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Short communication

Lanthanum cholate fibres: A novel adsorbent for fluoride removal

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A R T I C L E I N F O

Keywords:
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A B S T R A C T

Lanthanum cholate (LaC) synthesized from bile salt sodium cholate and Lanthanum was studied for its defluoridation capacity. The influence of pH, LaC dosage, fluoride concentration, and equilibration time on the defluoridation process was examined. The adsorption isotherm and adsorption kinetic models were studied to get an insight into the adsorption process of fluoride onto LaC. LaC demonstrated Langmuir monolayer adsorption capacity of 49.26 mg/g and its effectiveness for de-fluoridation of ground water samples was demonstrated. Presence of anions like HCO_3^-, CO_3^{2-}, Cl^-, SO_4^{2-}, NO_3^- had minimal effect on the fluoride removal. LaC and fluoride loaded LaC (LaCF) were characterised by Scanning Electron Microscopy (SEM)-Energy Dispersive X-Ray (EDX) Analysis, Infrared Spectroscopy and X-Ray Diffraction techniques.

1. Introduction

Fluoride in the environment occurs due to its natural presence as fluorite, biotites, topaz, mica etc., as well as from industrial effluents [1]. In drinking water, the optimum level of fluoride should be 0.5–1.0 mg/L (WHO standard) [2,3].

Defluoridation techniques include electrodialysis [4], ion exchange [5], membrane processes [6,7], as well as precipitation [8]. The widely used method for fluoride removal among all these methods is adsorption as it is the most promising, efficient process. Moreover, it provides eco-friendly approach towards fluoride removal [9–13].

Sodium cholate (NaC), a bile salt is an amphiphilic molecule forming aggregates in aqueous solution and is involved in the transport and absorption of cholesterol, lipids, and fat-soluble vitamins. Bile salt derived hydrogels [14] with rigid helical superstructures are amenable for the synthesis of novel nanomaterials [15–17] with applications as catalysts for synthesis of chiral materials, biosensors, and non-linear optics.

NaC, (3α-,7α-, and 12α-trihydroxy) does not form a gel due to its higher water-solubility. Bhaumik et al. for the first time synthesised a hydrogel of sodium cholate for the first time, driven by lanthanide [17]. Yan Qiao et al. synthesized one-dimensional LaC hierarchical architectures such as nanotubes, coil and rope like structures; nano ribbons and helical structures under controlled temperature conditions [18]. The authors believed that hydrogen bond formation between water and cholate could have facilitated the lanthanum cholate self-assembly.

Further, rare earth metal, such as lanthanum is well known for its high affinity towards fluoride ions [19]. Colloidal lanthanum has been reported for removal of fluoride, but has a limitation of adsorbent recovery at the end of treatment for application in water treatment [20–23]. Lanthanum alginate beads with a defluoridation potential of 197.2 $mg \cdot g^{-1}$ was reported by Huo et al. [24]. Vences et al. used lanthanum oxyhydroxides anchored granular activated carbon [25] while Wang et al. used Lanthanum modified bone waste as adsorbents for fluoride [26]. A Mg/Fe/La hydrotalcite-like compound was fabricated and applied for defluoridation by Xu et al. [27]. Tamarix hispida biochar was amended with La by Habibi et al. for improved fluoride adsorption capacity [28]. Lanthanum and cerium based MOF comprising Benzene tricarboxylic acid has been studied by Jeyaseelan et al. for fluoride removal [29].

In the present work bile salt sodium cholate was used to form Lanthanum cholate gel (LaC) with lanthanum and its defluoridation potential was investigated for the first time. No such investigation has been performed till date to the best of our knowledge. The synthesized LaC was effective for removal of fluoride over a wide pH range of 3–9.

2. Materials and methods

2.1. Chemicals

All reagents were prepared using analytical grade chemicals. The working solutions of desired concentrations of fluoride were prepared by suitable dilution of 1000 mg/L of fluoride solution.

