

Article

Template-Free Synthesis of Magnetic La-Mn-Fe Tri-Metal Oxide Nanofibers for Efficient Fluoride Remediation: Kinetics, Isotherms, Thermodynamics and Reusability

Shaoju Jian ¹, Yuhuang Chen ¹, Fengshuo Shi ¹, Yifei Liu ¹, Wenlong Jiang ¹, Jiapeng Hu ^{1,*}, Xiaoshuai Han ^{1,2}, Shaohua Jiang ^{1,2,*}  and Weisen Yang ^{1,*}

¹ Fujian Key Laboratory of Eco-Industrial Green Technology, Key Laboratory of Green Chemical Technology of Fujian Province University, College of Ecology and Resources Engineering, Wuyi University, Wuyishan 354300, China

² Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, International Innovation Center for Forest Chemicals and Materials, College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China

* Correspondence: wyuwqhjp@163.com (J.H.); shaohua.jiang@njfu.edu.cn (S.J.); yangweisen@126.com (W.Y.)

Abstract: The occurrence of fluoride contamination in drinking water has gained substantial concern owing to its serious threat to human health. Traditional adsorbents have shortcomings such as low adsorption capacity and poor selectivity, so it is urgent to develop new adsorbents with high adsorption capacity, renewable and no secondary pollution. In this work, magnetic electrospun La-Mn-Fe tri-metal oxide nanofibers (LMF NFs) for fluoride recovery were developed via electrospinning and heat treatment, and its defluoridation property was evaluated in batch trials. Modern analytical tools (SEM, BET, XRD, FTIR) were adopted to characterize the properties of the optimized adsorbent, i.e., LMF11 NFs with a La:Mn molar ratio of 1:1. The surface area calculated via BET method and pH_{pzc} assessed using pH drift method of LMF11 NFs were $55.81 \text{ m}^2 \text{ g}^{-1}$ and 6.47, respectively. The results indicated that the adsorption amount was highly dependent on the pH of the solution, and reached the highest value at $pH = 3$. The kinetic behavior of defluoridation on LMF11 NFs was dominated by the PSO model with the highest fitted determination coefficients of 0.9999. Compared with the other three isotherm models, the Langmuir model described defluoridation characteristics well with larger correlation coefficients of 0.9997, 0.9990, 0.9987 and 0.9976 at 15°C , 25°C , 35°C and 45°C , respectively. The optimized LMF11 NFs exhibited superior monolayer defluoridation capacities for $173.30\text{--}199.60 \text{ mg F}^-/\text{g}$ at $pH 3$ at $15\text{--}45^\circ\text{C}$ according to the Langmuir isotherm model. A thermodynamic study proved that the defluoridation by LMF11 NFs is a spontaneous, endothermic along with entropy increase process. In addition, the LMF11 NFs still showed high defluoridation performance after three reused cycles. These findings unveil that the synthesized LMF11 NFs adsorbent is a good adsorbent for fluoride remediation from wastewater owing to its low cost, high defluoridation performance and easy operation.

Keywords: La-Mn-Fe tri-metal oxides nanofibers; defluoridation; electrospinning; kinetics; wastewater treatment



Citation: Jian, S.; Chen, Y.; Shi, F.; Liu, Y.; Jiang, W.; Hu, J.; Han, X.; Jiang, S.; Yang, W. Template-Free Synthesis of Magnetic La-Mn-Fe Tri-Metal Oxide Nanofibers for Efficient Fluoride Remediation: Kinetics, Isotherms, Thermodynamics and Reusability. *Polymers* **2022**, *14*, 5417. <https://doi.org/10.3390/polym14245417>

Academic Editors: Ming Chen and Xiaoqiang Cao

Received: 14 November 2022

Accepted: 3 December 2022

Published: 11 December 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Fluoride contamination in groundwater caused by the processes of natural geochemical and human production activities is a burning issue, which has attracted substantial attention since it is closely related to the safety and health issue for humans [1–6]. An appropriate amount of F^- can enhance the hardness of teeth and the mineralization of hard tissues and prevent dental caries. Surplus fluoride in drinking water may lead to irremediable diseases in humans, namely fluorosis. The tolerance level of fluoride in drinking water recommended by the World Health Organization is no more than 1.5 mg/L [7,8]. However, endemic levels of fluorosis have been reported in 32 nations worldwide, and more than

200 million people especially in poor rural areas have been consuming water contaminated with high fluoride concentration for a long time. Accordingly, it is highly required to establish the deep treatment of fluoride-rich water. Adsorption is a promising way for fluoride decontamination since it possesses high adsorption capacity, high selectivity, handy operation and relative cost-effectiveness [9–14], compared with other defluoridation strategies, e.g., membrane, precipitation, and electrocoagulation [15]. A variety of defluoridation materials have been developed to remove excess F^- , namely carbon-based materials [16], activated alumina [17], carbonaceous materials [18], polymer-based materials [19], etc. Whereas the inherent shortcomings such as poor removal efficiency and low selectivity, have been encountered in practical applications for most of these adsorbents.

As far as we know, Belcher R. [20,21] in 1959 and Leonard et al. [22] in 1960 discovered for the first time that the coordination water in the complexes formed by rare earth elements Ce(III) and La(III) with alizarin complexone could exchange with F^- to form colored complexes with high selectivity, respectively. It provided a new way for scientists to remove fluoride from wastewater. Since then, various materials, such as compounds of multivalent metal elements such as La(III), Ce(III) and Ce(IV) in the form of oxides, hydrous oxides and basic carbonate [23], lanthanum impregnate silica gel [24], La(III) and Y(III)-impregnated alumina [25], La-chitosan [26], Mn-La metal composite [27], Fe-La-Ce tri-metallic composite [28], La-MOFs [29], La-MOF@x%PANI [30], had been exploited for remediation of fluoride. Among them, bi-metallic or tri-metallic oxides based on high valent lanthanum possessed high fluoride adsorption. However, the cost of La is relatively high. In order to reduce the cost and keep high defluoridation performance, adsorbents for fluoride remediation were fabricated by mixing other cheaper multivalent metal elements (i.e., Mg, Al, Mn, Fe) with La owing to the advantage and synergism of two or three metal oxides [31–34]. Mg-Fe-La tri-metal adsorbent (molar ratio: 25/1/4) developed by Wang et al. [32] via facile co-precipitation method possessed the highest uptake of 112.17 mg F^- /g for fluoride. Cotton-like Ca-Al-La adsorbent with optimal Ca/Al/La molar ratio of 1/4/2 exhibited the largest fluoride binding amount of 29.30 mg F^- /g [35]. Similarly, Gasparotto et al., stated that La-Al-Fe trioxide composites synthesized via the co-precipitation method presented a maximum fluoride uptake of 28.06 mg F^- /g at 25 °C and pH 8.25 [36]. Although the above adsorbents possess good defluoridation performance, it is difficult to separate them from aqueous solution quickly due to their nanoscale size. Additionally, the nano-adsorbents are easy to agglomerate, resulting in the decline of adsorption capacity.

Ease in localization and separation can promote the recovery and reuse of materials for successive treatment cycles. Due to the good magnetic responsiveness of Fe_3O_4 [37,38], its use in composite adsorbents for various pollutants removal can enhance their recovery rate and efficiency by a magnet [39,40]. Whereas, easy agglomeration is the major obstacle for the large-scale application of Fe_3O_4 nanoparticles. To overcome the limit of Fe_3O_4 nanoparticles, numerous magnetic adsorbents were fabricated by coating metal oxides on Fe_3O_4 nanoparticles to form core-shell composites or by loading Fe_3O_4 and other metal oxides on the carrier [41]. For example, graphene oxide (GO) supported Fe-Al oxide adsorbent (IAO/GO) fabricated by Liu et al. [42] showed a maximum binding amount of 64.72 mg F^- /g for fluoride. The use of magnetic La_2O_3 - CeO_2 - Fe_3O_4 nanofibers for fluoride removal from aqueous solution has been investigated by our group [43], the maximum uptakes are 202–230 mg F^- /g at 15–35 °C, and the adsorbent can be easily and quickly separated from the solution by an external magnet. The obstacles to the industrial application of La_2O_3 - CeO_2 - Fe_3O_4 nanofibers are the scarcity and relatively high cost of rare earth elements. There is no literature about the defluoridation by magnetically separable electrospun La-Mn-Fe tri-metal oxide nanofibers in wastewater. In view of the high affinity of La towards fluoride ions and the low cost of metals Mn and Fe, this research is to fabricate a new magnetic tri-metallic adsorbent (i.e., electrospun La-Mn-Fe tri-metal oxide nanofibers) with less expenditure, which can exhibit structural stability, high defluoridation efficiency, excellent recyclability and reusability.

In this study, magnetically separable electrospun La-Mn-Fe tri-metal oxide nanofibers (LMF NFs) were prepared by electrospinning and heat treatment. The LMF NFs were used as a new type of adsorbent for fluoride remediation. The magnetic Fe_3O_4 NPs are evenly dispersed along the nanofiber axis without obvious agglomeration. Moreover, the magnetic fibrous LMF NFs can effectively prevent the agglomeration of adsorbent during the defluoridation process and can be quickly separated from the solution using an external magnet after adsorption. The effects of the molar ratio of La/Mn, initial F^- concentration, pH, LMF11 NFs dosage, shaking time, interfering anions, isotherm models and adsorption kinetics were investigated in detail.

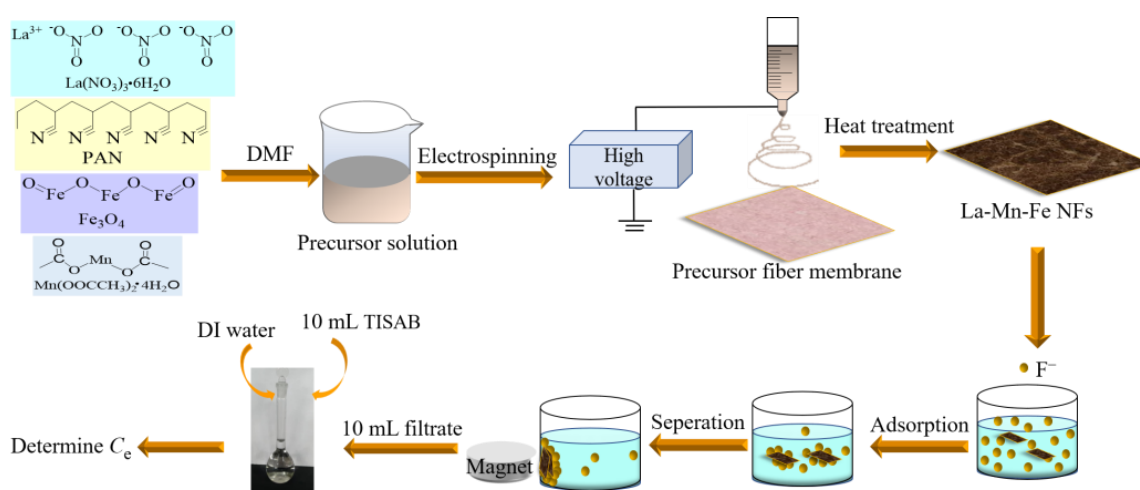
2. Materials and Methods

2.1. Chemicals

NaF , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, NaCl , DMF, Na_2CO_3 , NaNO_3 , Na_3PO_4 , CH_3COOH , $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, Na_2SO_4 , HCl , NaOH , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{HOCH}_2\text{CH}_2\text{OH}$ and CH_3COONa were acquired from Aladdin Chemical Reagent Co., Ltd. (Shanghai, China) and used as received. Polyacrylonitrile (PAN, $M_n = 2.5 \times 10^5$) was purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Preparation of La-Mn-Fe Tri-Metal Oxide Nanofibers

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were mixed in a beaker with La:Mn molar ratios of 2:1, 1:1 and 1:2, then completely dissolved in a small amount of DMF. Afterward, 1.8 g PAN powder, 10 mL DMF and 0.075 g Fe_3O_4 nanoparticles (via a solvothermal method [44]) were injected into each sample to form precursor solutions namely $(\text{La}(\text{NO}_3)_3/\text{Mn}(\text{CH}_3\text{COO})_2/\text{Fe}_3\text{O}_4/\text{PAN}/\text{DMF})$. The electrospinning processes were conducted to produce precursor fibers [33,43,45,46]. Briefly, the precursor solution was added into a 5 mL syringe with a metal needle, then the electrospinning of the precursor solution was performed with an applied electric field of 150 kV m^{-1} and a flow rate of 1.2 mL h^{-1} at room temperature, to generate precursor nanofibers. After electrospinning, the resulting precursor nanofibers were dehydrated for 8 h and then put into a tube furnace for heat treatment at 500°C for 2 h to prepare La-Mn-Fe tri-metal oxide nanofibers under an air atmosphere. La-Mn-Fe tri-metal oxide nanofibers with molar ratios of La/Mn being 2/1, 1/1 and 1/2 were noted as LMF21 NFs, LMF11 NFs and LMF12 NFs, respectively. The graphic plan of the fabrication process of electrospun LMF NFs and the adsorption of fluoride is portrayed in Scheme 1.



