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Highly Efficient Fluoride Extraction from Simulant Leachate of Spent Potlining via La-Loaded Chelating Resin. An Equilibrium Study

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Abstract

Spent potlining (SPL) hazardous waste is a potentially valuable source of fluoride, which may be recovered through chemical leaching and adsorption with a selective sorbent. For this purpose, the commercially available chelating resin Purolite® S950+ was loaded with lanthanum ions, to create a novel ligand-exchange sorbent. The equilibrium fluoride uptake behaviour of the resin was thoroughly investigated, using NaF solution and a simulant leachate of SPL waste. The resin exhibited a large maximum defluoridation capacity of 187 ± 15 mg g^{-1} *from NaF solution and 126 ± 10 mg g*$^{-1}$ *from the leachate, with solution pH being strongly influential to uptake performance. Isotherm and spectral data indicated that both chemisorption and unexpected physisorption processes were involved in the fluoride extraction and suggested that the major uptake mechanism differed in each matrix. The resin demonstrates significant potential in the recovery of fluoride from aqueous waste-streams.*

Keywords: spent potlining, Purolite S950+, chelating resin, fluoride uptake, lanthanum.

1. Introduction

Spent pot-lining (SPL) is a hazardous, carbonaceous waste product of the primary aluminium industry, formed from the exhausted cathodes of electrolytic cells. Over the lifespan of a cell, contaminants such as cryolite and AlF_3 diffuse through the graphite cathodic lining and ultimately into the refractory material below, causing a degradation in performance [1]. The cell is then decommissioned and the contaminated material excavated. The cathode material is known as “first-cut” SPL and the refractory shell as “second-cut”. The amount of SPL currently being generated worldwide is likely in excess of 1 MT yr^{-1} [2,3].

The composition of first-cut SPL includes ≤ 18% fluorides and ≤ 0.5% cyanides [4], thus presenting a risk of fluorosis and poisoning to both humans and animals [5,6]. SPL is however, a potentially valuable resource, partially because of its high fluoride concentration. Fluorspar (CaF_2) is the root of practically all major fluro-chemicals and was recognised by the European Union in 2014 as one of the 20 most crucial minerals to recycle effectively in the immediate future [7]. Numerous industrial processes have been devised for the treatment of SPL and recycling of minerals, but at present, only the Rio Tinto Alcan low-caustic leaching and lime (LCLL) process regenerates CaF_2. This involves leaching of ground and screened SPL with water, then evaporation to precipitate NaF, before a final treatment with $Ca(OH)_2$ [8]. A large percentage of fluoride-bearing compounds are not solublised by the initial wash [9] and must be leached by a combination of NaOH and H_2SO_4 to allow safe disposal of the solid residue, yet no fluoride recovery is attempted from these waste-streams. We propose an alternative strategy, in which the separate aqueous leachates are combined, then contacted with a sorbent material that selectively extracts the fluoride.

Many techniques exist for the defluoridation of water. Established precipitation methods however, result in large volumes of low-value slurry, from which fluoride recovery is difficult [10]. Adsorption and ion-exchange techniques are a promising alternative, as the fluoride may be selectively removed under mild conditions, with no waste generated. This has led to numerous fluoride uptake studies, using sorbents such as alumina [11], activated carbon [12], chitosan [13], synthesised microporous polymers [14] and layered double hydroxide clays [15]. Some sorbents may be repeatedly regenerated and reused, with hydroxide treatment being the most common strategy [14,16]. Commercial anion-exchange resins cannot produce selective uptake, since fluoride is the least selective of all common anions towards such materials [17]. This may be overcome via a cation-exchange or chelating resin, pre-loaded with metal ions, which have a high affinity for fluoride, thereby allowing uptake via the ligand-exchange processes shown in Eq. (1) [18,19].

$$[L\text{-}M(H_2O)_{n-m}(OH)_m]^{(n-2)-} + qF^- \rightleftharpoons [L\text{-}M(H_2O)_{n-m}(OH)_{m-q}F_q]^{(m-2)-} + qOH^- \qquad (1)$$

where L = resin functional group ligand, M = coordinated metal centre and q = 1 or 2. Al itself has been a popular metal for this purpose, given its light molecular weight, abundance and high stability constants associated with AlF_n complexes [20]. The highest reported uptake capacity for Al-loaded resins is ~12 mg fluoride per g resin [21].