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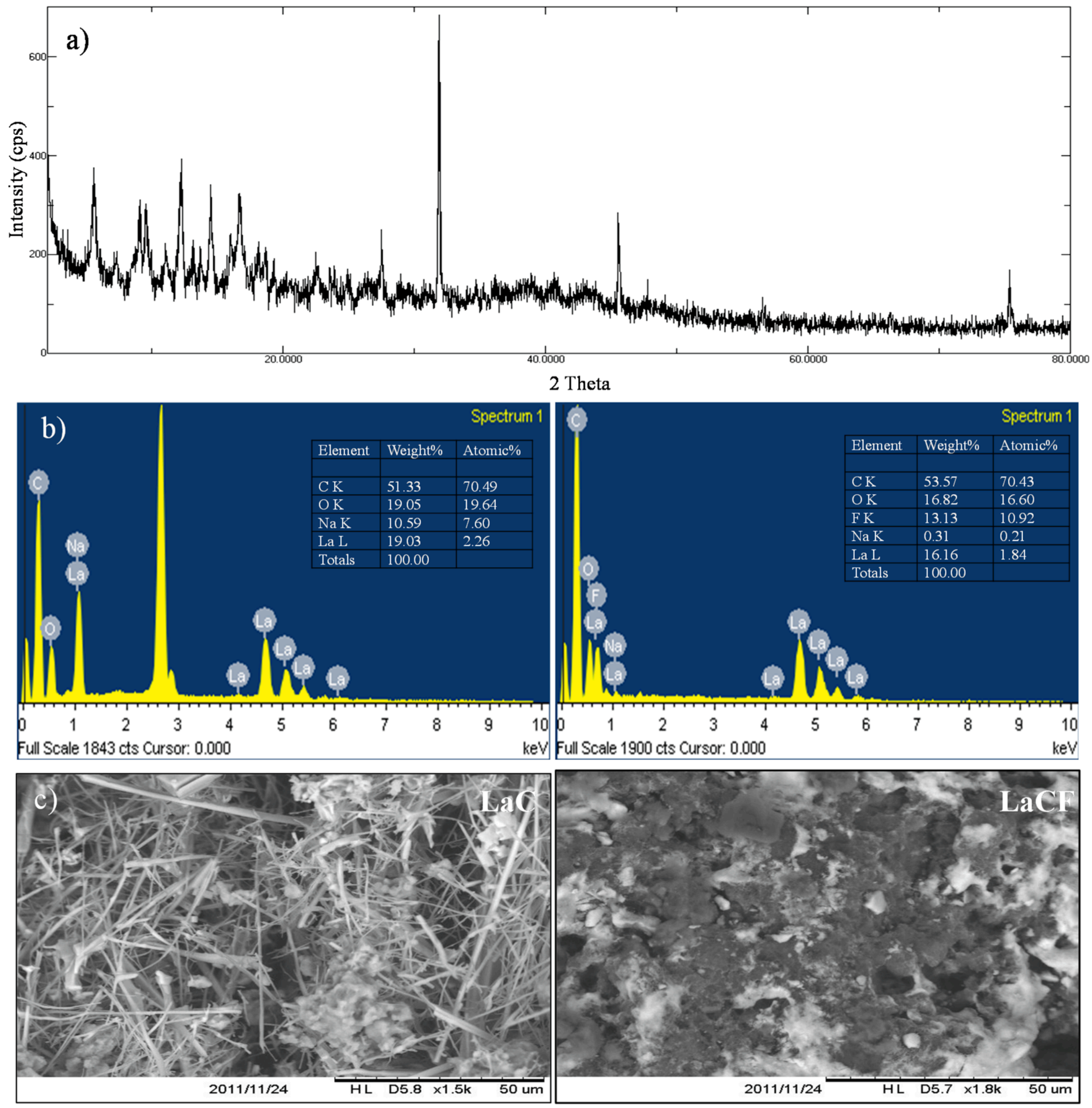

Fig. 1. a) XRD spectra of LaC, b) EDAX of LaC and LaCF, c) SEM images of LaC and LaCF.

2.2. *Synthesis of Lanthanum cholate self-assembly*

The self-assembly of hydrogel lanthanum cholate (LaC) was obtained by simple mixing of equal volume of 0.1 M Sodium cholate and 0.1 M Lanthanum chloride heptahydrate. The inverted test tube method was applied to investigate the hydrogelation. The hydrogel thus formed was opaque in nature which was further dried at 105 $\pm$ 2 °C and powdered for the use of fluoride adsorption experiments.

2.3. *Characterisation*

The IR spectral analysis of LaC, and LaCF was performed to investigate the vibrational frequency changes in the functional groups of LaC during fluoride removal using BRUKER ALPHA, FTIR spectrometer.

Thermogravimetric analysis (TGA) was done under nitrogen atmosphere using EXSTAR6000 TG/DTA 6300, to determine the thermal stability of LaC.