Scheme 1. Graphical procedure of fabrication of LMF NFs and the adsorption of fluoride.

2.3. Batch Adsorption Studies

The defluoridation performance of LMF NFs was evaluated using batch experiments (Scheme 1). Adsorption kinetics were performed in the time range from 1 to 60 min under

500 mL F^- solution with initial F^- concentrations of 20 and 50 mg F^- /L at 25 °C and pH 3. Adsorption isotherm studies were carried out at varying original F^- concentrations of 10–60 mg F^- /L at a temperature range of 15–45 °C with LMF11 NFs dosage of 0.2 g/L in 50 mL of respective solution. Various concentrations (10, 30, 50, 80 or 100 mg/L) of five commonly occurring anions, including nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), carbonate (CO_3^{2-}), phosphate (PO_4^{3-}) were studied under initial F^- concentration of 20 mg F^- /L with an adsorbent dosage of 0.2 g/L at 25 °C and pH 3 for 12 h. The effect of pH (2–9) along with LMF11 NFs dosage (0.2–0.6 g/L) on adsorption property was assessed under 50 mL initial F^- concentration of 20 mg F^- /L at 25 °C for 12 h.

2.4. Reusability Test

The reusability of the F^- adsorbed magnetic LMF11 NFs was determined to quantify the cost-effectiveness of the adsorbent for F^- remediation in the successive adsorption–desorption cycles. The original concentration of F^- was 20 mg F^- /L at pH 3 and 25 °C for 8 h for each regeneration cycle. The F^- adsorbed magnetic LMF11 NFs were recovered by an external magnet, and then eluted with 100 mL of 0.1 M NaOH to regeneration [43,47,48], vacuum-dried and used for a new run.

2.5. Characterization of Adsorbent

The crystal structures of LMF11 NFs before and after adsorption were established by X-ray diffraction (XRD, D8 ADVANCE X, Bruker, Saarbrücken, Germany). The BET specific surface area of the LMF11 NFs adsorbent was examined using a Micromeritics ASAP 2020 analyzer (Micromeritics, Norcross, GA, USA). The TEM and SEM images of the magnetic electrospun LMF11 NFs were acquired from TEM JEM 2100 (JEOL, Tokyo, Japan) and SEM 300U (VEGA, Tescan, Brno, Czech Republic). The point of zero charge of LMF11 NFs was assessed via a pH drift method [49].

3. Result and Discussion

3.1. Characterization of Adsorbent

The morphological details of $La(NO_3)_3/Mn(CH_3COO)_2/Fe_3O_4/PAN$ and LMF11 NFs were determined by SEM, as portrayed in Figure 1a,b. Obviously, the surfaces of $La(NO_3)_3/Mn(CH_3COO)_2/Fe_3O_4/PAN$ fibers are continuous and smooth with an average diameter of $1.28 \pm 0.10 \mu m$. Fe_3O_4 NPs are evenly distributed on the surface of the $La(NO_3)_3/Mn(CH_3COO)_2/Fe_3O_4/PAN$ and LMF11 NFs. After heat treatment, the volume and diameter of fibers decline due to the decomposition of $Mn(CH_3COO)_2$, $La(NO_3)_3$ and PAN. The continuous LMF11 NFs are hollow and rougher compared to that before calcination, which possess an average diameter of $626 \pm 57 nm$. Figure 1d displays the TEM image of LMF11 NFs, it is obvious that the spherical Fe_3O_4 NPs are uniformly dispersed along the fiber axis without obvious agglomeration. The chemical composition of LMF11 NFs is verified by EDS analysis, as shown in Figure 1c. EDS illustrates that the LMF11 NFs consist of La (14.02%), Mn (13.22%), Fe (4.45%) and O (68.31%) elements. Apparently, the detected La/Mn molar ratio in the sample is quite consistent with the designed value. The BET surface area and BJH pore distribution of LMF11 NFs are analyzed by N_2 adsorption–desorption isotherm (Figure 1e). The total pore volume and surface area of LMF11 NFs are $0.276 cm^3 g^{-1}$ and $55.81 m^2 g^{-1}$. The inset of Figure 1e states that the main pore sizes of LMF11 NFs locate at 3.06 nm and 17.39 nm, indicative of numerous mesopores in the adsorbent [29]. The isoelectric point (pH_{pzc}) of LMF11 NFs calculated according to the literature [50] is 6.47 (Figure 1f). This signifies that the surface charge of LMF11 NFs is positive and protonated at $pH < 6.47$ while negative at $pH > 6.47$. Thus, negative ions such as F^- can be easily absorbed into the positively charged LMF11 NFs owing to their coulombic attractions at a pH range below pH_{pzc} [51].

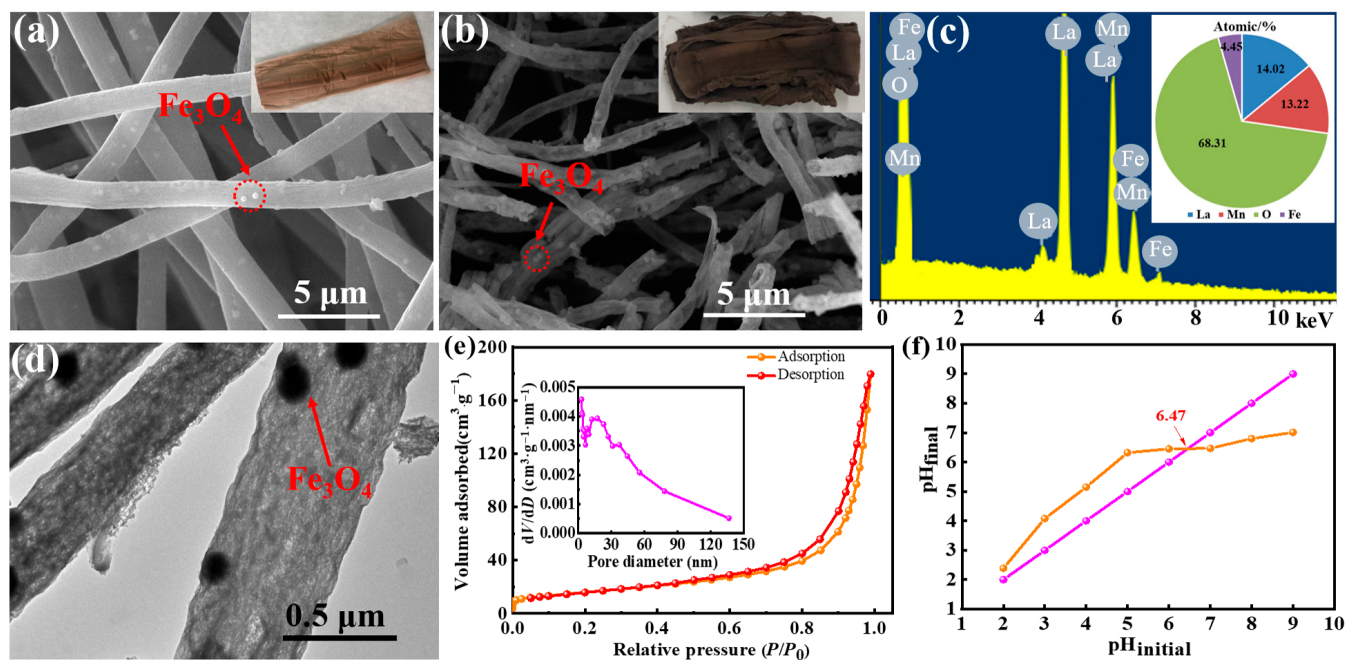


Figure 1. SEM images of $\text{La}(\text{NO}_3)_3/\text{Mn}(\text{CH}_3\text{COO})_2/\text{Fe}_3\text{O}_4/\text{PAN}$ (a) and LMF11 NFs (b), EDS analysis (c), TEM image (d), N_2 adsorption–desorption isotherm (e) and (f) pH_{pzc} of LMF11 NFs.

3.2. Preparation Optimization

The capture capacities of F^- on as-prepared adsorbents involving La NFs, LMF21 NFs, LMF11 NFs, LMF12 NFs, Mn NFs and Fe_3O_4 NPs were determined. Then, 0.2 g/L of adsorbents were placed into 50 mL fluoride solutions with a concentration of 20 mg F^- /L for the adsorption test, the temperature of 25 °C, pH of 3 and shaking time for 12 h were adopted, respectively. The fluoride binding amounts were determined, as portrayed in Figure 2. The maximum fluoride uptakes of La NFs, Mn NFs and Fe_3O_4 NPs are 104.12, 30.71 and 15.71 mg F^- /g, respectively. While the maximum uptakes of F^- on LMF21 NFs, LMF11 NFs, LMF12 NFs are 147.68, 182.03 and 131.67 mg F^- /g, respectively. Evidently, the LMF NFs possess higher adsorption capacity than those of single metal oxide due to the synergistic effect of La, Mn and Fe [33,34]. The fluoride uptake of LMF11 adsorbent with La/Mn molar ratio being 1/1 is the highest. Hence, LMF11 NFs is designed as fluoride scavenger in the subsequent experiments.

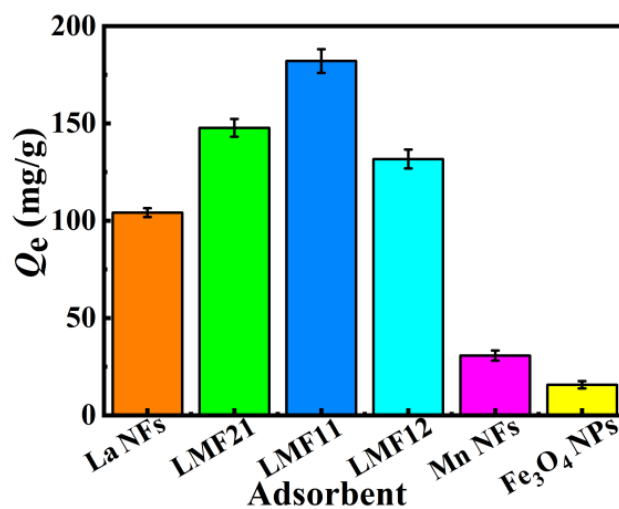
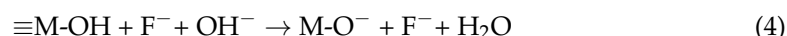
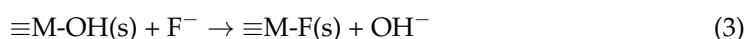
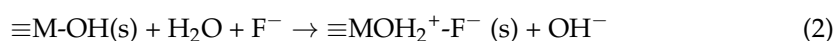
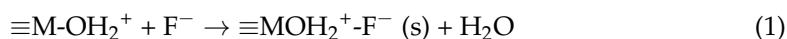


Figure 2. Impact of La/Mn molar ratio on the defluoridation performance of LMF NFs.

