

Article

# Rapid Removal and Efficient Recovery of Tetracycline Antibiotics in Aqueous Solution Using Layered Double Hydroxide Components in an In Situ-Adsorption Process

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**Abstract:** This work demonstrates a simple approach for the efficient removal of tetracycline (TC) antibiotic from an aqueous solution. The in situ-adsorption removal method involved instant precipitation formation of mixed metal hydroxides (MMHs), which could immediately act as a sorbent for capturing TC from an aqueous solution, by employing layered double hydroxide (LDH) components including magnesium and aluminum ions in alkaline conditions. By using this approach, 100% removal of TC can be accomplished within 4 min under optimized conditions. The fast removal possibly resulted from an instantaneous adsorption of TC molecules onto the charged surface of MMHs via hydrogen bonding and electrostatically induced attraction. The results revealed that our removal technique was superior to the use of LDH as a sorbent in terms of both removal kinetics and efficiency. Moreover, the recovery of captured TC was tested under the influence of various common anions. It was found that 98% recovery could be simply achieved by using phosphate, possibly due to its highly charged density. Furthermore, this method was successful for efficient removal of TC in real environmental water samples.

**Keywords:** tetracycline; metal hydroxides; layered double hydroxides; removal; water sample

## 1. Introduction

The contamination of antibiotics in environmental water is a global concern, as they are potentially toxic and harmful to both the ecosystem and human life [1]. One of the most commonly found antibiotics is tetracycline (TC), widely used in a variety of animal livestock in order to promote growth and kill bacteria [2]. It also plays a significant role in human therapy. As a result of its misuse, TC is commonly released as an agricultural or community effluent into the environment [3,4]. Furthermore, TC can be transferred from the community to a water source such as a lake. Therefore, the purification of wastewater by the removal of TC prior to release into environmental water is still necessary.

Even though treatment methods have been developed in wastewater management, most of them such as coagulation [5], ion exchange [6], and photocatalytic degradation [7] involve intensive energy and a high cost of operation, complex procedures, and production of possible toxic products. Above all reported methods, adsorption is the most reliable and effective means, with various sorbent materials being employed. For example, multi-walled carbon nanotubes (MWCNTs) as an adsorbent provided 99.8% removal of TC within 20 min [8]. High adsorption efficiency resulted from abundant  $\pi$ - $\pi$  interactions found from the  $\pi$  systems on the MWCNT surface, and benzene rings and double bonds,

both C=C and C=O, in TC molecules. Similarly, it was reported that graphene oxide functionalized with magnetic particles gave 98% removal efficiency within 10 min as a consequence of strong  $\pi$ - $\pi$  interactions between sorbent and target molecules [9]. Furthermore, zeolitic imidazolate metal organic framework ZIF-8 nanoparticles were used as an adsorbent and gave a removal efficiency of 90% as a result of a weak electrostatic interaction [10]. Furthermore, the removal of TC using Fe/Ni nanoparticle sorbent in an aqueous solution reached 97.4% removal within 2 h. [11]. In this sorbent-based adsorption technique, the removal efficiency of TC is chiefly dependent on the applied sorbents as well as their properties.

Among all these adsorbents, layered double hydroxide (LDH) has been considered as environmentally benign, and an effective adsorbent due to its high surface area and excellent anion exchangeability [12,13]. This material fundamentally consists of layers of mixed metal hydroxides linked with water molecules located in the interlayer space. The formula of LDH is generally symbolized as  $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(A^{n-})_{x/n}\cdot m\text{H}_2\text{O}$ , where  $M^{2+}$  and  $M^{3+}$  are divalent and trivalent cations, respectively.  $x$  is a molar ratio of  $M^{3+}/(M^{2+} + M^{3+})$  and  $A$  is an anion located at interlayers with the negative charge  $n$ . LDH has been employed as a sorbent or functionalized for the removal of various pollutants [14–21]. However, the synthesis and characterization of LDH sorbents are commonly required. Unavoidably, these steps are commonly time- and energy-consuming.

