7.5 ppm SeCN with Ratio = 0.5 and Dose = 1 g/l

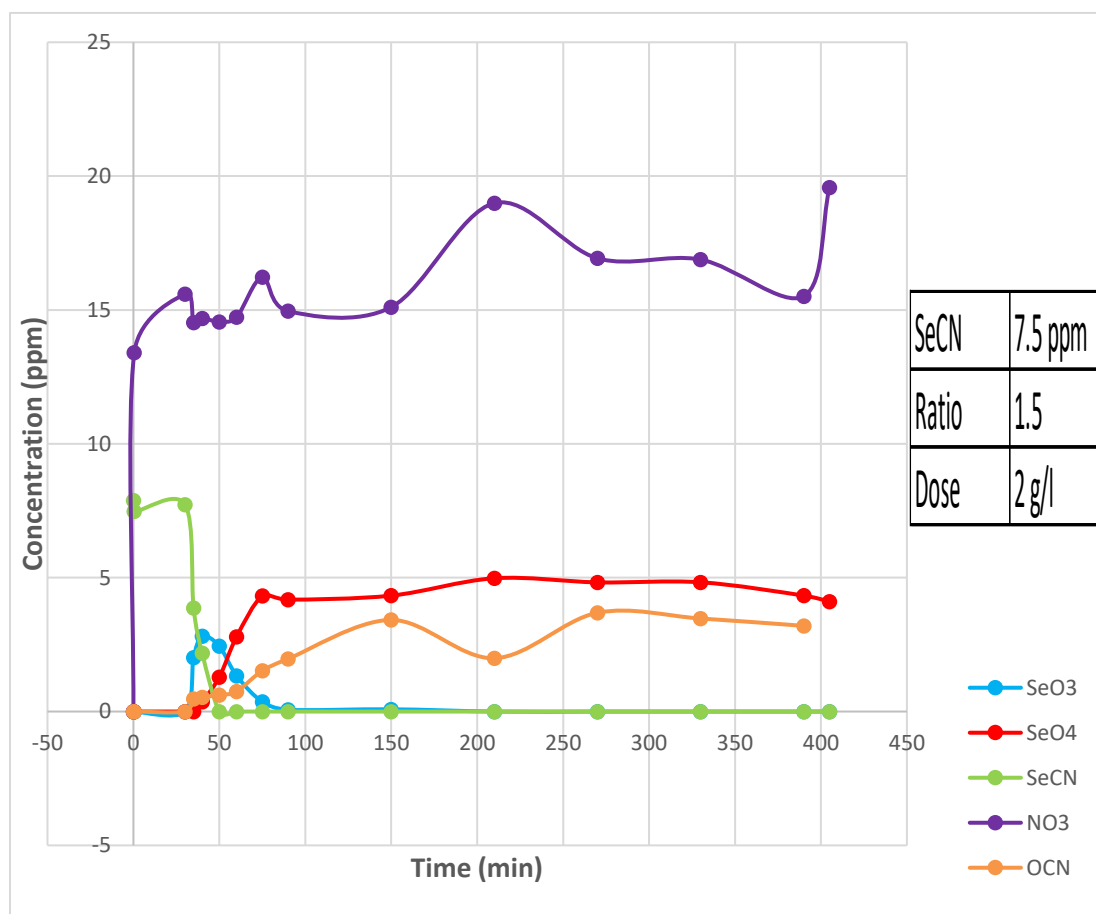


Figure 5.67 Photocatalytic Degradation of 7.5 ppm of SeCN with Ratio = 1.5 and Dose = 2 g/l