Rare earths have been similarly investigated, as they are hard metals, therefore strongly binding fluoride ligands [22]. A barrier to their industrial use for this purpose is their perceived scarcity and high cost. However, this is applicable mainly to Pr and Nd, which are desirable for production of lightweight magnets, used in hybrid car engines [23]. La and Ce in particular, have more limited industrial uses and this is reflected in the market value for their oxides, which remained in the region of £1400-

1600 T^{-1} throughout 2017. In contrast, Nd and Pr oxide prices were > £30000 T^{-1} [24].

The most common resin functional groups for La-loading have been either sulfonic or aminophosphonic acids [19,25,26], with highest reported uptake capacities being higher than for the Al-loaded equivalents; in the region of 25-30 mg g^{-1} [27]. Most literature studies on aqueous fluoride extraction focus on uptake from analytical grade NaF solutions [28,29], sometimes with controlled amounts of competing anions added, or mildly contaminated water from aquifers [26, 29]. However, data for concentrated waste-streams, containing multivalent cations, which may complex fluoride and displace resin-bound metals is lacking. Indeed, this factor compelled us to choose a more expensive chelating resin for the intended purpose, as in solutions of high ionic-strength, the loaded species of a conventional strong acid cation exchanger would be displaced by other cations in the aqueous waste, according to concentration gradients and order of selectivity, hence ruining the fluoride affinity of the resin. The only studies on actual SPL industrial leachate used calcite as a sorbent and focussed on modelling the kinetics of the uptake process [30,31]. To the best of our knowledge, no work exists on the selective removal of fluoride from leachate of SPL via metal-loaded chelating resin. Additionally, uptake behaviour has only been studied over initial fluoride concentrations < 100 mg L^{-1} (Supporting Information, Table S1), whereas the leaching of SPL produces aqueous waste of fluoride concentration > 2 orders of magnitude higher [9,32]. Therefore, from a water-conservation perspective, it is desirable to investigate such uptake conditions, even though the mechanisms of uptake may be complicated. The same applies for simpler NaF-based waste-streams.

Purolite® S950+ is a macroporous, weak acid, chelating resin, consisting of a styrene/divinylbenzene backbone, with aminophosphonic acid functional groups. The Al-loaded form has previously been investigated for fluoride-removal capabilities [21]. A similar Al-loaded resin has been commercialised for industrial use [33], although only as a final water-polishing step, rather than as part of a fluoride-recovery loop. Rare earth-loading has not yet been trialled. We envisage a treatment system (Fig. 1) for SPL leachate, using La-modified S950+ columns, with NaOH treatment to elute the fluoride as NaF, then precipitation of CaF_2 with $Ca(OH)_2$ [34]. However, the thermodynamics and kinetics of uptake in such an unusual sample matrix as spent potlining leachate must first be understood. Thus we report here an investigation into the isotherm behaviour of fluoride uptake on to La-loaded Purolite® S950+, with detailed comparison between PLS and NaF solution matrices.