The surface morphology and composition of LaC and LaCF were investigated using JEOL 1600 Scanning Electron Microscope and Energy Dispersive X-ray (EDX) (Carl Zeiss, EVO18) techniques.

XRD analysis of LaC was carried out using a Bruker PANalytical Diffractometer with Cu-Kα radiation. Zeta Plus 90Plus Brook Haven Zetasizer was used to measure surface charge on LaC.

2.4. *Adsorptive removal of fluoride*

Batch adsorption experiments were performed by taking known concentrations of fluoride solutions in polypropylene flasks to investigate the fluoride adsorption capacity of Lanthanum cholate. The flasks were agitated in an electrical shaker set to 150 rotations / minute at room temperature (30 $\pm$ 5 °C) for 3 h. All experiments were conducted at neutral pH except for pH studies wherein the pH was adjusted to desired values using NaOH or HCl.

The adsorbent was removed by filtration after equilibration and the un-adsorbed fluoride in the solution was analysed by ion selective electrode (ORION STAR A214). The pH of the solution was maintained

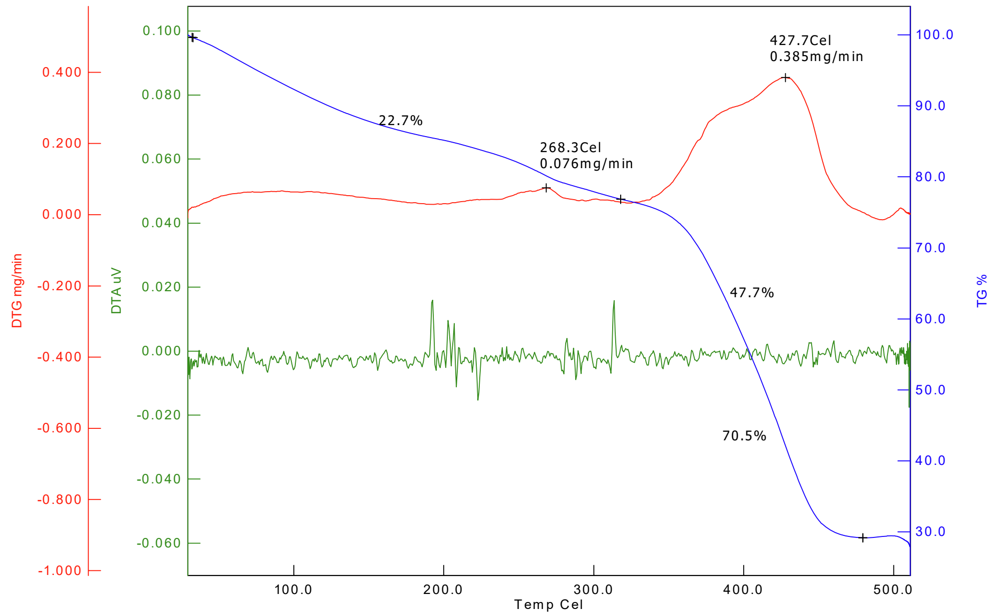

Fig. 2. Thermogravimetric analysis of LaC.

at 5–7 using TISAB buffer. The percent fluoride removed was obtained using the formula:

$q_e = C_i - C_e / m * 100$

where q_e = amount of fluoride adsorbed (mg/g).

C_i and Ce = initial and equilibrium fluoride concentrations (mg/L) respectively.

m = mass of LaC (mg).

Kinetic and isotherm modelling were performed on the obtained adsorption data (Table S1) to get an insight into the adsorption process.

3. Results and discussion:

3.1. Characterisation of LaC

The LaC XRD spectral pattern exhibited (Fig. 1a) distinct diffraction peaks at 16.1°, 26.2°, 30.4°, 39.8°, 46.8°, 56.2° which were assigned to (0 0 1), (1 0 0), (1 0 1), (1 0 2), (1 1 0), (1 1 2) lattice planes of lanthanum. Similar peaks were observed by researchers in lanthanum modified carbon and lanthanum modified bone waste [26,30]. The EDAX spectra (Fig. 1b) confirmed the presence of La in LaC and Lanthanum and Fluoride in LaCF. The SEM image (Fig. 1c) indicated fibrous nature of LaC. The length of the twisted ribbons was about 15 µm. It was observed that the fibrillar network of cholate collapsed after fluoride adsorption.