This study presents an in situ method for removal of TC antibiotics from an aqueous solution by employing the LDH components to generate instantly formed mixed metal hydroxides (MMHs), which simultaneously act as a sorbent to capture TC molecules from an aqueous solution during their precipitation formation. Unlike other sorbent-based removal techniques, our method was simple, efficient, rapid, and eco-friendly, as the synthesis of sorbent and its characterization can be avoided, thus saving time, energy, and cost. The parameters affecting the removal efficiency were investigated thoroughly. For comparison, a kinetic removal of this contaminant with LDH used as sorbent in a conventional route was also studied. The recovery of captured TC through an ionic interfering effect was demonstrated. Additionally, the removal of TC was carried out in real natural water samples.

## 2. Materials and Methods

### 2.1. Chemicals and Reagents

Tetracycline hydrochloride ( $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8\cdot\text{HCl}$ ) was obtained from Sigma-Aldrich (Hong Kong, China). Aluminium chloride hexahydrate ( $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ ) and magnesium chloride hexahydrate ( $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ ) were purchased from Sigma-Aldrich (St Louis, Missouri, USA). Sodium hydroxide (NaOH), sodium acetate ( $\text{CH}_3\text{COONa}$ ), sodium nitrate ( $\text{NaNO}_3$ ), and sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) were obtained from Carlo Erba (France). Sodium chloride (NaCl) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) were purchased from Ajax Finechem (Australia). Di-potassium hydrogen phosphate ( $\text{HK}_2\text{PO}_4$ ) was obtained from BDH Prolabo (England). Methanol ( $\text{CH}_3\text{OH}$ ) was purchased from LiChrosolv® (Darmstadt, Germany). All chemicals and reagents were of at least analytical grade and used as received without further purification. Deionized (DI) water was used throughout. A 1000 mg  $\text{L}^{-1}$  stock solution of TC was freshly prepared by dissolving 0.1000 g of  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8\cdot\text{HCl}$  in 100 mL of a mixed methanol:water solution (30:70% v/v). The solutions of mixed metal solutions ( $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ ) with varied mole ratios were prepared by a dissolution of an appropriate amount of  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  and  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$  in DI water.

### 2.2. Synthesis of LDH

As a comparative study, the removal of TC from an aqueous solution with LDH sorbent was investigated. First, LDH with a 3:1 mole ratio of Mg:Al was synthesized by co-precipitation as explained elsewhere [22]. Typically, a solution containing 0.0681 mol of  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$  (13.84 g) and 0.0227 mol of  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$  (5.48 g) in 200 mL DI was prepared. Then, 150 mL of an aqueous solution of 4.45 g NaCl was added slowly under stirring at room temperature and then 3 M NaOH was added to adjust the pH to 12. The mixture was then transferred into the Teflon coated stainless steel autoclave for

hydrothermal treatment at 120 °C for 48 h. Next, the precipitates were filtered, washed thoroughly with DI water, and dried at 90 °C for 24 h.

### 2.3. Measurement and Characterization

To evaluate the removal efficiency, the absorption spectra of TC residuals were recorded by an Agilent 8453 UV-vis spectrophotometer (Agilent Technologies, Waldbronn, Germany). A centrifuge (H-11n, Kokusan, Tokyo) with 15 mL calibrated tubes was used for the phase separation. Power X-ray diffraction (XRD, D8 Advance, Bruker, Bremen, Germany) and attenuated total reflection Fourier transform infrared spectroscope (ATR-FTIR; Tensor 27, Bruker, Germany) were used. Scanning electron microscopy (SEM) was completed using a SNE-4500M microscope (SEC Co., Ltd, Seoul, South Korea). In addition, the surface charge of MMHs was assured by Zeta potential measurement using the Zetasizer Nano S (Malvern Instruments Ltd, Malvern, UK).