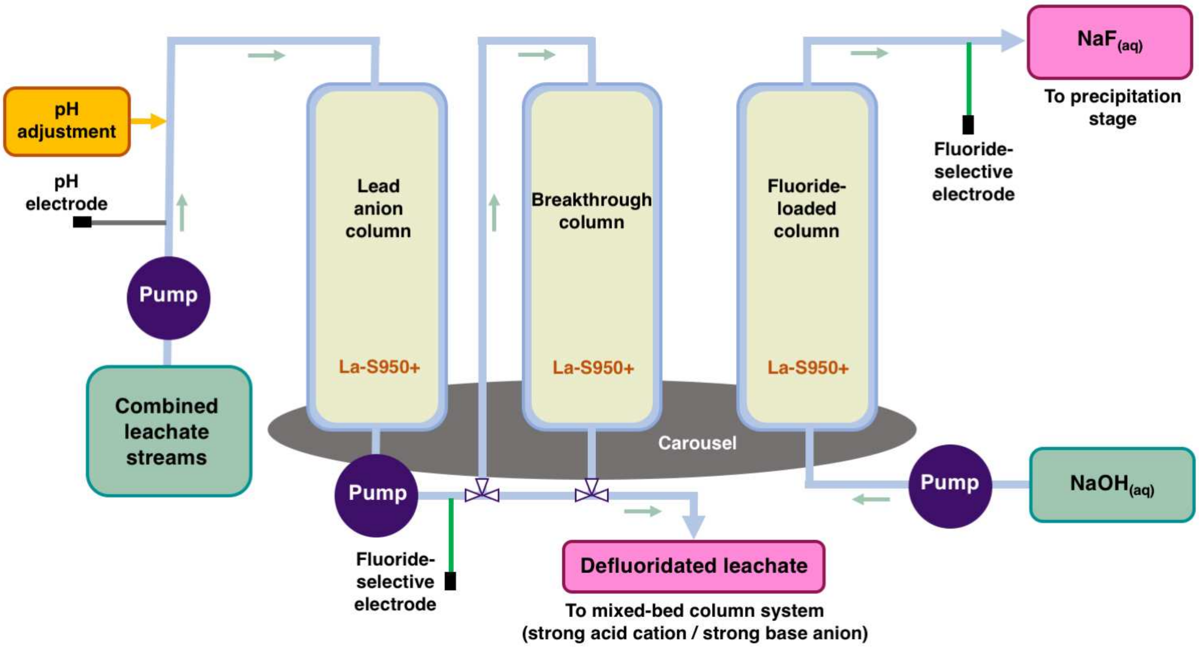

Fig. 1. Proposed ion-exchange treatment system for SPL leachate.

2. Experimental

2.1. Reagents and stock solutions

A simulant pregnant leach solution (PLS) of first-cut SPL was prepared, with concentrations calculated from characterisation work of Holywell & Bréault [4], Mahadevan & Ramachandran [35] and Pong *et al.* [36]. The major components of this liquor are given in Table 1.

Table 1. Composition of SPL simulant leachate pregnant leach solution (PLS).

Component	**Concentration (mg L^{-1})**
Fluoride (F^-)	1500
Carbonate (CO_3^{2-})	750
Chloride (Cl^-)	50
Cyanate (CNO^-)	50
Ferrocyanide ($[Fe(CN)_6]^{4-}$)	50
Sulfate (SO_4^{2-})	2200
Aluminium (Al^{3+})	1200
Calcium (Ca^{2+})	200

NaF, $NaHCO_3$, NaCl, NaCNO, $K_4[Fe(CN)_6]$, $(NH_4)_2SO_4$, $Al_2(SO_4)_3$ and $Ca(OH)_2$ (analytical reagent grade) were purchased from commercial suppliers and used without further purification. Sodium and sulfate salts were used where possible, to reflect the leaching agents used in the LCLL process [8]. Reagents were dissolved in deionised water in a polypropylene beaker. The ionic strength of the undiluted leachate was 24.8 mmol L^{-1}, compared to 6.23 mmol L^{-1} for a NaF solution of equivalent fluoride concentration. The pH was 5.5. Aqueous speciation was carried out using the Aqion software package v6.4.7 [37]. Full methodology is shown in the Supporting Information, p2.

2.2. Pre-conditioning and metal-loading of the resin

Purolite® S950+ resin was kindly donated by the manufacturer in Na form. Specifications are given in Supporting Information, Table S3. Conversion to H form [38], was achieved by contacting 25 g resin (wet mass) with 1 L of 1 M HCl in a Nalgene bottle, which was sealed and placed on an orbital shaker for ≥ 8 h at 100 rpm. The resin was then washed with 5 x 200 bed volumes of deionised water (bed volume = minimum volume of water required to fully wet the mass of resin).

The H-S950+ resin was loaded with La by contacting 25 g (wet mass) with 1 L of 10000 mg L^{-1} La^{3+} solution, made by dissolving $LaCl_3.7H_2O$ in deionised water. These were agitated and washed, as before, then dried in a 50 ^{O}C air-flow oven for a minimum of 24 h. This resulted in the La-loaded Purolite® S950+ resin, hereafter referred to as La-S950+. La uptake by H-950+ was determined by analysis of 2000-15000 mg L^{-1} La^{3+} solutions, before and after contact with the resin with a Thermo Scientific iCAP 6000 ICP-OES. Samples were analysed in duplicate and error determined from 2 x standard deviation. Results were compared with similar experimentation, using Ca^{2+} solutions, to gauge the efficiency of La-loading, this being the manufacturer's recommended procedure for determination of S950+ capacity [39].