3.3. Adsorption Study

3.3.1. The Effect of pH

The effect of pH on the defluoridation performance of LMF11 NFs was evaluated at various pH values from 2 to 9 (Figure 3). The maximum binding amount (47.79 mg F[−]/g) and removal efficiency (95.58%) for LMF11 NFs occurs at a pH of 3 owing to the columbic attractions (Equation (1)). LMF11 NFs show a dramatic decrease in defluoridation property at pH > 3 and pH < 3. Most fluoride ions exist in the form of electrically neutral HF (pK_a^{HF} = 2.95) [52] when pH < 3, which can reduce the columbic forces between LMF11 NFs and adsorbate [42]. Meanwhile, the diminished binding amount at higher pH conditions is attributed to electrostatic repulsion between F[−] and negatively charged LMF11 NFs along with the competition between F[−] and OH[−] for active sites [41]. Additionally, the equilibrium pH of the F[−] solution changed from 2 to 2.18, 3–5.49, 4–6.59, 5–6.75, 6–6.59, 7–6.34, 8–6.83, 9–7.14 after adsorption, respectively. The improvement of pH after adsorption in an initial pH range of 2–6 suggests the existence of an ion exchange of hydroxyl groups bonded on the surface of the adsorbent with fluoride ions (Equations (2) and (3)). While the decline of pH after adsorption in an initial pH range from 7 to 9 (>pH_{pzc}) is mainly ascribed to the competitive adsorption between hydroxyl groups and adsorbate (F[−]) (Equation (4)). A pH of 3 was chosen to utilize for subsequent studies.



where $\equiv\text{M}$ indicative of La, Fe and Mn metal ions.

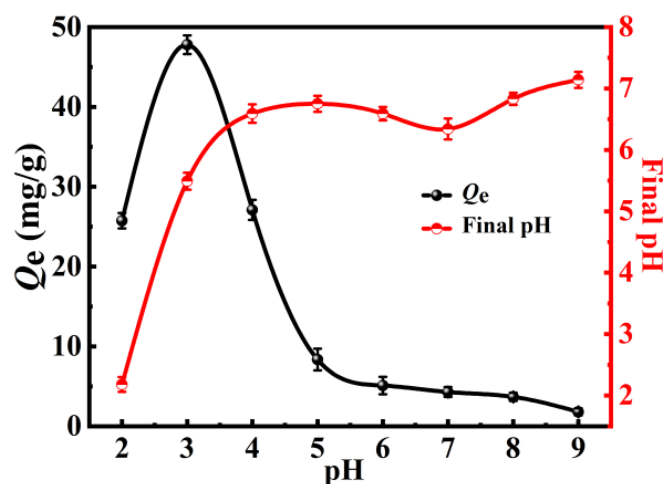


Figure 3. pH effect on defluoridation performance on LMF11 NFs and the final pH of the solution.

3.3.2. The Effect of LMF11 NFs Dosage

The effect of LMF11 NFs dosage on the defluoridation was studied. Appropriate mass (0.01, 0.015, 0.02, 0.025, or 0.03 g) of LMF11 NFs was poured into a 50 mL of 50 mg F[−]/L fluoride solution at 25 °C. Evidently, the adsorption uptakes at an adsorbent dosage of 0.2, 0.3, 0.4, 0.5 and 0.6 g L^{−1} are 188.21, 153.44, 123.81, 99.33 and 82.77 mg F[−]/g, the fluoride removal percentages are 75.29%, 92.07%, 99.05%, 99.32% and 99.33%, respectively (Figure 4). It can be concluded that the binding amount descends progressively with ascending LMF11 NFs dosage at a fixed concentration of F[−]; the removal efficiency shows is an increasing trend. The number of the binding sites on LMF11 NFs rises with the increase in the LMF11 NFs dosage, the solution, resulting in an obvious increase in fluoride removal percentage.

However, the initial concentration of F^- keeps constant and fails to saturate the binding sites on LMF11 NFs. It means that the binding sites cannot be fully used. In addition, the binding sites may be agglomerated together, leading to partial binding sites covering each other, and then the unit adsorption capacity cuts down [41]. The adsorbent dosage is selected as 0.2 g/L in the following defluoridation experiments in light of the economy and practicability of the adsorbent.

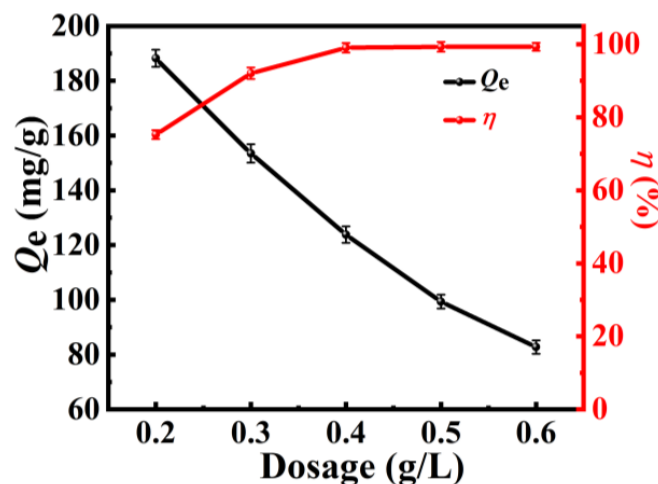


Figure 4. Effect of adsorbent dosage on the defluoridation performance of LMF11 NFs.

3.3.3. The Effect of Initial F^- Concentration (C_0)

The fluoride uptake significantly depends on the initial concentration of F^- . As shown in Figure 5, the fluoride uptake of LMF11 NFs elevates gradually with an increase in C_0 (10 mg F^- /L to 45 mg F^- /L). The reason is that with the increase in F^- concentration, the number of fluoride ions near the surface of the LMF11 NFs increases apparently, and the binding sites on the surface of LMF11 NFs are more fully surrounded by fluoride ions, thus, more fluoride ions are adsorbed by the adsorbent, resulting in the increasing of fluoride binding amount [53]. Then it approaches saturation at higher C_0 due to the saturation of active sites. While the fluoride removal efficiency declines with the rise of fluoride concentration. It is because the LMF11 NFs adsorbent have a limited adsorption uptake. When LMF11 NFs adsorbent achieve adsorption saturation, the removal percentage will decline with the rise of the initial fluoride concentration. In addition, at $C_0 = 60$ mg F^- /L, the binding amount leaps from 175.82 mg F^- /g at 15 °C to 193.53 mg F^- /g at 45 °C. The higher the temperature of the adsorption system, the larger the binding amount, validating the endothermic nature of the defluoridation process [29].

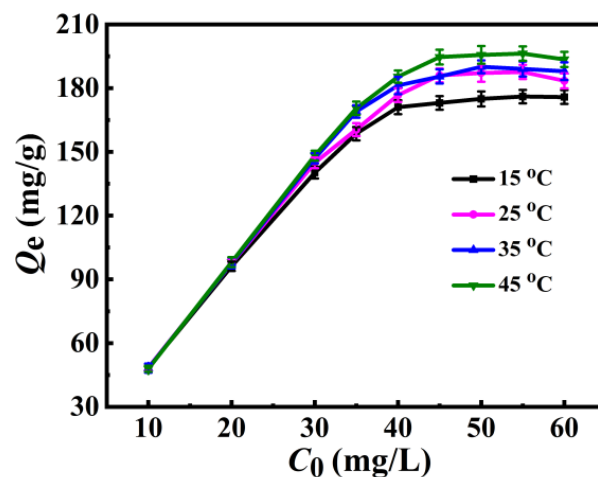


Figure 5. Influence of initial concentration of F^- on the defluoridation performance of LMF11 NFs.

3.3.4. The Effect of Contact Time

The defluoridation experiments were kinetically conducted towards F^- removal on LMF11 NFs by varying the time intervals in the range of 0–60 min using an adsorbent dosage of 0.2 g/L with given concentrations ($C_0 = 20$ and 50 mg F^- /L) at 25 °C and pH = 3. As depicted in Figure 6, exceeding 70% of F^- could be removed within the first 20 min at $C_0 = 20$ and 50 mg F^- /L, showing an excellent defluoridation property. In this stage, numerous binding sites in LMF11 NFs and the high concentration of fluoride ions in the solution decide the rapid adsorption rate. Hence the larger adsorption rate in the incipient step is ascribed to the strengthening of the diffusion rate of F^- provided by concentration gradient along with the existence of numerous available binding sites on the LMF11 NFs [54]. The adsorption tends to dynamic equilibrium after 10 min in 20 mg F^- /L solution and 30 min in 50 mg F^- /L solution. Clearly, at higher C_0 , it takes longer shaking time to attain equilibrium. Based on the aforementioned analysis, the effect of pH (A), initial concentration of F^- (B) and LMF11 NFs dosage (C) (Supplementary Materials, Tables S1 and S2) was determined using response surface methodology (RSM) to optimize the adsorption parameters [55,56]. It is clear that the experimental results of the single factor variable are very close to the RSM results (Supplementary Materials, Table S3, Figures S1 and S2).

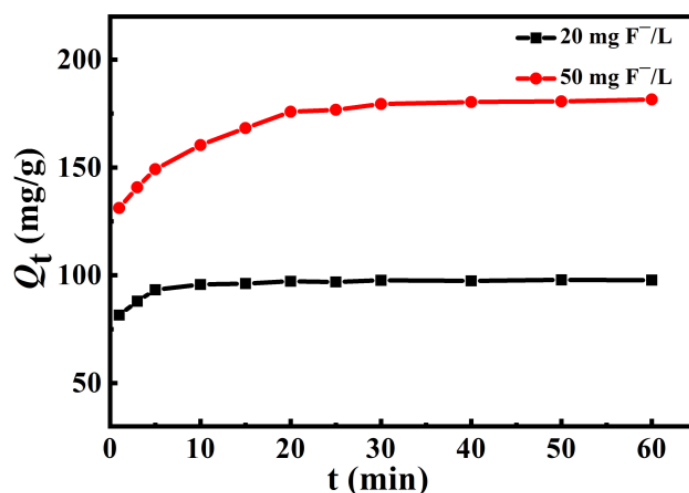


Figure 6. Influence of shaking time and initial F^- concentration on defluoridation performance.

3.3.5. The Effect of Interfering Anions

One of the major barriers that limit the widespread application of adsorption technology in practical water treatment is the selectivity of adsorbent. The effects of five commonly occurring anions including nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), carbonate (CO_3^{2-}) and phosphate (PO_4^{3-}) on defluoridation by LMF11 NFs were investigated. The competitive experiments were conducted by weighing 0.01 g LMF11 NFs into a binary system that contained 50 mL 10 mg F^- /L F^- paired with different concentrations (10, 30, 50, 80 or 100 mg/L) of the interfering anions, respectively. The result is depicted in Figure 7. Obviously, NO_3^- , Cl^- , SO_4^{2-} and CO_3^{2-} anions at all concentrations of 10–100 mg/L almost do not prevent the F^- removal, illustrating the excellent selectivity and stability of LMF11 NFs adsorbent. Whereas the binding capacity drops quickly from 98.20 to 52.16 mg F^- /g with the rise of PO_4^{3-} concentration from 0 to 100 mg/L, manifesting a remarkable competitive effect of PO_4^{3-} on defluoridation. This may be explained by the K_{sp} of $LaPO_4$ (3.7×10^{-23}) [54], which favors PO_4^{3-} to displace the adsorbed F^- on LMF11 NFs compared with that of LaF_3 , thereby deteriorating the fluoride binding capacity. The same result has also been reported by several studies using rare earth element-based materials for fluoride remediation [27,57].

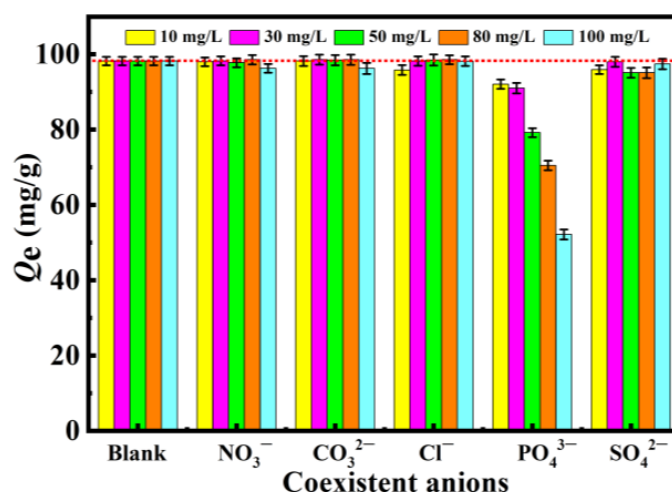


Figure 7. Effect of interfering anions on the fluoride adsorption density by using LMF11 NFs.