### 2.4. Removal Procedure

It can be noted that other divalent and trivalent cations such as  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$ , and  $Fe^{3+}$  can be employed [23–25]. However, the rate of precipitation of metal hydroxides should be considered as it can result in the kinetic removal of TC. From the cost and toxicity point of view,  $Mg^{2+}$  and  $Al^{3+}$  ions were selected in this study. The removal of TC molecules from an aqueous solution was studied in a batch experiment. First, a simulated water sample containing 30 mg L<sup>-1</sup> TC was prepared and then conditioned with 1M NaOH. To initiate the removal of TC, a solution of  $Mg^{2+}/Al^{3+}$  ions with a fixed mole ratio of 3:1 was then added into 10 mL of TC solution. After a certain contact time, the TC-MMH particles were separated from the solution by centrifuging at 6000 rpm for 2 min. The residual TC in the solution was monitored by UV-vis measurement. The absorbance at 384 nm was used to evaluate the removal efficiency (%R) based on the following expression:

$$\%R = [(A_0 - A)/A_0] \times 100$$

where  $A_0$  and  $A$  are the absorbance of TC before and after the removal at any time, respectively. The effects of all factors on the removal efficiency including the volume of the mixed metal solution, the volume of NaOH, mole ratio of  $Mg^{2+}/Al^{3+}$ , and the removal time were studied.

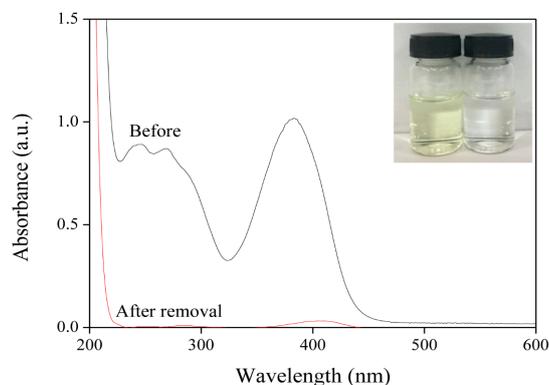
For a comparative study, the kinetic removal of TC by the LDH sorbent was investigated. The experiment was performed in a batch system with a total volume of 10 mL of 30 mg L<sup>-1</sup> of TC and 0.0131 g of LDH sorbent. After a certain contact time from 15 s to 150 min, 1 mL of the solution was withdrawn for UV-vis measurement and 1 mL of DI water was introduced into the studied system. The removal efficiency was calculated by using the above expression.

## 3. Results and Discussion

### 3.1. Removal of TC

In this study, the in situ-adsorption removal strategy was based on the usage of LDH components in order to generate the mixed metal hydroxides (MMHs), which can simultaneously capture the TC molecules during their precipitation formation. First, the removal of TC from an aqueous solution was simply tested by introducing a metal solution containing both  $Mg^{2+}$  and  $Al^{3+}$  ions into an alkaline TC solution. In general, regarding its  $pK_a$  values (3.3, 7.7, and 9.7), TC is present in the aqueous solution in various forms depending on the pH of solution [26]. TC is in the  $TCH_2$  neutral form when the pH falls in the range of 3.3–7.7. However, it is protonated and in a positively-charged  $TCH_3^+$  form in a solution with a pH less than 3.3 and it is negatively-charged as the  $TCH^-$  form in alkaline conditions (pH > 10). As our strategy was performed in an alkaline solution at a pH of about 12, a removal of TC from an aqueous solution was accomplished through an interaction with instantly formed MMH acting as a sorbent. The removal resulted from an adsorption of TC molecules on the surface of MMHs