2.3. Batch fluoride extraction from various media

All experiments were carried out at ambient temperature. In a typical procedure, ~100 mg of La-S950+ (dry mass) was contacted with 25 mL solution of known fluoride concentration in a 50 mL polypropylene screw-top tube (NaF or PLS solutions were diluted appropriately to achieve the required fluoride concentrations). This was sealed and placed on an orbital shaker at 100 rpm for 24 h. In controlled pH experiments, the liquor pH was maintained by being adjusted at 10 minute intervals with 0.01-1 M solutions of HCl and NaOH until equilibrium was reached. In all cases, equilibrium pH was within 0.01 unit of initial pH. The fluoride concentration of the solution, before and after resin contact, was determined using a Cole-Palmer fluoride ion-selective electrode. (Supporting Information, p 3). The equilibrium fluoride uptake capacity of the resin in mg g^{-1} (q_e) was determined using Eq (2):

$$q_e = (C_i - C_e) \, x \, V/W \qquad (2)$$

where C_i is the initial fluoride concentration of the solution in mg L^{-1}, C_e is the fluoride concentration of the solution at equilibrium in mg L^{-1}, V is the volume of solution contacted in L and W is the dry mass of resin used in g.

2.4. Determination of uptake behaviour by fitting to isotherm

The uptake behaviour of the system was expected to be dominated by the ligand exchange of aqua and hydroxyl groups for fluorides, coordinated to a finite number of degenerate La centres. We thus fitted batch uptake data to the two-parameter Langmuir isotherm model, represented by Eq. (3):

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{3}$$

where K_L is a Langmuir isotherm constant and q_{max} is the theoretical saturation capacity of the resin in mg g^{-1}.

It was however, thought likely that fluoride ions might be bound via multiple interactions with the functionality of the resin, including potentially the protonated amine group at, lower pH, and multiple H-bonding interactions [40]. Hence we also investigated fitting to the empirical Freundlich model (Eq. (4)), which accounts for surface heterogeneity.

$$q_e = K_F \, C_e^{1/n} \tag{4}$$

where K_F and n are Freundlich isotherm constants. All other terms as per Eqs. (2) and (3).

Because of the potential for a non-degenerate energy of adsorption, we also fitted data to the Dubinin-Radushkevich (D-R) isotherm (Eq. (5)), which allows calculation of the desorption energy of uptake, based on a Gaussian distribution [41].

$$q_e = (q_{max}) \, exp\left(-B_D \, \left[RTln\left(1 + \frac{1}{C_e}\right)\right]^2\right) \tag{5}$$

where B_D is a D-R isotherm constant in mol^2 J^2, R is the gas constant (8.314 J K^{-1} mol^{-1}) and T is the temperature in K. The bracket $[RTln(1 + 1/C_e)]$ is often described by a single term ε (the Polyani potential) in J mol^{-1}. All other terms as per Eq. (2).

We finally attempted fitting to the Temkin isotherm (Eq. (6)), which operates on the assumption that the energy of sorption decreases linearly as a function of surface coverage, taking into account possible sorbate-sorbate interactions [41].

$$q_e = B \ln A_T + B \ln C_e \tag{6}$$

where A_T is the equilibrium binding constant and B is a heat of sorption constant in J mol^{-1}. All other terms as per Eq. (2).

Loading isotherms were determined by the previously described procedure for batch extraction, with solutions of NaF or PLS over a C_i range of 1.5-1500 mg L^{-1}. Results were averaged from 3 replicate samples. Error in C_e values were calculated from 2 x standard deviation and propagated accordingly. Isotherm fitting was achieved with the SOLVER Microsoft Excel programme, following the method of Billo [42].

2.5. Co-extraction of other anions and cations

In the case of the PLS, post-resin-contact sample solutions were analysed in comparison to the parent solution, to determine uptake of competing anions and also cations in the system. Cl^-, NO_3^- and SO_4^{2-} were quantified using a Thermo Fisher ICS-900 ion chromatography system (Supporting Information, p6); Al, Ca and Fe via ICP-OES. Leaching of La^{3+} during solution contact was also checked in these analyses.