3.3.6. Fluoride Adsorption Isotherm

The equilibrium data generated from the adsorption experiment at temperatures of 15 to 45 °C (Figure 5) are fitted by four classical isotherm modes viz., Langmuir, Freundlich, D-R and Temkin [29]. The as-estimated relevant factors are listed in Table 1. As portrayed in Figure 8a–d, the order of the fitted determination coefficients (R^2) at 15 to 45 °C is Langmuir (0.9997, 0.9990, 0.9987 and 0.9976) > Temkin (0.8708, 0.8358, 0.6854 and 0.6161) > D-R (0.8402, 0.7725, 0.5981 and 0.4976) > Freundlich (0.7863, 0.7252, 0.5627 and 0.4791), illustrating that the homogeneous and single-layer adsorbed on LMF11 NFs dominates the defluoridation process [29,58]. The evaluated Q_m values range from 173.30–199.60 mg F^-/g at 15 to 45 °C, exceedingly higher than many reported adsorbents including MOFs such as La-BTC (105.2 mg/g), La-BPDC (125.9 mg/g), La-BHTA (145.5 mg/g), La-PMA (158.9 mg/g) and La-BDC (171.7 mg/g) [29], Uio-66 (20 mg/g) [59], Amine functionalized electrospun cellulose nanofibers (5.31 mg/g) [60], electrospun alumina nanofibers (1.2 mg/g) [61] and double (Ce-Fe bimetal oxides, 60.97 mg/g [62]) or tri-metal oxide-based materials (SA-CMAZ, 31.72 mg/g [63]; Mg/Ce/Mn, 12.99 mg/g [64]). Table 2 lists the fluoride adsorption capacities of the LMF11 NFs and other adsorbents based on rare earth elements for comparison. It is conspicuously seen that LMF11 NFs show excellent fluoride adsorption capacity. Additionally, the dimensionless constant (R_L) > 1 means unfavorable adsorption, while R_L < 1 indicates favorable adsorption processes [65]. All the attained values of R_L at evaluated temperatures lie between 0 and 1 (Table 1), reflecting favorable adsorption by LMF11 NFs in this study.

The values of $1/n$ (0.1961–0.2543) established from the Freundlich model lie in the range of $0 < 1/n < 1$ at 15 to 45 °C, signifying beneficial adsorption by LMF11 NFs under studied conditions [52]. The E value derived from the D-R model represents free energy. E values in ranges of 1–8 kJ mol^{-1} , 8–16 kJ mol^{-1} and greater than 16 kJ mol^{-1} are indicative of electrostatic physical adsorption, electrostatic interaction or synergy and chemical adsorption, respectively [65]. The E value calculated from the D-R model gradually elevates from 14.06 to 17.96 kJ/mol with ascending the temperature from 15 to 45 °C, which denotes that the defluoridation on LMF11 NFs proceeds from ion exchange to chemisorption [66].

Table 1. Four classical isotherms constants for defluoridation on LMF11 NFs at 15 to 45 °C.

Models	Parameters	T (°C)			
		15	25	35	45
Langmuir	Q_m (mg g ⁻¹)	173.30	189.03	193.05	199.60
	K_L (L mg ⁻¹)	1.7445	2.2383	2.4904	2.5825
	R^2	0.9997	0.9990	0.9987	0.9976
	R_L	0.0095–0.0542	0.0073–0.0427	0.0066–0.0386	0.0064–0.0373
Freundlich	K_F (L g ⁻¹)	93.54	104.01	114.66	123.20
	$1/n$	0.2543	0.2460	0.2117	0.1961
	R^2	0.7863	0.7252	0.5627	0.4791
D-R	$k_{ad}' \times 10^2$ (mol ² kJ ⁻²)	0.2530	0.2250	0.1820	0.1550
	E (kJ mol ⁻¹)	14.06	14.91	16.58	17.96
	R^2	0.8402	0.7725	0.5981	0.4976
Temkin	K_T (L g ⁻¹)	44.39	61.11	158.11	261.92
	B_T (J mol ⁻¹)	89.64	90.26	104.64	110.95
	R^2	0.8708	0.8358	0.6854	0.6161

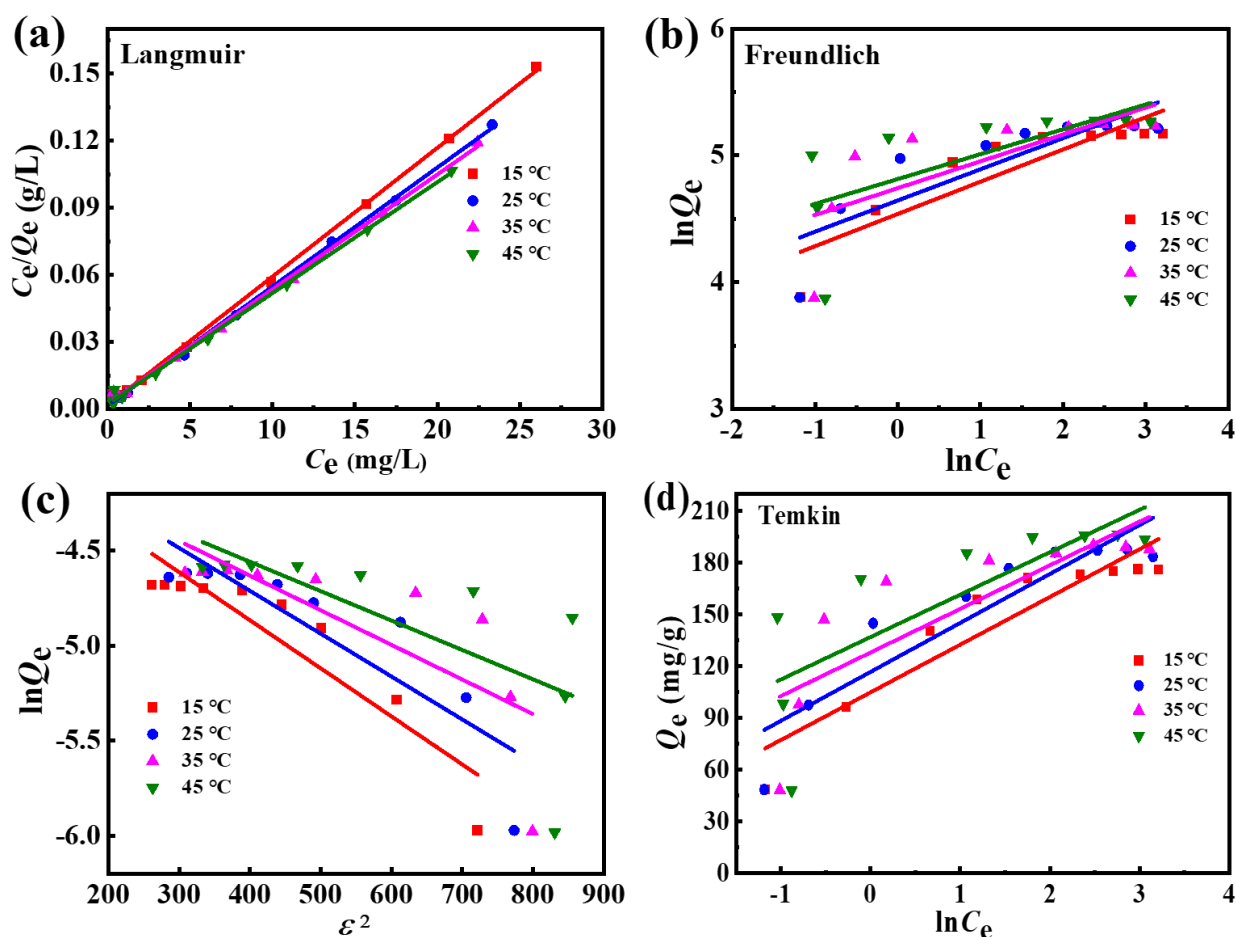
**Figure 8.** Adsorption isotherms of F^- on LMF11 NFs, (a) Langmuir, (b) Freundlich, (c) D-R and (d) Temkin at 15–45 °C.

Table 2. Comparison of various adsorbents based on rare earth elements for defluoridation.

Adsorbents	pH	C ₀ (mg L ⁻¹)	Equilibrium Time/(h)	Q _m (mg g ⁻¹)	References
Ce-AlOOH	3	10–1000	2	62.8	[67]
Fe-Mg-La tri-metal nanocomposite	7	10–300	4	47.20	[66]
Fe-Al-Ce tri-metal oxide	5.8	2–110	24	195	[68]
Mg-Fe-La tri-metal composite	neutral pH	10–150	6	112.17	[32]
Bx-Ce-La@500	3	10–50	3	88.13	[69]
Fe-La-Ce tri-metallic composite	4	10–100	2	303.03	[28]
Zr-La/PP	3	2–50	8.3	32.5	[70]
Layered Zr-Al-La tri-metal composite	3	20–200	6.6	90.48	[71]
Granular TiO ₂ -La	3–9	0.5–2830	–	78.4	[72]
La/Mg/Si-loaded palm shell-based activated carbon	7	100	2	285.7	[73]
La-Mn bimetal oxide nanofibers	3	10–55	1.5	189.39	[33]
Powdered Ce-Mn oxide	6	10–100	3	137.5	[74]
La-Mn-Fe NFs	3	10–60	1	199.60	This study

3.3.7. Adsorption Kinetic

Figure 9 depicts four linear adsorption kinetic curves namely PFO, PSO, Elovich and Weber and Morris models [53] of LMF11 NFs for fluoride at C₀ = 20 and 50 mg F⁻/L and pH = 3. Correlative parameters are listed in Table 3. The highest regression coefficients (i.e., 0.9999 at 20 mg F⁻/L and 0.9999 at 50 mg F⁻/L) derived from the PSO model are larger than those of PFO (0.7212 and 0.9019) and Elovich (0.8714 and 0.9698) models, elucidating the chemisorption behavior plays a critical role in defluoridation process, which is consistent with the reported results of fluoride removal on other La-based adsorbents [32,75]. The theoretical fluoride capture capacities (Q_{e, cal}, 98.23 and 184.50 mg F⁻/g at 20 and 50 mg F⁻/L) derived from the PSO model are in agreement with measured adsorption amounts (Q_{e, exp}, 97.76 and 181.49 mg F⁻/g at 20 and 50 mg F⁻/L). The second-order rate constants (k₂) are 3.7012 × 10⁻² and 0.5236 × 10⁻² g mg⁻¹ min⁻¹ at C₀ = 20 and 50 mg F⁻/L and 25 °C, respectively. This indicates that LMF11 NFs exhibit a higher fluoride removal rate at a lower F⁻ concentration, resulting in a shorter time needed to attain the adsorption equilibrium. Similar results were observed in other La-modified adsorbents [54]. In addition, on the basis of the three-segment linear fitting Weber and Morris model, the intercepts (C) are not zero (Figure 9d), reflecting that the defluoridation mechanism of LMF11 NFs is complex and composed of surface adsorption, intraparticle diffusion along with external liquid film diffusion [48]. The order of k_{int} is k_{int1} > k_{int2} > k_{int3} at C₀ = 20 and 50 mg F⁻/L, revealing that the surface or film diffusion is a rate-controlling step. The fluoride ions adsorb quickly on the external surface of LMF11 NFs at beginning. Pore diffusion or intraparticle is a rate-limiting step at the second stage and the diffusion into mesopores/micropores is dominant and then achieves equilibrium on the exterior surface at the third stage, where intraparticle diffusion decreases owing to the extremely low F⁻ concentration in the adsorption system [43,48].