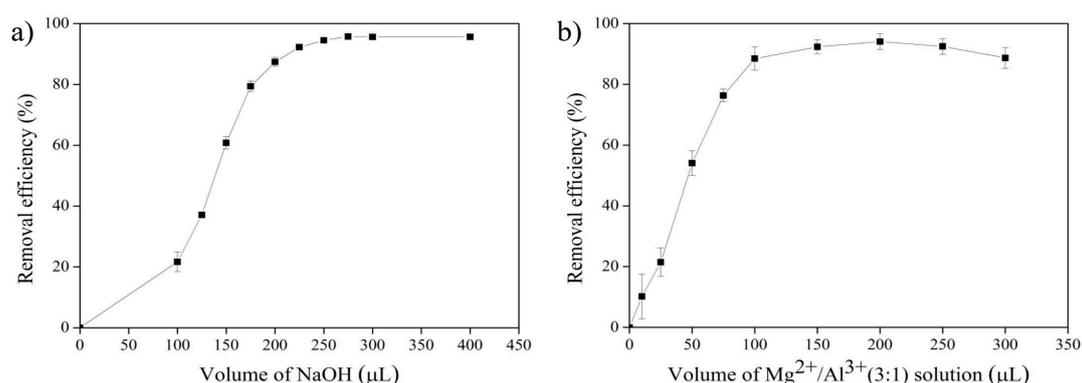
as a consequence of an electrostatic interaction and H-bonding [27]. The UV-vis spectra of  $30 \text{ mg L}^{-1}$  TC before and after the removal for 4 min of contact time is presented in Figure 1. It was found that the absorbance of TC was reduced tremendously after the removal. This indicated the potential of the present approach for TC removal.



**Figure 1.** UV-vis absorption spectra of TC in aqueous solution at an initial concentration of  $30 \text{ mg L}^{-1}$ ; before and after removal for 4 min contact time, with corresponding photograph images of the solution (inset).

### 3.2. Optimization of the Removal of TC

This method involved the use of LDH components to initiate the removal of TC from an aqueous solution. Accordingly, the main parameters including the amount of hydroxyl and metal ions were studied. These precursors could have an impact on the precipitation formation of MMHs, thereby affecting the removal efficiency. First, the impact of  $\text{OH}^-$  on the removal of  $30 \text{ mg L}^{-1}$  TC was investigated by varying the amount of  $\text{OH}^-$ , while other factors were fixed. Figure 2a shows that the removal efficiency of TC was enhanced rapidly, when increasing the amount of  $\text{OH}^-$  up to 200 mmol (200 mL). Then, the removal slightly improved until an addition of 275 mmol (275 mL)  $\text{OH}^-$ . After that, a further addition of  $\text{OH}^-$  did not benefit the removal of TC molecules. Thus, the amount of 275 mmol (275 mL) of  $\text{OH}^-$  was optimal.



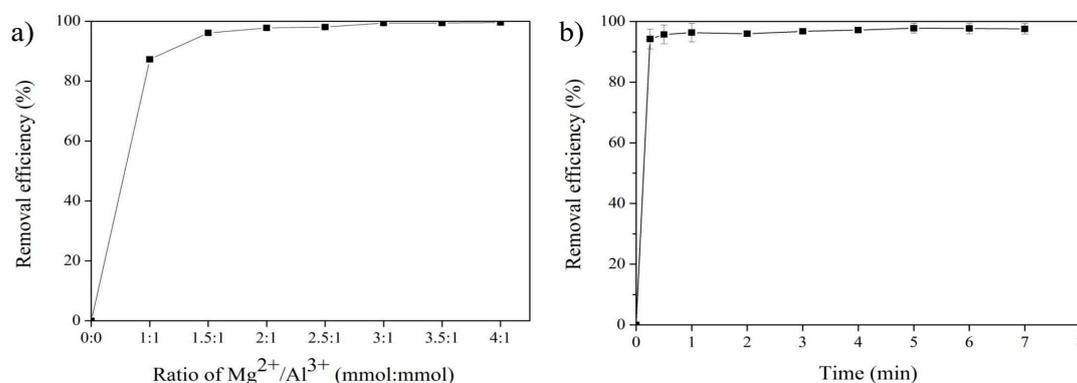
**Figure 2.** The effect of (a) the volume of 1 M NaOH and (b) the volume of mixed metal solution on the removal efficiency of TC in aqueous solution at an initial concentration of  $30 \text{ mg L}^{-1}$ .

The effect of both  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  ions on the removal of TC was also examined. The mole ratio of  $\text{Mg}^{2+}:\text{Al}^{3+}$  was fixed at 3:1 as an optimal ratio, while the volume of these ions was varied and other parameters were kept constant. As presented in Figure 2b, the removal efficiency of TC was improved with increasing the volume of the mixed metal solution up to 200  $\mu\text{L}$ . After that, the removal of TC became slightly lower. Similar to  $\text{OH}^-$ , an increase of  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  content enhanced the

precipitation formation of MMHs, thereby improving the interaction with TC in the solution. Thus, the removal efficiency increased when the components used to produce MMH sorbent increased as the removal is commonly dependent on the content of sorbent.