The thermogram of LaC (Fig. 2) exhibited a weight loss of 22.7% at ~ 234̊C attributed to disintegration of cholate network bound to lanthanum followed by a weight loss of ~ 47.7% in the temperature range between 350 and 520 °C attributed to the decomposition of cholate molecules.

Fig. 3 shows the FTIR spectral analysis of sodium cholate, LaC and LaCF. The broad band in sodium cholate and Lanthanum cholate at 3380 cm^{-1} was ascribed to hydroxyl stretching mode [18]. The bands at 1578 and 1404 cm^{-1} in sodium cholate were ascribed to asymmetric and symmetric stretching modes of carboxyl group respectively, with a frequency separation $\Delta\nu$ of 174 cm^{-1}. On the other hand, in lanthanum cholate, the absorption peaks were observed at 1536 and 1418 cm^{-1} respectively, wherein $\Delta\nu$ is 118 cm^{-1} (Fig. 3b). The smaller $\Delta\nu$ value of lanthanum-cholate than that of sodium cholate indicated that lanthanum bound to carboxyl group in a bidentate chelating fashion. The assignment of bands at 1645 cm^{-1}, 856 cm^{-1} and 1039 cm^{-1} in LaC was to C = O, O-La stretching and C-O bending modes respectively.

After adsorption of fluoride a blue shift from 3380 cm^{-1} to 3360 cm^{-1} was observed, that may be attributed to a change in gel structure. Further, the asymmetric and symmetric stretching modes of carboxyl group were observed at 1550 and 1409 cm^{-1} respectively, wherein $\Delta\nu$ of 139 cm^{-1} was close to pristine sodium cholate indicating the weakening of La carboxylate binding. The peak observed at 856 cm^{-1}, attributed to La–O stretching vibration, shifted to 861 cm^{-1} in LaCF indicating interaction between LaC and fluoride. The vibrational band at 562 cm^{-1} was ascribed to La-F stretching mode.

Fig. 4 exhibits the XPS spectra of LaC and LaCF. Peaks attributed to Lanthanum, Sodium, Oxygen and Carbon were observed in the spectrum [31]. The additional peak at 686.38 eV in LaCF indicated that fluoride was effectively adsorbed onto LaC.

3.2. Effect of pH

The change in adsorptive potential of 0.1 g of LaC for 50 mg/L of fluoride contained in 25 mL solution in the pH range 1.0–11.0 was investigated by equilibrating for 3 h. The adsorptive removal of fluoride by LaC was observed to be independent of pH (Fig. 5). The PZC of LaC was observed to be at pH ~ 2. The removal efficiency would have been maximum upto pH 2 if the removal process was electrostatic in nature, due to $F^- \cdots OH_2^+$ interaction and would have decreased above pH 2 due to repulsion between O^- and F^-. The adsorption being independent of pH clearly indicated that some other mechanisms such as ion exchange, hard acid hard base interaction between lanthanum and fluoride resulting in complex formation were also involved in the fluoride adsorption process.

3.3. Kinetic studies

The fluoride adsorption kinetics was studied by equilibrating 25 mL of solution containing 100 mg/L of fluoride, under neutral conditions for different time intervals with 50 mg of LaC (figure S1). Significant removal of fluoride occurred in the first 20 min, followed by slow attainment of equilibrium in 3 h. The initial fast adsorption might be due to vacant adsorption sites in the presence of a high solute concentration gradient followed by a slow rate due to occupancy of the available adsorption sites [31].