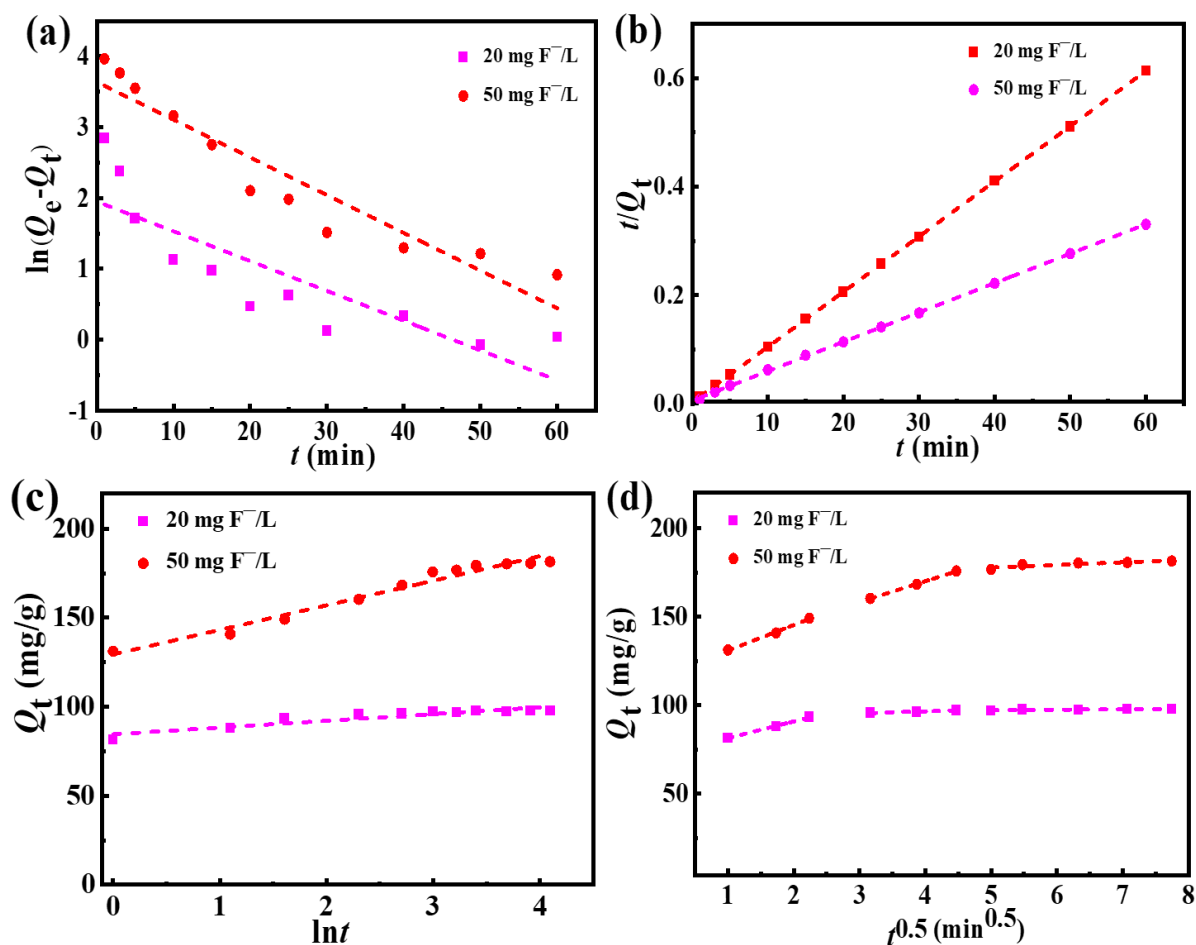


Figure 9. Linear kinetic models of F^- adsorption on LMF11 NFs, (a) PFO, (b) PSO, (c) Elovich and (d) W-M model.

Table 3. Kinetic constants for defluoridation on LMF11 NFs.

Models	Parameters	C_0 (mg/L)	
		20	50
PFO	$k_1 \times 10^2$ (min^{-1})	4.2040	5.3240
	Q_e (mg g^{-1})	7.04	38.03
	R^2	0.7212	0.9019
PSO	$k_2 \times 10^2$ ($\text{g mg}^{-1} \text{min}^{-1}$)	3.7012	0.5236
	$Q_{e, \text{cal}}$ (mg g^{-1})	98.23	184.50
	$Q_{e, \text{exp}}$ (mg g^{-1})	97.76	181.49
	R^2	0.9999	0.9999
Elovich	α ($\text{mg g}^{-1} \text{min}^{-1}$)	1.8793×10^{10}	1.6323×10^5
	β (g mg^{-1})	0.2642	0.0725
	R^2	0.8714	0.9698
Weber–Morris	k_{int1} ($\text{mg g}^{-1} \text{min}^{-0.5}$)	9.4357	14.4288
	R^2	0.9974	0.9954
	C	71.97	116.48
	k_{int2} ($\text{mg g}^{-1} \text{min}^{-0.5}$)	1.1282	11.77
	R^2	0.9207	0.9988
	C	92.02	112.98
	k_{int3} ($\text{mg g}^{-1} \text{min}^{-0.5}$)	0.2503	1.4632
	R^2	0.5567	0.8091
	C	95.94	170.48

3.3.8. Thermodynamic Study

The thermodynamic factors (namely ΔG^0 , ΔH^0 and ΔS^0) derived from the plot of $\ln K_D$ versus $10^3/T$ (Figure 10) are tabulated in Table 4. The ΔG^0 values at 15–45 °C are assessed at -5.89 , -6.69 , -7.08 and -7.64 kJ mol $^{-1}$, respectively. The values of ΔG^0 are negative, signifying the defluorination process by LMF11 NFs is feasible and spontaneous [75]. The positive ΔH^0 (10.45 kJ mol $^{-1}$) and ΔS^0 (69.12 J mol $^{-1}$ K $^{-1}$) confirm the defluorination by LMF11 NFs is endothermic along with an entropy increase process [76].

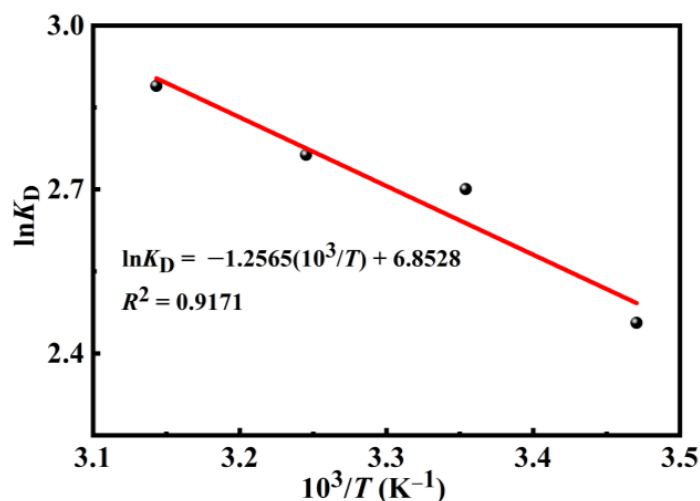


Figure 10. The linear relationship between $\ln K_D$ and $10^3/T$.

Table 4. Thermodynamic factors of defluorination by LMF11 NFs.

T (°C)	ΔG^0 (kJ mol $^{-1}$)	$\ln K_D$	ΔH^0 (kJ mol $^{-1}$)	ΔS^0 (J mol $^{-1}$ K $^{-1}$)
15	-5.89	2.46	10.45	69.12
25	-6.69	2.70		
35	-7.08	2.76		
45	-7.64	2.89		

3.3.9. Reusability

For an ideal adsorbent, it is vital to possess high reusability without a significant loss of removal efficiency. Figure 11 shows the renewability of LMF11 NFs. Notably, the F^- uptakes of LMF11 NFs are 97.50, 96.46, 95.73 and 94.76 mg F^- /g at the original, first, second and third cycles, respectively. It can be concluded that the defluorination performance is still effective for up to three consecutive reuse–regeneration cycles. The result states that LMF11 adsorbent exhibits sufficient chemical stability and reusability, thereby it is suitable for F^- removal from wastewater.

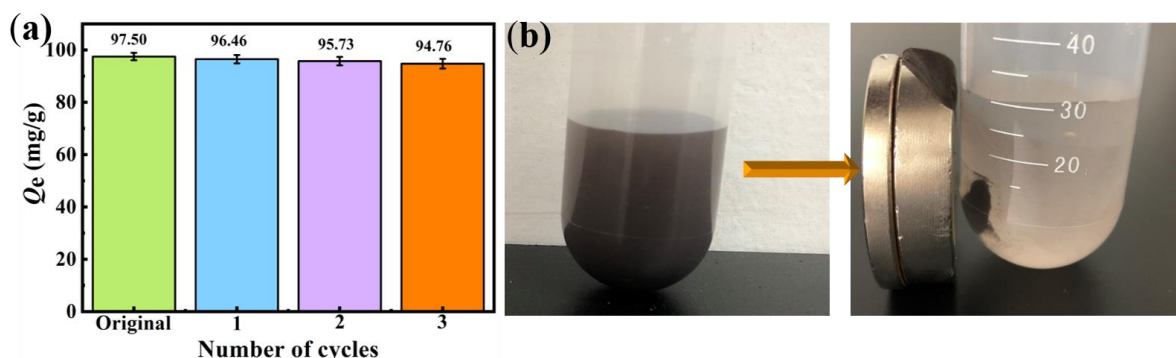


Figure 11. Reusability of LMF11 NFs (a) and photo of magnetic separation (b).

3.4. Adsorption Mechanism

The defluorination mechanism of LMF11 NFs was analyzed by PXRD and FTIR. Figure 12a shows the PXRD spectra of the LMF11 NFs and F^- adsorbed LMF11 NFs. Seven characteristic peaks appearing at $2\theta = 23.0^\circ, 32.8^\circ, 40.5^\circ, 47.1^\circ, 58.2^\circ, 68.6^\circ$ and 77.8° , assigned to peak indices of (100), (110), (111), (200), (211), (220) and (310), respectively, portray the cubic perovskite phase of $LaMnO_3$ (JCPDS NO. 74-0440) [33,77]. The detected characteristic peaks occur at $2\theta = 30.7^\circ$ (220), 35.8° (311) and 62.9° (440), signifying that the cubic phase of Fe_3O_4 has been generated [44]. Meanwhile, the wide peak located at $2\theta = 29.5^\circ$ (220) [78] assigns to La_2O_3 . In summary, the LMF11 NFs are composed of La_2O_3 , $LaMnO_3$ and Fe_3O_4 . After defluorination, the disappearance of the diffraction peak ascribed to La_2O_3 and the presence of new reflections belonged to the hexagonal structure of LaF_3 (PDF No.32-0483) [43] state that the ion exchange between $-OH$ on the surface of LMF11 NFs and F^- is the dominating defluorination mechanism of hydrous La_2O_3 in adsorption system. Moreover, the reflection intensity of Fe_3O_4 and $LaMnO_3$ turns slightly weak after fluoride uptake owing to the decrease in crystallinity caused by the entry of F^- into the crystal lattice.