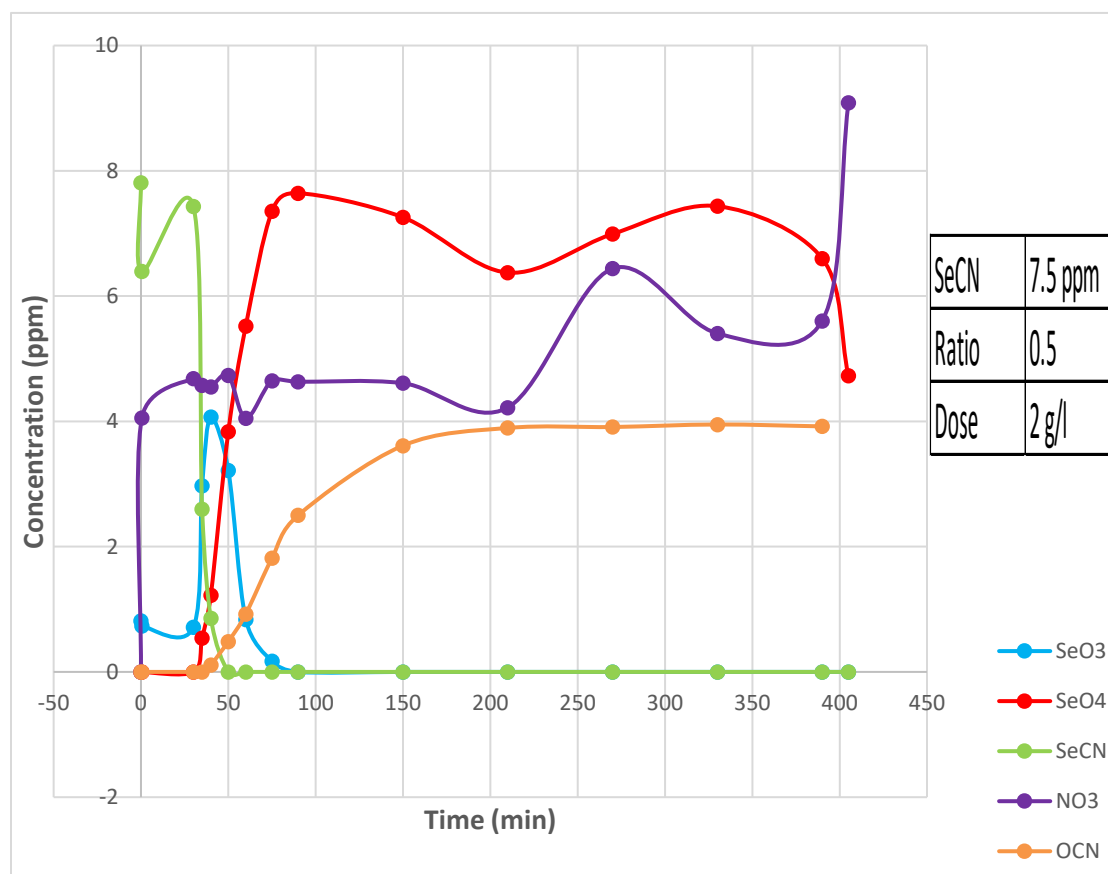


Figure 5.68 Photocatalytic Degradation of 7.5 ppm of SeCN with Ratio = 0.5 and Dose = 2 g/l