The adsorption kinetic data (Table 1) exhibited close correlation of

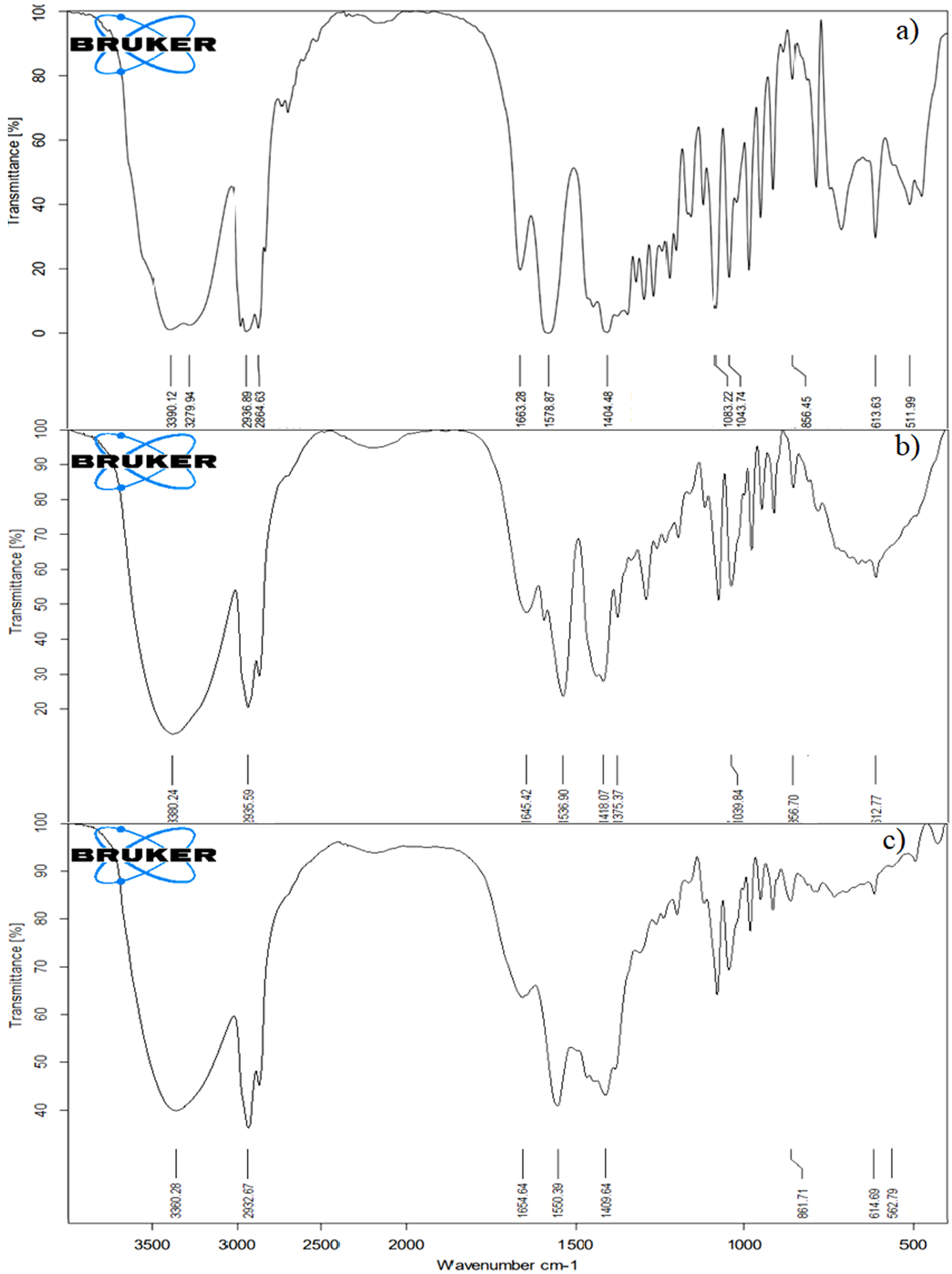

Fig. 3. FTIR study of a) Sodium cholate, b) LaC and c) LaCF.

experimental q_e values with calculated q_e values when fitted to pseudo-second order model indicating a diffusion-controlled process. The intraparticle diffusion model indicated that fluoride adsorption onto LaC involved two steps - rapid fluoride adsorption onto LaC in the first 20 min. by boundary layer or macro-pore diffusion followed by a slow intraparticle or micro-pore diffusion attaining equilibrium (Fig. 6).

3.4. Adsorption isotherm studies

The defluoridation potential of LaC in the concentration range 10–200 mg/L was investigated (Figure S2) and the data were further fitted and modelled by Langmuir and Freundlich isotherm equations (Table 2, Fig. 6).