2.6. Solid-state analysis of resin

Samples of resin were first washed of residual NaF or PLS with 10 x 200 bed volumes of deionised water, then ground to a fine slurry, using a mortar and pestle, then dried in an air-flow oven at 50°C for a minimum of 24 h. XRD analysis was performed using a Bruker D2 Phaser X-ray diffractometer. XRD data was matched using the International Center for Diffraction Data (ICDD) PDF-4+ database [43]. X-ray Photoelectron Spectroscopy (XPS) was carried out using a Kratos Supra instrument. Full operating conditions are detailed in the Supporting Information, p 3.

3. Results and discussion

3.1. Metal-loading of the resin

ICP-OES results determined the Ca^{2+} capacity of the H form of the resin to be 71.3 ± 2.5 mg g^{-1} (1.78 ± 0.06 mmol g^{-1}), in close agreement with manufacturer specifications [39]. Similarly, the La^{3+} capacity was found to be 256 ± 2 mg g^{-1} (1.84 ± 0.01 mmol g^{-1}). This compares favourably with literature data for aminophosphonic acid resins [25] and for specifically-designed polyacrylamidoxime [44] and amide [45] resins for lanthanide and actinide extraction. A contact solution of 10000 mg L^{-1} La^{3+} resulted in optimum loading.

Spectroscopic evidence has suggested that 6-and higher-coordinate metals may chelate to the resin via interactions with both O and N atoms [46]. In this instance, the N 1s XPS spectra (Supporting Information, p 4-6) demonstrated that there was no interaction between the amines and coordinated metals. Therefore, the La-loading mechanism is likely as shown in Fig. 2.

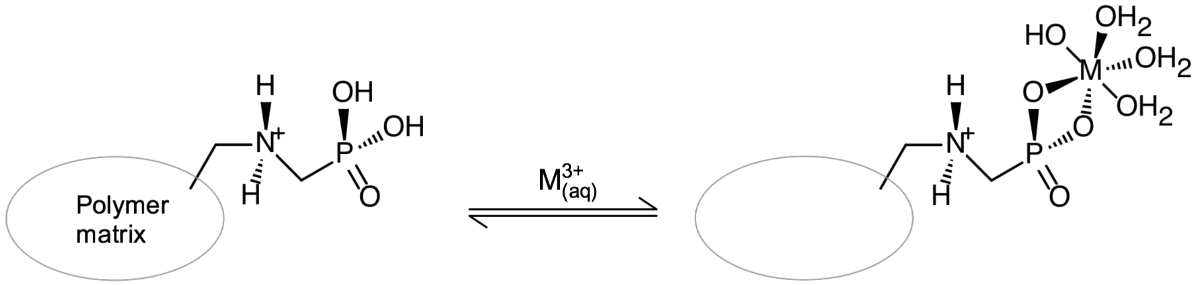

Fig. 2. Loading mechanism for La-S950+.

3.2. Effect of pH on fluoride uptake

The fluoride uptake of La-S950+ over a pH range of 1-10 is shown in Fig. 3.

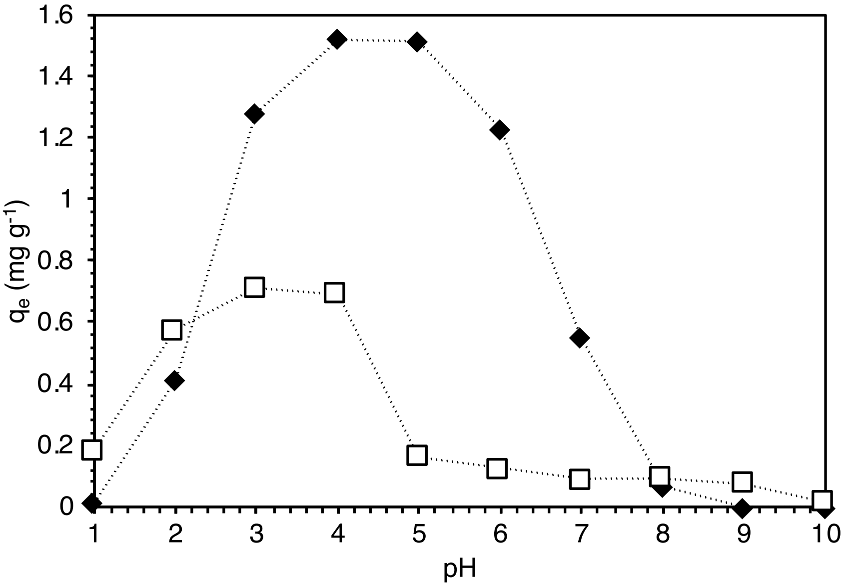

Fig. 3. Fluoride uptake of La-S950+ over a pH range of 1-10. F^- C_i = 15 mg L^{-1}. Error is too small to be graphically represented. Data points represent final equilibrium solution pH. ◆ = PLS. □ = NaF solution.