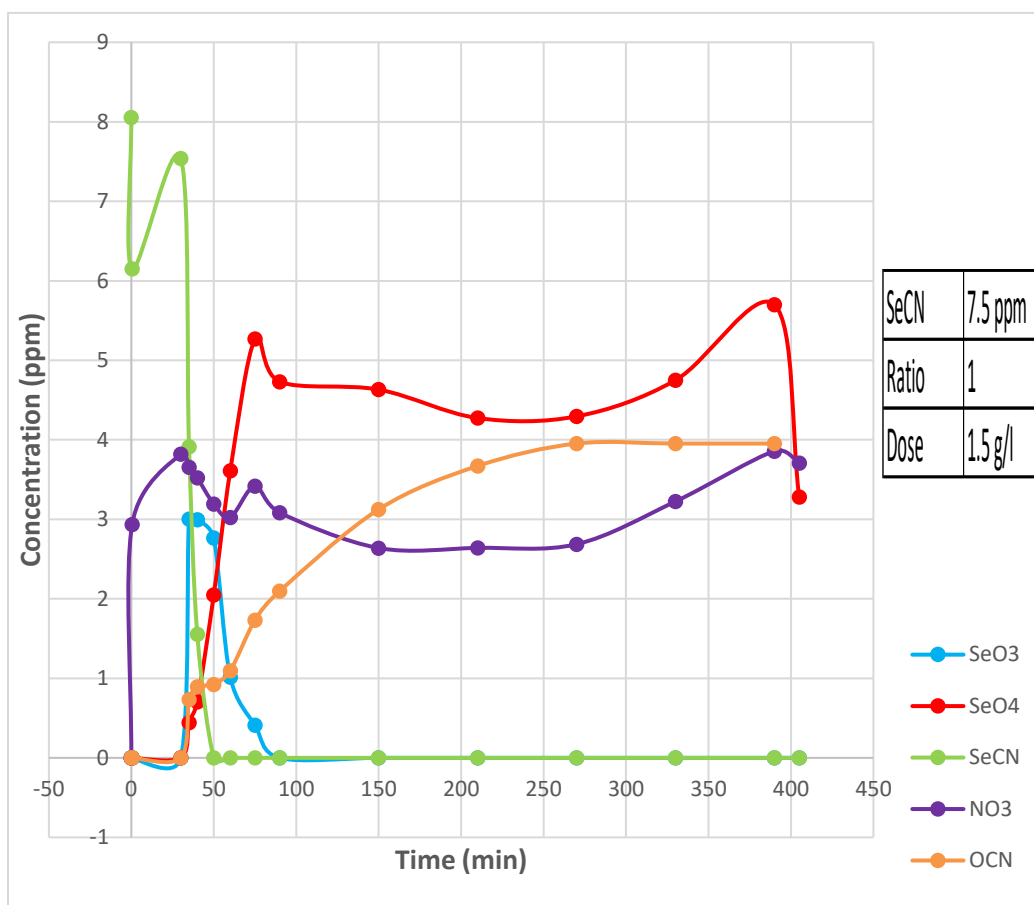


Figure 5.69 Photocatalytic Degradation of 7.5 ppm of SeCN with Ratio = 1 and Dose = 1.5 g/l

## CHAPTER 6

### CONCLUSION AND RECOMMENDATIONS

#### 6.1 Conclusion

This study investigated the removal of selenocyanate using  $\text{TiO}_2$  modified by Mg/Fe LDH in combined photocatalytic degradation (PCD) and adsorption system. First, the adsorption capacity of LDH for selenium species ( $\text{SeO}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{SeCN}^-$ ) was investigated by studying the effect of calcination temperature of LDH, LDH dosage, and concentration of respective selenium species on their respective removal efficiency. Adsorption results showed that the removal efficiency of selenite and selenate increased with an increase in the LDH calcination temperature and LDH dosage, whereas the maximum removal efficiency for both was achieved for LDH calcined at 500 °C and 1.5 g/l dosage of LDH. For selenocyanate, the highest removal efficiency was noted for LDH calcined at 250 °C. The selenium removal efficiency using the combined  $\text{TiO}_2$  LDH photocatalytic degradation and adsorption system was investigated by studying the effects of weight ratio of LDH: $\text{TiO}_2$  (w/w), the dose of adsorbent, and selenocyanate concentration. The rapid degradation of selenocyanate was observed during photocatalysis using 250 °C calcined Mg/Fe LDH with selenocyanate disappearing within 20 min. The photocatalytic degradation experiments showed that the removal efficiency of selenocyanate increased with an increase in the LDH: $\text{TiO}_2$  (w/w) ratio and the adsorbent dosage. Selenite and selenate resulting from the selenocyanate degradation were subsequently taken up by Mg/Fe LDH.

## **6.2 Recommendations**

- 1- Application of Mg/Fe LDH prepared at temperatures higher than 250 °C along with TiO<sub>2</sub> for selenocyanate treatment should be investigated.
- 2- The use of other dopants such as zinc to prepare modified LDH for respective selenocyanate treatment should be investigated.

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