The equilibrium data best fitted to Langmuir adsorption isotherm [r^2 = 0.99] rather than Freundlich adsorption isotherm model [r^2 = 0.96]

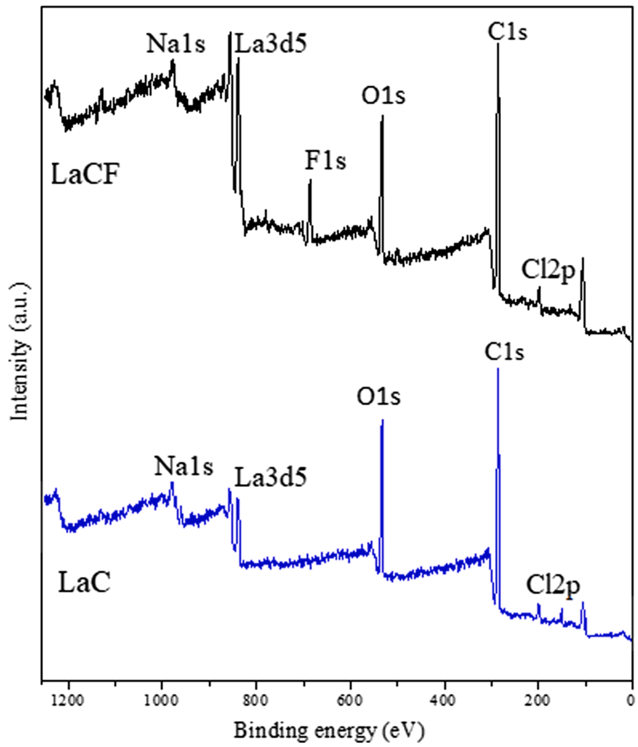

Fig. 4. XPS spectra of LaC and LaCF.

indicating monolayer adsorption. Comparison with literature reported adsorbents for fluoride (Table 3) indicated that the Langmuir monolayer adsorption capacity (q_{max} = 49.26 mg/g) was comparable at neutral pH in a reasonable time interval of 3 h. Though adsorption was higher with some of the reported adsorbents, they either required longer time to achieve equilibrium or required acidic pH conditions while LaC was effective as adsorbent over a wide pH (3–10) range. However, Mg/Fe/La CHLc hydrotalcite [32] and lanthanum-loaded magnetic cationic hydrogel composite [33] proved to be more effective adsorbents.

3.5. Effect of competing anions

In general, the wastewater stream or ground water and various other sources of drinking water contain several other anions besides fluoride. Hence, the effect of other commonly occurring anions on removal of 50 mg/L of fluoride by LaC was studied using 4 g/L LaC. It was observed that fluoride uptake was not affected by 50 mg/L and 100 mg/L of Cl^-, SO_4^{2-}, NO_3^-, CO_3^{2-} and HCO_3^- anions (Fig. 7).

3.6. Application to ground water sample

LaC was applied for de-fluoridation of real ground water sample collected from Fatehpura, Vadodara. Because of the low fluoride content in the groundwater, the samples were spiked with 5 to 100 mg L^{-1} of fluoride. The defluoridation was performed at optimum experimental conditions at neutral pH, 100 mg dose, 3 h contact time. The extent of removal of fluoride by LaC from the spiked samples is given in Table 4. The results indicated that LaC could effectively remove fluoride from ground water samples.

The physicochemical characteristics of the ground water were found to be pH 9.2, total alkalinity 60 mg/L, total hardness 260 mg/L, chemical oxygen demand (COD) 16 mg/L, total dissolved solids (TDS) 3670 mg/L, conductivity 7340 μS/cm, nitrate 620 mg/L, nitrite 42.89 mg/L, sulphate 161.3 mg/L, chloride 1497 mg/L, fluoride 1.49 mg/L.

The quantitative removal of fluoride in the presence of high concentration of ions suggested the possibility of formation of an inner sphere Lanthanum fluoride complex [40].

4. Conclusions

In summary, LaC has been successfully fabricated and its surface nature and properties were investigated by XRD, XPS, TGA, EDAX, SEM and FTIR spectroscopic techniques. Efficient adsorption of fluoride by LaC occurred over a wide pH range with adsorptive potential of 49.26 mg/g. LaC exhibited potential for de-fluoridation of ground water with no interference due to competing sulphate, carbonate, chloride, nitrate and bicarbonate ions.

In addition, the adsorption equilibrium was attained in about 3 h with maximum adsorption occurring within 20 min. The removal process may be through ion exchange and complex formation.