The solution pH for both sample matrices was significant to the performance of the resin. At low pH, fluoride exists mainly as the stable ion-pair F^-/H_3O^+, making removal from aqueous solution unfavourable [47]. The relatively high uptake from NaF solution at pH 2 was therefore surprising, as the ratio here of HF:F^- was calculated as 1.4:1 [37]. This possibly shows the effect of increased electrostatic attraction, with protonation of the resin surface [48] At higher pH, the hydroxide ion is a significant competitor for fluoride-binding sites [15,21]. However, at pH 8, where uptake was negligible for both matrices, the fluoride concentration was still 2 orders of magnitude higher than hydroxide concentration (Supporting Information, Table S2). The pK_a of La^{3+} aqua complexes is 8.63 ± 0.05 in 2 M $NaClO_4$ [49]. Therefore $La(OH)_3$ precipitation at a pH > 8.5 may be predicted. However, fluoride exchange clearly became unfavourable at a lower pH than this, indicating modification of the La^{3+} pK_a by the hydrophobic resin surface [50]. The literature shows variance in optimum pH for fluoride uptake on to La-loaded resins, from 2.5 to 7 [21,27], indicating the specific environment created by the resin support may indeed be influential. There is also evidence that pK_a values for metal complexes bound to chelating ligands are lower than for monodentate complexes [51]. Notably, over the pH range for favourable adsorption, a large proportion of fluoride in the PLS system exists as AlF^{2+}, AlF_2^+ and AlF_3 (Supporting Information, Table S2), consistent with the literature [48]. This however appeared to enhance, rather than suppress the uptake, which suggested an alternative uptake mechanism was occurring. This will be discussed in due course.

3.3. Practical Operating conditions

Following contact with the resin, the pH of NaF and PLS solutions were observed to quickly decrease to ~ 4 and prior adjustment of pH to this value had no influence on performance. Therefore, rather than lengthen the resin-washing procedure, which would not be practical industrially, subsequent experiments were run at the natural pH of the sample solutions. It was found that the alteration of pH during contact was independent of fluoride uptake, which was expected, since the ligand-exchange mechanism actually releases hydroxide [28,29]. XPS data (Supporting Information, p 5-6) indicated that partial deprotonation of the quarternised amines dictated the pH behaviour. The amine functionality of aminophosphonic acid resins is known to act as an anion-exchange site [46]. However, uptake experiments (Supporting Information, Fig. S3)) confirmed that uptake of common anions by H-S950+ was negligible (< 1 mg g^{-1} in most cases). Therefore the amine, and indeed the presence of any uncoordinated phosphonic acid groups were insignificant to the performance of La-S950+.

In accordance with the literature [13,26], the uptake efficiency of the resin decreased with increasing resin:solution ratio, although the % extraction increased and easily reached ~100 % at a ratio of 1 g to 25 mL (Supporting Information, Fig. S4). A ratio of ~100 mg La-S950+ to 25 mL solution was used to ensure high resin efficiency and reasonable accuracy of electrode measurements.

3.4. Isotherm behaviour

The fitting of data for fluoride uptake by La-S950+ from NaF solution and from the PLS to the various isotherm models is shown in Figs. 4-5. Fig. 4 models the data over a low C_i range of 1.5-50 mg L^{-1}, to allow comparison with the literature. Fig. 5 models the data over a higher C_i range, to more closely simulate industrial conditions. Isotherm parameters were extracted and presented in Tables 2 and 3. The equilibrium parameter R_L was calculated from Langmuir isotherms, using Eq. (6):

$$R_L = \frac{1}{1+(1+K_L C_i)} \tag{6}$$

The mean free energy of desorption (E_{des}), was calculated from the D-R isotherms using Eq. (7):

$$E_{des} = \frac{1}{\sqrt{2B_D}} \tag{7}$$

Temkin and D-R fitting were poor at higher C_i and the associated parameters were not considered valid and are not presented.