The mole ratio of  $Mg^{2+}:Al^{3+}$  was also investigated. In general, LDHs are synthesized by the hydrothermal method at a 2:1 and 3:1 mole ratio of  $Mg^{2+}:Al^{3+}$ . In this study, we simulated the formation of LDHs and employed their components to generate the simultaneous removal of TC from the solution. Under our studied conditions, the mole ratios of these ions varied from 1:1 to 4:1, while other parameters were kept constant. As can be seen in Figure 3a, the TC removal efficiency was sharply boosted by extending the mole ratio of  $Mg^{2+}:Al^{3+}$  ions up to 2:1. It was noticed that the strong precipitation of MMHs probably depended on the content of  $Mg^{2+}$  more than  $Al^{3+}$ . This resulted in an increase in the removal of TC when the content of  $Mg^{2+}$  ions was increased. However, the removal of TC reached the maximum value with the  $Mg^{2+}:Al^{3+}$  mole ratio of 3:1. Therefore,  $Mg^{2+}:Al^{3+}$  with a mole ratio of 3:1 was appropriate for the removal of TC by this approach.

The kinetic removal of TC by the proposed method was studied. The removal experiments were carried out at various contact times. The contact time was described as the time required for TC removal after the introduction of a mixed metal solution into the studied system. The experiments were tested under an optimization condition including 275  $\mu$ L of NaOH, 200  $\mu$ L of  $Mg^{2+}:Al^{3+}$  at a 3:1 mole ratio and an initial TC concentration of 30  $mg L^{-1}$ . Figure 3b shows the kinetic removal of TC by our method. It was observed that the removal efficiency of TC increased rapidly and slightly improved after 15 s. However, almost complete removal of TC was achieved after 4 min of contact time. The comparison of the removal of TC by the proposed method with other methods is summarized in Table 1. The results indicated that the proposed technique was more efficient and rapid than other removal methods. In addition, our method required no synthetic step of sorbents or catalysts, thus saving time, chemicals and energy.



**Figure 3.** The effect of (a) mixed metal concentrations and (b) contact time on the removal efficiency of TC in aqueous solution at an initial concentration of 30  $mg L^{-1}$ .

**Table 1.** Comparison of the removal of TC by the proposed method with other methods.

Material	Removal Method	Removal Time (min)	Removal Efficiency (%)	Ref.
GO/AC hybrid membrane	filtration	19	98.9	[28]
g-C <sub>3</sub> N <sub>4</sub> /Bi <sub>3</sub> TaO <sub>7</sub>	photocatalytic	90	89.2	[29]
Carbon doped g-C <sub>3</sub> N <sub>4</sub>	photocatalytic	90	90	[30]
ZnO@montmorillonite	photocatalytic	75	94	[31]
MWCNTs	adsorption	20	99.8	[8]
GO-MPs	adsorption	10	98	[9]
Fe/Ni BNPs	adsorption	120	97.4	[11]
MMHs	<i>in situ</i> -adsorption	4	99.8	This study