CRediT authorship contribution statement

Mohini Sadhu: Formal analysis, Investigation, Methodology, Writing – original draft. **P. Padmaja Sudhakar:** Conceptualization, Data curation, Funding acquisition, Methodology, Project

Table 1
Kinetic parameters.

q_e(exp): 29.38 mg/g	q_e(calc)	K	r^2
Pseudo First order	3.4158	0.0483	0.8443
Pseudo Second order	29.585	0.0371	1.0

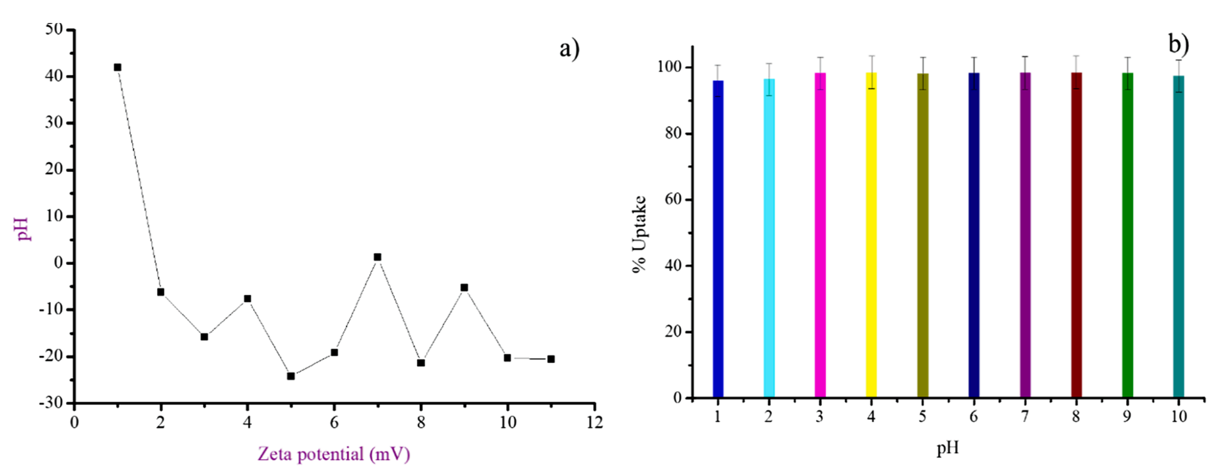

Fig. 5. a) Zeta potential of LaC, b) Effect of pH on defluoridation potential of LaC (dose: 50 mg, time: 3 h, conc.: 50 ppm).