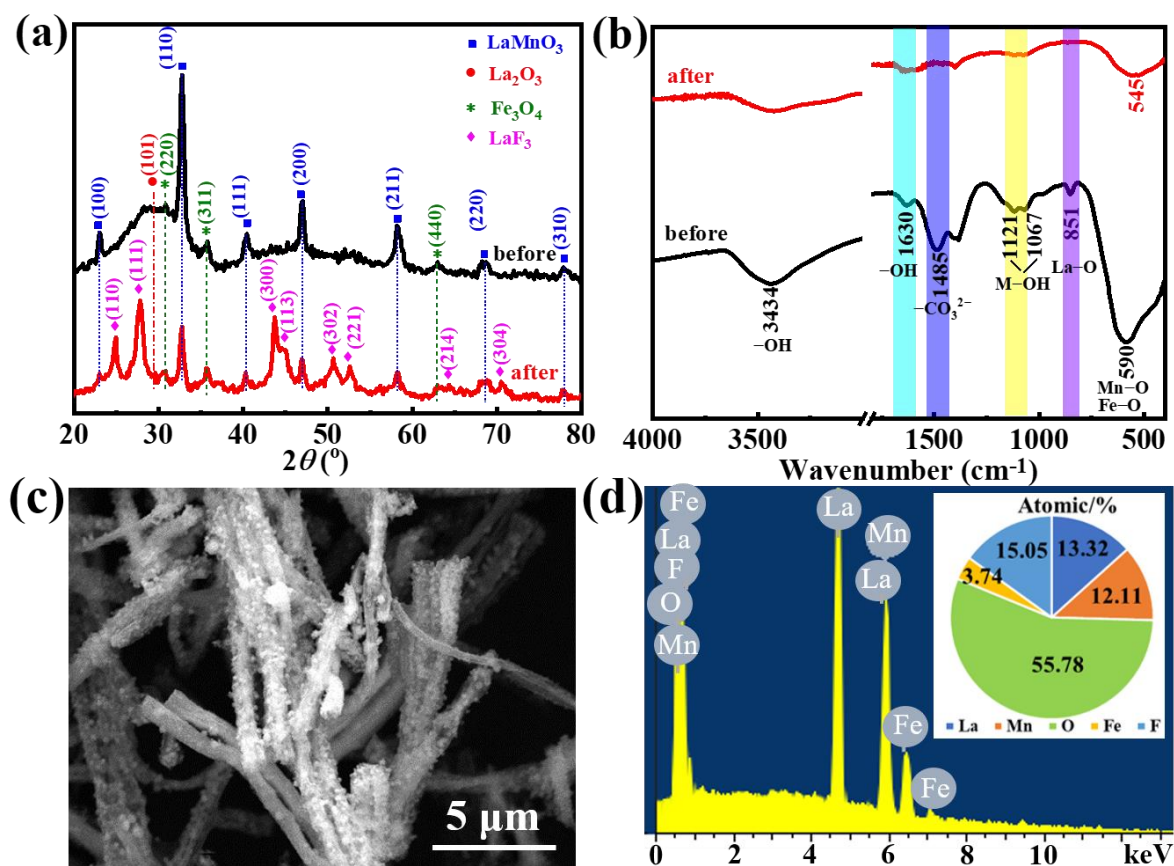


Figure 12. PXRD patterns (a) and FTIR spectra (b) of LMF11 NFs before and after F^- loaded, SEM image (c) and EDS (d) of LMF11 NFs after F^- uptake.

As seen from the FTIR spectrum of the neat LMF11 NFs (Figure 12b), the bands at 3434, 1630, 1485, 851 and 590 cm^{-1} assign to the surface hydroxyl groups stretching mode, chemisorbed water bending mode, CO_3^{2-} stretching mode, La-O stretching mode, and Mn-O along with Fe-O stretching mode [44,77,79]. Meanwhile, the two peaks ascribed to the metal hydroxyl bond (M-OH) [67,80] at 1121 and 1067 cm^{-1} are detected. After fluoride uptake, the bands at 3430 and 1632 cm^{-1} turn obviously weak and two peaks at 1127 and 1067 cm^{-1} are not detected, validating that the bonding of fluoride through electrostatic interaction as well as the replacement of $-OH$ by F^- via ion exchange [81].

Moreover, the La-O band vanishes and the M-O bands (i.e., Mn-O and Fe-O) significantly change, revealing that metal-oxygen bands (La-O, Mn-O and Fe-O) are participated in defluoridation process [82].

F[−] loaded LMF11 adsorbent was further verified by SEM and EDS (Figure 12c,d). The used LMF11 NFs have preserved fibrous morphology. However, the morphological surface of the used LMF11 NFs acquires modified, since there are lots of nanoparticles on the surface of F[−] loaded LMF11 NFs after fluoride adsorption, indicating that fluoride ions have covered the LMF11 NFs surface and LaF₃ nanoparticles have been yielded via ion exchange during the defluoridation process, which is consistent with PXRD analysis. Apparently, the EDS spectrum of F[−] loaded LMF11 NFs portrayed in Figure 12d suggests the presence of La (13.32%), Mn (12.11%), F (15.05%), Fe (3.74%) and O (55.78%) in the used LCF11 NFs.

The pH and pH_{pzc} investigation of LMF11 NFs on F[−] removal reveal that it is more prone to higher removal efficiency in the acidic condition, owing to opposite charges on LMF11 NFs surface and F[−] which is responsible for columbic attractions. The values of E_{DR} calculated by D-R isotherm are 14.06, 14.91, 16.58 and 17.96 kJ mol^{−1}, respectively, at 15, 25, 35 and 45 °C, confirming that the F[−] adsorption is owing to both ion exchange and chemisorption [29,83]. In a word, the defluoridation process onto LMF11 NFs is significantly governed by hydrogen bond, columbic interaction, as well as ion exchange. The plausible defluoridation mechanism by LMF11 NFs is depicted in Figure 13.

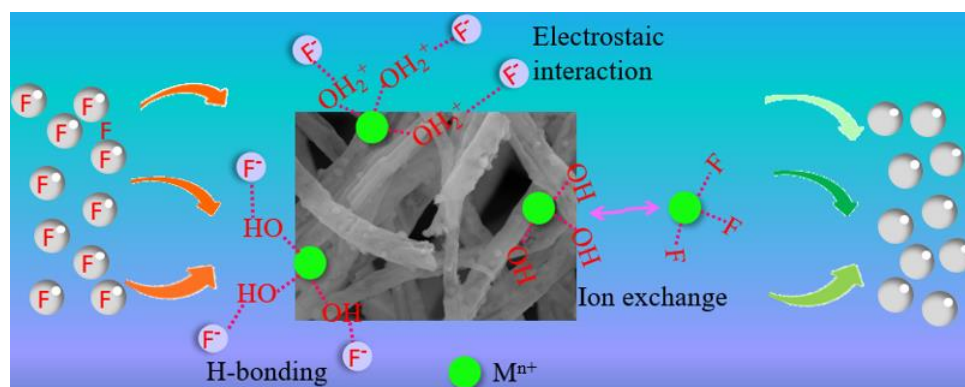


Figure 13. Possible F[−] adsorption mechanism of LMF11 NFs.

4. Conclusions

In this study, magnetic electrospun La-Mn-Fe tri-metal oxide nanofibers (LMF NFs) were developed through electrospinning and heat treatment and used for fluoride recovery. The prepared LMF11 NFs with a La:Mn molar ratio of 1:1 gained the highest fluoride adsorption amount. The results of the investigation were summarized as follows:

- (1) The LMF11 NFs presented fiber morphology with an average diameter of 626 ± 57 nm. The results showed that the spherical Fe₃O₄ NPs were uniformly dispersed along the fiber axis without obvious agglomeration, and the total pore volume and surface area of LMF11 NFs were 0.276 cm³ g^{−1} and 55.81 m² g^{−1}, respectively. The isoelectric point (pH_{pzc}) of LMF11 NFs was 6.47.
- (2) The responsible factors such as initial pH values, shaking time, interfering ions, temperature, initial concentration of adsorbate and adsorbent for fluoride retention on LMF11 NFs were systematically conducted. The maximum adsorption amount of LMF11 NFs achieved at a pH of 3. With ascending LMF11 NFs dosage, the adsorption uptake descended from 188.21 to 82.77 mg F[−]/g, and the adsorption amount of LMF11 NFs increased with the ascend of initial fluoride and then reached equilibrium. The fluoride adsorption by the LMF11 NFs does not affect by the interfering anions, such as NO₃[−], Cl[−], SO₄^{2−} and CO₃^{2−}, with the exception of PO₄^{3−} anions.

- (3) The Langmuir isotherm and PSO model were favored divulging that the F^- adsorption on LMF11 NFs was seen as a single-layer chemisorption. The maximum binding amount calculated from the Langmuir isotherm model was as high as 173.30–199.60 mg F^- /g at pH = 3 at 15–45 °C. A thermodynamic study proved that the defluoridation by LMF11 NFs is a spontaneous, endothermic as well as entropy increase process. The regeneration of the F^- loaded LMF11 NFs exhibited a high defluoridation efficiency of 94.76 mg F^- /g at $C_0 = 20$ mg F^- /L up to three repetitions.
- (4) On the basis of the isoelectric point, FTIR and PXRD analysis, it was confirmed that LMF11 NFs worked with the defluoridation mechanisms including hydrogen bonding, electrostatic attraction and ion exchange.

In summary, the fabricated LMF11 NFs possessed good defluoridation performance and high selective adsorption ability, indicating that the material has great potential as a promising adsorbent for fluoride decontamination. Further study will be conducted on the removal of phosphate, arsenate and other pollutants in the future.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym14245417/s1>, Table S1. Factors and their levels; Table S2. The design of experiment for the adsorption of fluoride and the actual and predicted responses; Table S3. ANOVA results for adsorption capacity; Figure S1. (a) Normal probability plot; (b) Comparison between actual and predicted adsorption efficiency; Figure S2. 3D surface model graphs of fluoride adsorption. Refs. [55,56,84–86].

Author Contributions: Conceptualization, investigation, writing—original draft preparation, W.Y., W.J. and S.J. (Shaoju Jian); analysis, F.S. and Y.L.; data curation, Y.C. and X.H.; writing—review and editing, S.J. (Shaohua Jiang); methodology and project administration and supervision, J.H. All authors have read and agreed to the published version of the manuscript.

Funding: The work is financially supported by the National Natural Science Foundation of China (51903123); Natural Science Foundation of Fujian Province (No. 2020J01419, No. 2020J01393 and No. 2020J05220); National College Students' innovation and entrepreneurship training program (202210397017); Natural Science Foundation of Jiangsu Province (BK20180770 and BK20190760); and The Open Fund of Fujian Provincial Key Laboratory of Eco-Industrial Green Technology (WYKF-EIGT2022-1); The Open Fund of Key Laboratory of Green Chemical Technology of Fujian Province University (WYKF-GCT2022-4, WYKF-GCT2021-1).

Data Availability Statement: The data are included within the article.

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

References

1. Ali, S.; Thakur, S.K.; Sarkar, A.; Shekhar, S. Worldwide contamination of water by fluoride. *Environ. Chem. Lett.* **2016**, *14*, 291–315. [CrossRef]
2. Wang, J.; Sun, Y.; Zhao, X.; Chen, L.; Peng, S.; Ma, C.; Duan, G.; Liu, Z.; Wang, H.; Yuan, Y.; et al. A poly(amidoxime)-modified MOF macroporous membrane for high-efficient uranium extraction from seawater. *e-Polymers* **2022**, *22*, 399–410. [CrossRef]
3. Chen, L.; Sun, Y.; Wang, J.; Ma, C.; Peng, S.; Cao, X.; Yang, L.; Ma, C.; Duan, G.; Liu, Z. A wood-mimetic porous MXene/gelatin hydrogel for electric field/sunlight bi-enhanced uranium adsorption. *e-Polymers* **2022**, *22*, 468–477. [CrossRef]
4. Xu, Y.; Hu, J.; Zhang, X.; Yuan, D.; Duan, G.; Li, Y. Robust and multifunctional natural polyphenolic composites for water remediation. *Mater. Horiz.* **2022**, *9*, 2496–2517. [CrossRef]
5. Amini, M.; Mueller, K.; Abbaspour, K.C.; Rosenberg, T.; Afyuni, M.; Møller, K.N.; Sarr, M.; Johnson, C.A. Statistical modeling of global geogenic fluoride contamination in groundwaters. *Environ. Sci. Technol.* **2008**, *42*, 3662–3668. [CrossRef] [PubMed]
6. Wang, M.; Yin, C.; Jinlan, C.; Zhu, W. Application of AHP-FCE evaluation on the pulping and papermaking water pollution control technology. *J. For. Eng.* **2021**, *6*, 107–113. [CrossRef]
7. Chen, X.; Wan, C.; Yu, R.; Meng, L.; Wang, D.; Chen, W.; Duan, T.; Li, L. A novel carboxylated polyacrylonitrile nanofibrous membrane with high adsorption capacity for fluoride removal from water. *J. Hazard. Mater.* **2021**, *411*, 125113. [CrossRef]
8. Jeyaseelan, A.; Viswanathan, N.; Naushad, M.; Bathula, C. Fabrication of Multi-functionalized Graphene Oxide Doped Alginate Hybrid Spheres for Enhanced Fluoride Adsorption. *J. Inorg. Organomet. Polym. Mater.* **2021**, *32*, 216–228. [CrossRef]
9. Guo, R.; Jiang, S.; Hu, M.; Zhan, Y.; Cheng, K.; Duan, G. Adsorption of volatile benzene series compounds by surface-modified glass fibers: Kinetics, thermodynamic adsorption efficiencies, and mechanisms. *Environ. Sci. Pollut. Res.* **2021**, *28*, 30898–30907. [CrossRef]