### 3.3. Characterization of MMH Sorbent and Confirmation for TC Removal

To confirm the removal of TC by our strategy, an instantly formed MMH sorbent was collected and then characterized. First, the surface charge of MMH was confirmed by the Zeta potential measurement. The result indicated that the surface of MMH particles was positively-charged with +19 mV. In the presence of TC, it was observed that the surface charge of MMH particles was reduced to  $-0.1$  mV. The reduction of surface charge possibly resulted from the adsorption of TC molecules, present as a negative form ( $\text{TCH}^-$ ) in the studied alkaline conditions, on the surface of MMH. The interaction of MMH with TC was also investigated by FT-IR measurement. As presented in Figure 4, when compared with the spectra of TC and MMH sorbent (without TC removal), a decrease in the intensity of the sharp peak at approximately  $3700\text{ cm}^{-1}$ , corresponding to the  $-\text{OH}$  group in the MMH sorbent after removal of TC, was observed. This possibly implied a surface interaction of MMH with TC molecules via hydrogen bonding. It was also found that after the removal of TC, a characteristic peak at  $1524\text{ cm}^{-1}$ , which was attributed to the vibration of the  $\text{NH}_2$  group of TC molecules, shifted to  $1597\text{ cm}^{-1}$ . These results confirmed the interaction between TC and MMH particles instantly generated in the system. Moreover, the presence of TC on the surface of MMH was also investigated by SEM measurement. As displayed in Figure 5, it was revealed that TC appeared on the surface of the MMH sorbent, confirming the interaction of TC molecules with MMH sorbent.

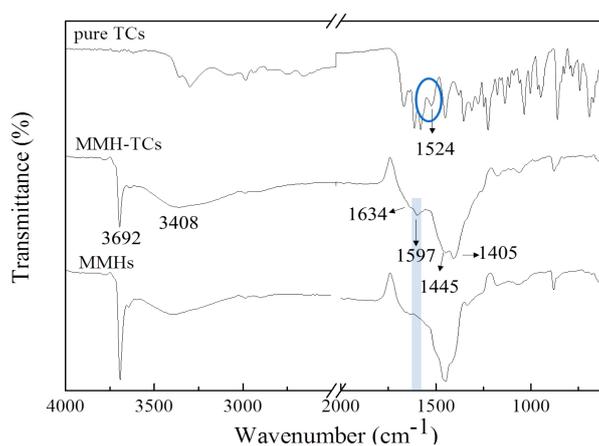


Figure 4. FT-IR spectra of pure TC, MMHs, and TC-MMHs.

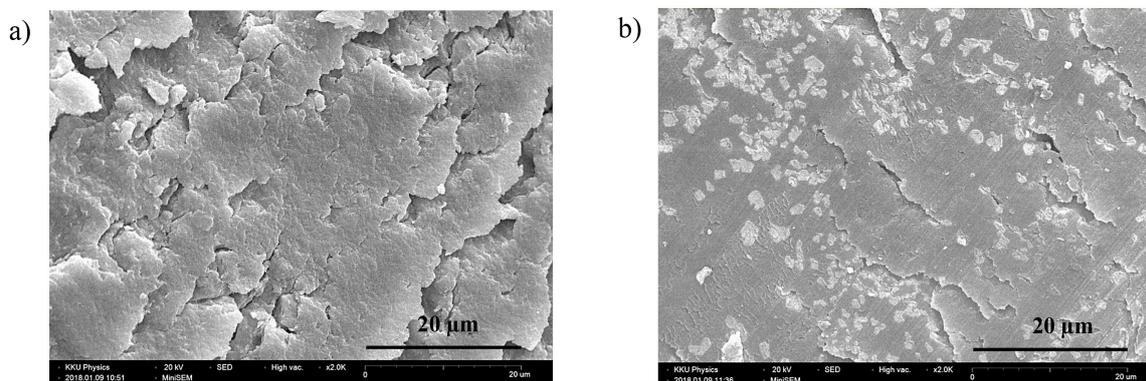
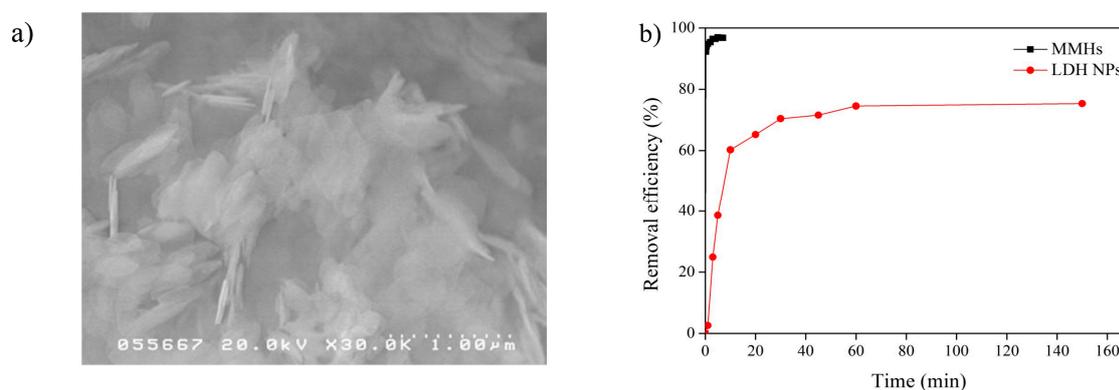