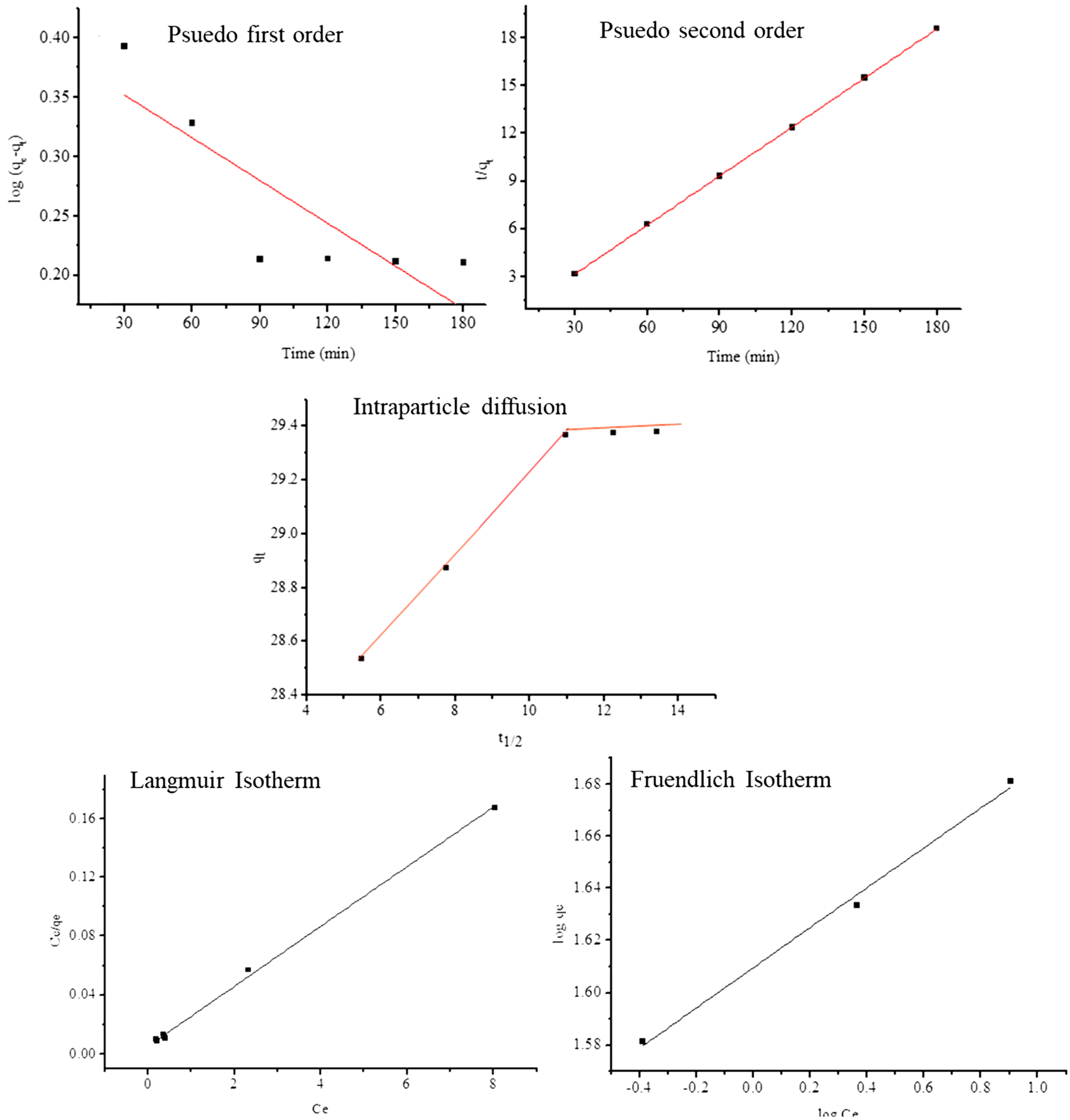

Fig. 6. Kinetic models and isotherm models for fluoride adsorption onto LaC.

Table 2
Isotherm parameters.

	Parameters		
Langmuir	Qm	K_L (L.mmol^{-})	r^2
	49.26	3.9	0.99
Freundlich	N	k_F(Lg^{-1})	r^2
	13.42	40	0.96

administration, Resources, Supervision, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Table 3
Comparison of adsorptive potential of fluoride by LaC.

Adsorbent	pH	q_{max} (mg/g)	Equilibration period	Reference
Mg-Al-La hydrous oxide	7	41.746	40 min	[34]
La-Alginate beads	4	197.2	24 h	[24]
Hybrid La-activated carbon	7	6.2	1 h	[25]
La modified seaweed	7	94.34	240 min	[35]
Magnesium Lanthanum ferri hydrotalcite	6.8	59.34	100 min	[32]
La modified bone waste	2.5–10	8.96	20 min	[26]
Lanthanum hydroxide	7.2	242.2	72 h	[21]
Lanthanum impregnated bauxite	7	18.8	120 min	[36]
Rose stem doped with Lanthanum	6.5	2.26	48 h	[37]
Zirconium–Lanthanum complexed polyvinyl alcohol films	7	11.57	45 min	[38]
lanthanum-loaded magnetic cationic hydrogel composite	7	136.78	10 min	[33]
Lanthanum aluminium perovskite	2	87.75	10 min	[39]
Lanthanum cholate	3–10	49.26	180 min	This study

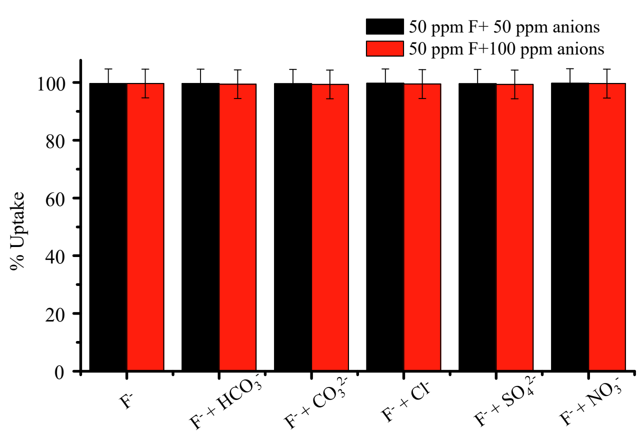

Fig. 7. Influence of competing anions on % uptake of fluoride.

Table 4
Spiking study.

Sample	F^- conc. remaining after adsorption(mg/L)
25 mL ground water	0.008
25 mL ground water + 5 mg/L F	0.012
25 mL ground water + 10 mg/L F	0.022
25 mL ground water + 15 mg/L F	0.025

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.inoche.2023.110429.

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