10. Yu, J.; Li, Y.; Duan, G.; Wen, P.; Zhou, W. Bio-templated fabrication of chain-spherical V_2O_5/C composites from dandelion fiber for high-efficiency electromagnetic wave absorption. *Vacuum* **2022**, *195*, 110683. [\[CrossRef\]](#)
11. Du, H.; Yue, M.; Huang, X.; Duan, G.; Yang, Z.; Huang, W.; Shen, W.; Yin, X. Preparation, Application and Enhancement Dyeing Properties of ZnO Nanoparticles in Silk Fabrics Dyed with Natural Dyes. *Nanomaterials* **2022**, *12*, 3953. [\[CrossRef\]](#)
12. Yu, J.; Li, Y.; Xu, X.; Duan, G.; Li, Y.; Zhou, W. Rambutan-like $Nb_2O_5@SHCs$ microspheres for improved microwave absorption performance. *Compos. Commun.* **2021**, *24*, 100643. [\[CrossRef\]](#)
13. Li, R.; Lou, Z.; Gu, S.; Wang, Q.; Liu, J.; Yanjun, L. Preparation of magnetic carbon with microwave absorption property using bamboo powder. *J. For. Eng.* **2021**, *6*, 112–120. [\[CrossRef\]](#)
14. Zhou, W.; Lin, P.; Xu, X.; Xie, Y. Sound absorption characteristics of the jute fiber felt and its application in automobiles. *J. For. Eng.* **2021**, *6*, 113–119. [\[CrossRef\]](#)
15. Hu, X.; Zhu, F.; Kong, L.; Peng, X. A novel precipitant for the selective removal of fluoride ion from strongly acidic wastewater: Synthesis, efficiency, and mechanism. *J. Hazard. Mater.* **2021**, *403*, 124039. [\[CrossRef\]](#)
16. Takmil, F.; Esmaili, H.; Mousavi, S.M.; Hashemi, S.A. Nano-magnetically modified activated carbon prepared by oak shell for treatment of wastewater containing fluoride ion. *Adv. Powder Technol. Int. J. Soc. Powder Technol. Jpn.* **2020**, *31*, 3236–3245. [\[CrossRef\]](#)
17. Xu, X.; Liao, Y.; Sun, J.; Wang, X.; Chen, S.; Lv, Z.; Song, J. Removal of Fluorides from Aqueous Solutions Using Fresh and Regenerated Activated Alumina. *Acta Phys. Chim. Sin.* **2019**, *35*, 317–326. [\[CrossRef\]](#)
18. Abe, I.; Iwasaki, S.; Tokimoto, T.; Kawasaki, N.; Nakamura, T.; Tanada, S. Adsorption of fluoride ions onto carbonaceous materials. *J. Colloid Interface Sci.* **2004**, *275*, 35–39. [\[CrossRef\]](#)
19. Raghav, S.; Jain, P.; Kumar, D. Assembly of cerium impregnated pectin/silica-gel biopolymeric material for effective utilization for fluoride adsorption studies. *Mater. Today Proc.* **2022**, *50*, 273–281. [\[CrossRef\]](#)
20. Belcher, R.; Leonard, M.A.; West, T.S. Submicro-methods for the analysis of organic compounds. Part X. Determination of fluorine. *J. Chem. Soc.* **1959**, *717*, 3577–3579. [\[CrossRef\]](#)
21. Belcher, R.; Leonard, M.A.; West, T.S. A new spot test for the detection of fluoride ion. *Talanta* **1959**, *2*, 92–93. [\[CrossRef\]](#)
22. Leonard, M.A.; West, T.S. Chelating reactions of 1,2-dihydroxyanthraquinon-3-ylmethyl-amine-NN-diacetic acid with metal cations in aqueous media. *J. Chem. Soc.* **1960**, *866*, 4477–4486. [\[CrossRef\]](#)
23. Tokunaga, S.; Haron, M.J.; Wasay, S.A.; Wong, K.F.; Laosangthum, K.; Uchiumi, A. Removal of fluoride ions from aqueous solutions by multivalent metal compounds. *Int. J. Environ. Stud.* **1995**, *48*, 17–28. [\[CrossRef\]](#)
24. Wasay, S.A.; Haran, M.J.; Tokunaga, S. Adsorption of fluoride, phosphate, and arsenate ions on lanthanum-impregnated silica gel. *Water Environ. Res.* **1996**, *68*, 295–300. [\[CrossRef\]](#)
25. Wasay, S.A.; Tokunaga, S.; Park, S.W. Removal of Hazardous Anions from Aqueous Solutions by La(III)- and Y(III)-Impregnated Alumina. *Sep. Sci. Technol.* **1996**, *31*, 1501–1514. [\[CrossRef\]](#)
26. Kamble, S.P.; Jagtap, S.; Labhsetwar, N.K.; Thakare, D.; Godfrey, S.; Devotta, S.; Rayalu, S.S. Defluoridation of drinking water using chitin, chitosan and lanthanum-modified chitosan. *Chem. Eng. J.* **2007**, *129*, 173–180. [\[CrossRef\]](#)
27. Yu, Y.; Chen, J.P. Fabrication and performance of a Mn–La metal composite for remarkable decontamination of fluoride. *J. Mater. Chem. A* **2014**, *2*, 8086. [\[CrossRef\]](#)
28. Thathsara, S.K.T.; Cooray, P.; Mudiyanse, T.K.; Kottegoda, N.; Ratnaweera, D.R. A novel Fe-La-Ce tri-metallic composite for the removal of fluoride ions from aqueous media. *J. Environ. Manag.* **2018**, *207*, 387–395. [\[CrossRef\]](#)
29. Yin, C.; Huang, Q.; Zhu, G.; Liu, L.; Li, S.; Yang, X.; Wang, S. High-performance lanthanum-based metal-organic framework with ligand tuning of the microstructures for removal of fluoride from water. *J. Colloid Interface Sci.* **2022**, *607*, 1762–1775. [\[CrossRef\]](#)
30. Govarthanan, M.; Jeon, C.H.; Kim, W. Synthesis and characterization of lanthanum-based metal organic framework decorated polyaniline for effective adsorption of lead ions from aqueous solutions. *Environ. Pollut.* **2022**, *303*, 119049. [\[CrossRef\]](#)
31. He, Y.; Zhang, L.; An, X.; Wan, G.; Zhu, W.; Luo, Y. Enhanced fluoride removal from water by rare earth (La and Ce) modified alumina: Adsorption isotherms, kinetics, thermodynamics and mechanism. *Sci. Total Environ.* **2019**, *688*, 184–198. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Wang, J.; Kang, D.; Yu, X.; Ge, M.; Chen, Y. Synthesis and characterization of Mg–Fe–La trimetal composite as an adsorbent for fluoride removal. *Chem. Eng. J.* **2015**, *264*, 506–513. [\[CrossRef\]](#)
33. Jian, S.; Cheng, Y.; Ma, X.; Guo, H.; Hu, J.; Zhang, K.; Jiang, S.; Yang, W.; Duan, G. Excellent fluoride removal performance by electrospun La–Mn bimetal oxide nanofibers. *New J. Chem.* **2022**, *46*, 490–497. [\[CrossRef\]](#)
34. Kong, L.; Tian, Y.; Pang, Z.; Huang, X.; Li, M.; Yang, R.; Li, N.; Zhang, J.; Zuo, W. Synchronous phosphate and fluoride removal from water by 3D rice-like lanthanum-doped La@MgAl nanocomposites. *Chem. Eng. J.* **2019**, *371*, 893–902. [\[CrossRef\]](#)
35. Xiang, W.; Zhang, G.; Zhang, Y.; Tang, D.; Wang, J. Synthesis and characterization of cotton-like Ca–Al–La composite as an adsorbent for fluoride removal. *Chem. Eng. J.* **2014**, *250*, 423–430. [\[CrossRef\]](#)
36. Gasparotto, J.M.; Roth, D.; Perilli, A.L.d.O.; Franco, D.S.P.; Carissimi, E.; Foletto, E.L.; Jahn, S.L.; Dotto, G.L. A novel Fe-Al-La trioxide composite: Synthesis, characterization, and application for fluoride ions removal from the water supply. *J. Environ. Chem. Eng.* **2021**, *9*, 106350. [\[CrossRef\]](#)
37. Liu, L.; Song, W.; Jiang, S.; Duan, G.; Qin, X. Giving Penetrable Remote-Control Ability to Thermoresponsive Fibrous Composite Actuator with Fast Response Induced by Alternative Magnetic Field. *Nanomaterials* **2021**, *12*, 53. [\[CrossRef\]](#)