Figure 5. SEM images of (a) MMHs and (b) TC-MMHs.

### 3.4. Comparison on TC Removal with LDH Sorbent

We also investigated the removal of TC by using an LDH sorbent. LDH was prepared by a hydrothermal method, as explained in Section 2.2. Figure 6a represents the SEM image of LDH. It was seen that typical plate-like particles were observed. In addition, the XRD pattern confirmed the

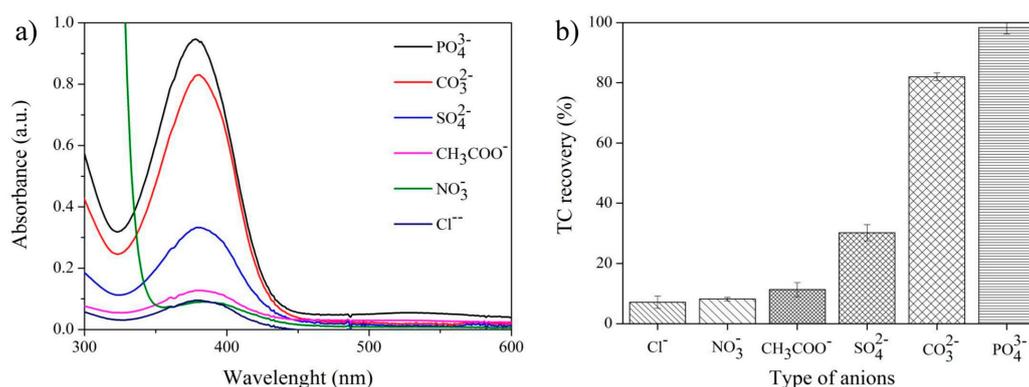
characteristics of LDH (see Figure S1 in Supplementary Materials). The experiments were conducted in a traditional way as a batch system at  $30 \text{ mg L}^{-1}$  of TC solution, as described in Section 2.4. An amount of LDH sorbent was calculated based on the optimized removal condition of the proposed method. LDH (0.0131 g) was obtained and further employed as a solid sorbent. The removal kinetics of LDH sorbent, in comparison with the proposed strategy, are displayed in Figure 6b. It was clearly seen that the removal of TC by LDH sorbent was quite slow. The removal reached an equilibrium after 60 min with a removal efficiency of 75%. This result indicated an incomplete removal of  $30 \text{ mg L}^{-1}$  of TC by the LDH sorbent. It is noted that the removal efficiency can be improved with increasing the amount of sorbent. However, this removal kinetic result implied that the present method was superior to the traditional sorbent-based removal method in terms of rapidness, efficiency, and cost-effectiveness as it eliminated the synthesis step of sorbent, thereby saving time, chemicals, and energy.



**Figure 6.** (a) SEM image of LDH sorbent and (b) its kinetic removal of TC in aqueous solution at an initial concentration of  $30 \text{ mg L}^{-1}$ , compared with MMHs.

### 3.5. Recovery of Captured TC

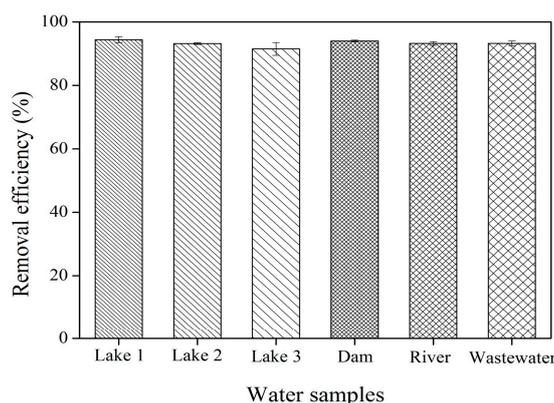
The ability of the proposed removal approach to recover TC from an aqueous solution was also tested. After the removal process, the precipitates containing TC were dispersed for 1 min in a solution containing an excess of various common anions (sodium salts) including  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{PO}_4^{3-}$ . After centrifugation for phase separation, the solution was then taken for analysis of TC content. These anions were employed as they could interfere with the adsorption ability of TC molecules on the surface of MMH particles. Thus, recovery of TC could be achieved. Figure 7 represents the UV-vis spectra of TC collected after the recovery step and the recovery efficiency regarding different anions used. It was found that the recoveries of TC were ordered with the use of  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{Cl}^-$ . The effect of these anions on both the precipitation formation of MMH particles and adsorption of TC possibly resulted from their charge density. Hence, 98% of recovery was obtained in the case of  $\text{PO}_4^{3-}$  used. In addition, this exhibited the advantage of the present removal strategy as the recovery of TC was simply obtained, regarding the loosely formed MMH sorbent.



**Figure 7.** (a) UV-vis absorption spectra of TC and (b) the recovery efficiency after recovery of TC with various anions.

### 3.6. Removal of TC in Real Environmental Water Samples

The applicability of the proposed method was further assessed by the removal of TC in environmental water samples. The water samples were collected from various water sources including Nam Pong River, Ubonratana Dam, Nong Kot Lake, Si Than Lake, Kaennakorn Lake, and the wastewater treatment pond located at Srinagarind Hospital, Khon Kaen, Thailand. It was found from an initial analysis that these water samples had a pH in the range of 6.6–7.5 without the presence of TC. Accordingly, to evaluate the applicability of the proposed method, all water samples were first filtrated and then spiked with  $30 \text{ mg L}^{-1}$  of TC. After removal using our strategy, the removal efficiency was reported, as presented in Figure 8. The results revealed that the removal of TC performed in every simulated water sample was 92%. The result indicated the applicability of our approach for the removal of TC in real water samples. High removal efficiencies were obtained even with the presence of other ionic species or contaminants, commonly found in natural water. Therefore, the interference of other compounds or ions is negligible. It can also be noted that other ionic species could facilitate the precipitation formation of MMHs, increasing the adsorption ability of TC. This led to an enhanced removal efficiency of TC from the aqueous solution.



**Figure 8.** Removal of TC added in various environmental water samples at an initial concentration of  $30 \text{ mg L}^{-1}$ .

## 4. Conclusions

This study demonstrates a simple strategy for the efficient removal of tetracycline (TC) antibiotic from an aqueous solution. The in situ-adsorption method involves the utilization of layered double hydroxide (LDH) components to initiate precipitation of mixed metal hydroxides (MMHs), concurrently acting as a sorbent for instant adsorption of TC molecules from an alkaline solution.  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$ ,

present as chloride forms, were used. Under optimized conditions, 99.5% removal efficiency can be obtained within 4 min due to a strong electrostatic interaction and hydrogen bonding between TC molecules and the positively-charged surface of MMHs. When compared with the removal adsorption by the LDH sorbent, our method is much better and faster. With our removal strategy, 98% recovery of TC captured by MMHs can be simply achieved by dispersion in a phosphate solution. Moreover, almost complete removal of TC from simulated environmental water samples including a dam, river, three lakes and wastewater plant can be obtained.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4352/9/7/342/s1>, Figure S1: XRD pattern of LDH

**Author Contributions:** Conceptualization, S.S. (Sira Sansuk); investigation, K.P. and M.S.; methodology, K.P. and M.S.; supervision, S.S. (Supalax Srijaranai); writing—original draft preparation, K.P.; writing—review and editing, S.S. (Sira Sansuk).

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**Conflicts of Interest:** The authors declare no conflict of interest.

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