38. Yang, X.; Qi, H.; Jiang, S.; Dong, X.; Duan, G. Di-aeolotropic electric conductive Janus nanobelts with up-/down-converting fluorescence and magnetism by sequential coaxial and side-by-side electrospinning. *Compos. Commun.* **2022**, *35*, 101307. [\[CrossRef\]](#)
39. Markeb, A.A.; Ordosgoitia, L.A.; Alonso, A.; Sánchez, A.; Font, X. Novel magnetic core-shell Ce-Ti@Fe₃O₄ nanoparticles as an adsorbent for water contaminants removal. *RSC Adv.* **2016**, *6*, 56913–56917. [\[CrossRef\]](#)
40. Kumari, S.; Singh, N.; Sharma, R.; Yadav, M.; Khan, S. Kinetics and isotherms of adsorption of fluoride onto Fe₃O₄/graphene/alginate nanocomposite hydrogel. *Environ. Nanotechnol. Monit. Manag.* **2021**, *16*, 100590. [\[CrossRef\]](#)
41. Zhou, G.; Meng, Q.; Li, S.; Song, R.; Wang, Q.; Xu, Z.; Xing, Z. Novel magnetic metal-organic framework derivative: An adsorbent for efficient removal of fluorine-containing wastewater in mines. *J. Environ. Chem. Eng.* **2022**, *10*, 108421. [\[CrossRef\]](#)
42. Liu, L.; Cui, Z.; Ma, Q.; Cui, W.; Zhang, X. One-step synthesis of magnetic iron-aluminum oxide/graphene oxide nanoparticles as a selective adsorbent for fluoride removal from aqueous solution. *RSC Adv.* **2016**, *6*, 10783–10791. [\[CrossRef\]](#)
43. Jian, S.; Shi, F.; Hu, R.; Liu, Y.; Chen, Y.; Jiang, W.; Yuan, X.; Hu, J.; Zhang, K.; Jiang, S.; et al. Electrospun magnetic La₂O₃-CeO₂-Fe₃O₄ composite nanofibers for removal of fluoride from aqueous solution. *Compos. Commun.* **2022**, *33*, 101194. [\[CrossRef\]](#)
44. Yang, W.; Wang, Y.; Wang, Q.; Wu, J.; Duan, G.; Xu, W.; Jian, S. Magnetically separable and recyclable Fe₃O₄@PDA covalent grafted by l-cysteine core-shell nanoparticles toward efficient removal of Pb²⁺. *Vacuum* **2021**, *189*, 110229. [\[CrossRef\]](#)
45. Duan, G.; Jin, M.; Wang, F.; Greiner, A.; Agarwal, S.; Jiang, S. Core effect on mechanical properties of one dimensional electrospun core-sheath composite fibers. *Compos. Commun.* **2021**, *25*, 100773. [\[CrossRef\]](#)
46. Yang, X.; Wang, J.; Guo, H.; Liu, L.; Xu, W.; Duan, G. Structural design toward functional materials by electrospinning: A review. *e-Polymers* **2020**, *20*, 682–712. [\[CrossRef\]](#)
47. Qiu, H.; Liang, C.; Yu, J.; Zhang, Q.; Song, M.; Chen, F. Preferable phosphate sequestration by nano-La(III) (hydr)oxides modified wheat straw with excellent properties in regeneration. *Chem. Eng. J.* **2017**, *315*, 345–354. [\[CrossRef\]](#)
48. Dong, S.; Wang, Y. Characterization and adsorption properties of a lanthanum-loaded magnetic cationic hydrogel composite for fluoride removal. *Water Res.* **2016**, *88*, 852–860. [\[CrossRef\]](#)
49. Zaidi, R.; Khan, S.U.; Farooqi, I.H.; Azam, A. Investigation of kinetics and adsorption isotherm for fluoride removal from aqueous solutions using mesoporous cerium-aluminum binary oxide nanomaterials. *RSC Adv.* **2021**, *11*, 28744–28760. [\[CrossRef\]](#)
50. Ma, X.; Zhao, S.; Tian, Z.; Duan, G.; Pan, H.; Yue, Y.; Li, S.; Jian, S.; Yang, W.; Liu, K.; et al. MOFs meet wood: Reusable magnetic hydrophilic composites toward efficient water treatment with super-high dye adsorption capacity at high dye concentration. *Chem. Eng. J.* **2022**, *446*, 136851. [\[CrossRef\]](#)
51. Liu, H.; Guo, W.; Liu, Z.; Li, X.; Wang, R. Effective adsorption of phosphate from aqueous solution by La-based metal-organic frameworks. *RSC Adv.* **2016**, *6*, 105282–105287. [\[CrossRef\]](#)
52. Parashar, K.; Ballav, N.; Debnath, S.; Pillay, K.; Maity, A. Rapid and efficient removal of fluoride ions from aqueous solution using a polypyrrole coated hydrous tin oxide nanocomposite. *J. Colloid Interface Sci.* **2016**, *476*, 103–118. [\[CrossRef\]](#) [\[PubMed\]](#)
53. Li, H.; Li, T.; Zhang, T.; Zhu, J.; Deng, W.; He, D. Construction and Adsorption Performance Study of GO-CNT/Activated Carbon Composites for High Efficient Adsorption of Pollutants in Wastewater. *Polymers* **2022**, *14*, 4951. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Xu, J.; Cui, Y.; Wang, R.; Shi, Z.; Wu, C.; Li, D. Mesoporous La-based nanorods synthesized from a novel IL-SFME for phosphate removal in aquatic systems. *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, *624*, 126689. [\[CrossRef\]](#)
55. Siyal, A.A.; Shamsuddin, M.R.; Khahro, S.H.; Low, A.; Ayoub, M. Optimization of synthesis of geopolymer adsorbent for the effective removal of anionic surfactant from aqueous solution. *J. Environ. Chem. Eng.* **2021**, *9*, 104949. [\[CrossRef\]](#)
56. Ghumman, A.S.M.; Shamsuddin, R.; Nasef, M.M.; Nisa Yahya, W.Z.; Abbasi, A. Optimization of synthesis of inverse vulcanized copolymers from rubber seed oil using response surface methodology. *Polymer* **2021**, *219*, 123553. [\[CrossRef\]](#)
57. Liu, H.; Deng, S.; Li, Z.; Yu, G.; Huang, J. Preparation of Al-Ce hybrid adsorbent and its application for defluoridation of drinking water. *J. Hazard. Mater.* **2010**, *179*, 424–430. [\[CrossRef\]](#)
58. Liu, M.; Li, S.; Tang, N.; Wang, Y.; Yang, X.; Wang, S. Highly efficient capture of phosphate from water via cerium-doped metal-organic frameworks. *J. Clean. Prod.* **2020**, *265*, 121782. [\[CrossRef\]](#)
59. Kamarehie, B.; Noraei, Z.; Jafari, A.; Ghaderpoori, M.; Karami, M.A.; Ghaderpoury, A. Data on the fluoride adsorption from aqueous solutions by metal-organic frameworks (ZIF-8 and UiO-66). *Data Brief* **2018**, *20*, 799–804. [\[CrossRef\]](#)
60. Araga, R.; Sharma, C.S. Amine Functionalized Electrospun Cellulose Nanofibers for Fluoride Adsorption from Drinking Water. *J. Polym. Environ.* **2019**, *27*, 816–826. [\[CrossRef\]](#)
61. Mahapatra, A.; Mishra, B.G.; Hota, G. Studies on Electrospun Alumina Nanofibers for the Removal of Chromium(VI) and Fluoride Toxic Ions from an Aqueous System. *Ind. Eng. Chem. Res.* **2013**, *52*, 1554–1561. [\[CrossRef\]](#)
62. Tang, D.; Zhang, G. Efficient removal of fluoride by hierarchical Ce-Fe bimetal oxides adsorbent: Thermodynamics, kinetics and mechanism. *Chem. Eng. J.* **2015**, *283*, 721–729. [\[CrossRef\]](#)
63. Wang, A.; Zhou, K.A.; Liu, X.A.; Liu, F.A.; Zhang, C.B.; Chen, Q.A. Granular tri-metal oxide adsorbent for fluoride uptake: Adsorption kinetic and equilibrium studies. *J. Colloid Interface Sci.* **2017**, *505*, 947–955. [\[CrossRef\]](#) [\[PubMed\]](#)
64. Gitari, W.M.; Izuagie, A.A.; Gumbo, J.R. Synthesis, characterization and batch assessment of groundwater fluoride removal capacity of trimetal Mg/Ce/Mn oxide-modified diatomaceous earth. *Arab. J. Chem.* **2020**, *13*, 1–16. [\[CrossRef\]](#)
65. Zhu, L.; Zhang, C.; Wang, L.; Zhang, J. The simple synthesis of metal organic frameworks with high fluoride adsorption performance from water. *J. Solid State Chem.* **2022**, *307*, 122866. [\[CrossRef\]](#)

66. Chen, P.; Wang, T.; Xiao, Y.; Tian, E.; Wang, W.; Zhao, Y.; Tian, L.; Jiang, H.; Luo, X. Efficient fluoride removal from aqueous solution by synthetic Fe Mg La tri-metal nanocomposite and the analysis of its adsorption mechanism. *J. Alloys Compd.* **2018**, *738*, 118–129. [\[CrossRef\]](#)
67. Tao, W.; Zhong, H.; Pan, X.; Wang, P.; Wang, H.; Huang, L. Removal of fluoride from wastewater solution using Ce-AlOOH with oxalic acid as modification. *J. Hazard. Mater.* **2020**, *384*, 121373. [\[CrossRef\]](#)
68. Wu, X.; Zhang, Y.; Dou, X.; Yang, M. Fluoride removal performance of a novel Fe-Al-Ce trimetal oxide adsorbent. *Chemosphere* **2007**, *69*, 1758–1764. [\[CrossRef\]](#)
69. Alhassan, S.I.; Wang, H.; He, Y.; Yan, L.; Jiang, Y.; Wu, B.; Wang, T.; Gang, H.; Huang, L.; Jin, L.; et al. Fluoride remediation from on-site wastewater using optimized bauxite nanocomposite (Bx-Ce-La@500): Synthesis maximization, and mechanism of F-removal. *J. Hazard. Mater.* **2022**, *430*, 128401. [\[CrossRef\]](#)
70. Shang, Y.; Xu, X.; Gao, B.; Yue, Q. Highly selective and efficient removal of fluoride from aqueous solution by Zr La dual-metal hydroxide anchored bio-sorbents. *J. Clean. Prod.* **2018**, *199*, 36–46. [\[CrossRef\]](#)
71. Zhou, J.; Zhu, W.; Yu, J.; Zhang, H.; Zhang, Y.; Lin, X.; Luo, X. Highly selective and efficient removal of fluoride from ground water by layered Al-Zr-La Tri-metal hydroxide. *Appl. Surf. Sci.* **2018**, *435*, 920–927. [\[CrossRef\]](#)
72. Yan, L.; Tu, H.; Chan, T.; Jing, C. Mechanistic study of simultaneous arsenic and fluoride removal using granular TiO₂-La adsorbent. *Chem. Eng. J.* **2017**, *313*, 983–992. [\[CrossRef\]](#)
73. Choong, C.E.; Kim, M.; Yoon, S.; Lee, G.; Park, C.M. Mesoporous La/Mg/Si-incorporated palm shell activated carbon for the highly efficient removal of aluminum and fluoride from water. *J. Taiwan Inst. Chem. Eng.* **2018**, *93*, 306–314. [\[CrossRef\]](#)
74. Deng, S.; Liu, H.; Zhou, W.; Huang, J.; Yu, G. Mn-Ce oxide as a high-capacity adsorbent for fluoride removal from water. *J. Hazard. Mater.* **2011**, *186*, 1360–1366. [\[CrossRef\]](#) [\[PubMed\]](#)
75. Yang, W.; Shi, F.; Jiang, W.; Chen, Y.; Zhang, K.; Jian, S.; Jiang, S.; Zhang, C.; Hu, J. Outstanding fluoride removal from aqueous solution by a La-based adsorbent. *RSC Adv.* **2022**, *12*, 30522–30528. [\[CrossRef\]](#) [\[PubMed\]](#)
76. Zheng, M.; Wang, J.; Fu, D.; Ren, B.; Song, X.; Kan, K.; Zhang, X. Anchored growth of highly dispersed LDHs nanosheets on expanded graphite for fluoride adsorption properties and mechanism. *J. Hazard. Mater.* **2023**, *442*, 130068. [\[CrossRef\]](#)
77. Zhu, W.; Hao, N.; Chen, C.; Qiu, Y.; Zuo, Y.; Wei, J.; Qian, J.; Wang, K. Hierarchical Regulation of LaMnO₃ Dual-Pathway Strategy for Excellent Room-Temperature Organocatalytic Oxidation Performance. *Inorg. Chem.* **2022**, *61*, 7459–7466. [\[CrossRef\]](#) [\[PubMed\]](#)
78. Hu, C.G.; Liu, H.; Dong, W.T.; Zhang, Y.Y.; Bao, G.; Lao, C.S.; Wang, Z.L. La(OH)₃ and La₂O₃ Nanobelts—Synthesis and Physical Properties. *Adv. Mater.* **2007**, *19*, 470–474. [\[CrossRef\]](#)
79. Afify, M.S.; El Faham, M.M.; Eldemerdash, U.; El Rouby, W.M.A.; El-Dek, S.I. Room temperature ferromagnetism in Ag doped LaMnO₃ nanoparticles. *J. Alloys Compd.* **2021**, *861*, 158570. [\[CrossRef\]](#)
80. Zhang, Y.; Qian, Y.; Li, W.; Gao, X.; Pan, B. Fluoride uptake by three lanthanum based nanomaterials: Behavior and mechanism dependent upon lanthanum species. *Sci. Total Environ.* **2019**, *683*, 609–616. [\[CrossRef\]](#)
81. Chen, J.; Yang, R.; Zhang, Z.; Wu, D. Removal of fluoride from water using aluminum hydroxide-loaded zeolite synthesized from coal fly ash. *J. Hazard. Mater.* **2022**, *421*, 126817. [\[CrossRef\]](#) [\[PubMed\]](#)
82. Zhang, J.; Chen, N.; Su, P.; Li, M.; Feng, C. Fluoride removal from aqueous solution by Zirconium-Chitosan/Graphene Oxide Membrane. *React. Funct. Polym.* **2017**, *114*, 127–135. [\[CrossRef\]](#)
83. Huang, Q.; Zhao, L.; Zhu, G.; Chen, D.; Ma, X.; Yang, X.; Wang, S. Outstanding performance of thiophene-based metal-organic frameworks for fluoride capture from wastewater. *Sep. Purif. Technol.* **2022**, *298*, 121567. [\[CrossRef\]](#)
84. Nguyen, D.T.C.; Vo, D.-V.N.; Nguyen, T.T.; Nguyen, T.T.T.; Nguyen, L.T.T.; Tran, T.V. Optimization of tetracycline ad-sorption onto zeolitic-imidazolate framework-based carbon using response surface methodology. *Surf. Interfaces* **2022**, *28*, 101549. [\[CrossRef\]](#)
85. Kalsido, A.W.; Meshesha, B.T.; Behailu, B.M.; Alemayehu, E. Optimization of Fluoride Adsorption on Acid Modified Bentonite Clay Using Fixed-Bed Column by Response Surface Method. *Molecules* **2021**, *26*, 7112. [\[CrossRef\]](#)
86. Yang, Y.; Li, X.; Gu, Y.; Lin, H.; Jie, B.; Zhang, Q.; Zhang, X. Adsorption property of fluoride in water by metal organic framework: Optimization of the process by response surface methodology technique. *Surf. Interfaces* **2022**, *28*, 101649. [\[CrossRef\]](#)