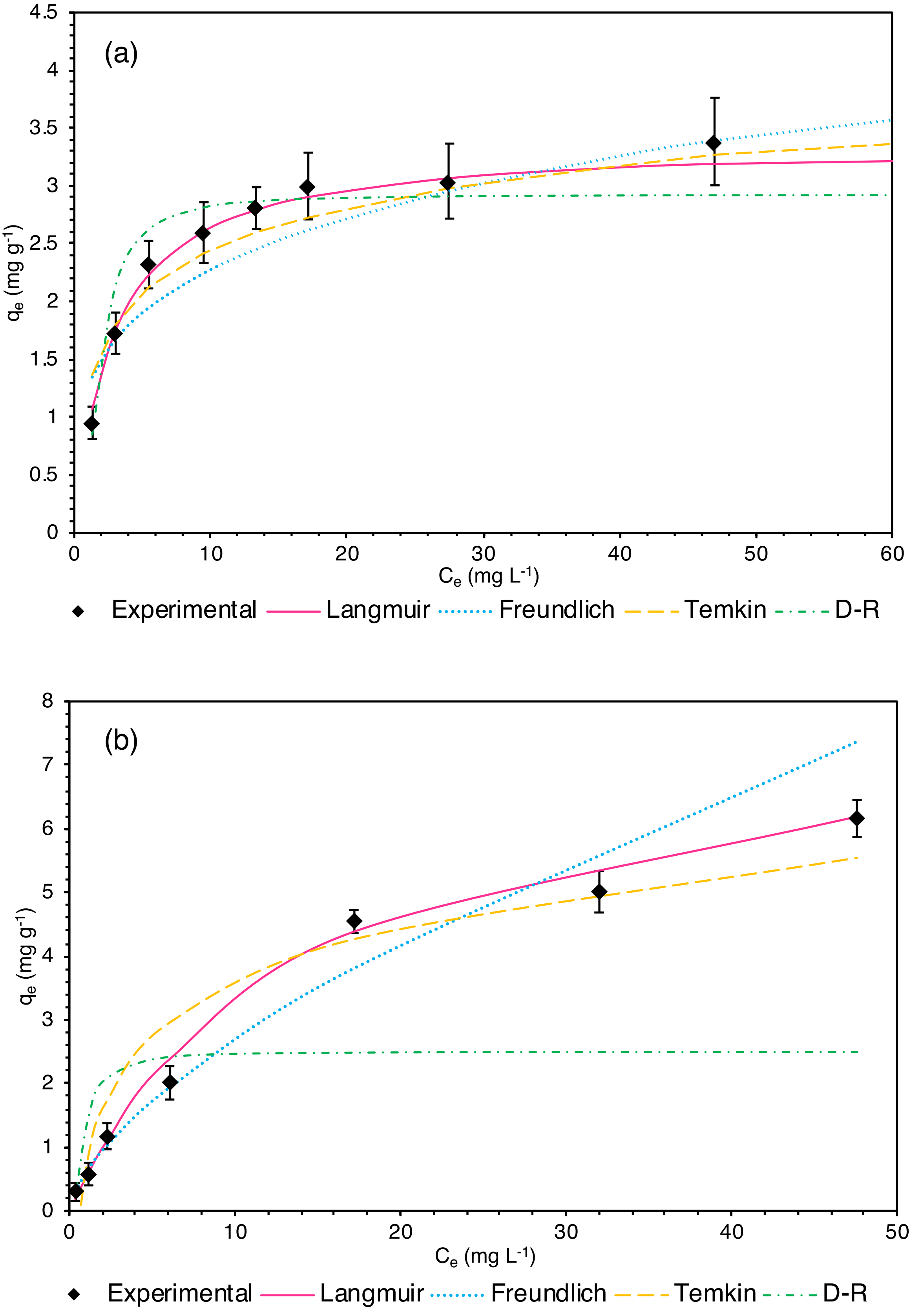

Fig. 4. Fluoride uptake of La S950+ fitted to isotherm models from (a) NaF solution and (b) PLS. F^- C_i range = 1.5-50 mg L^{-1}.

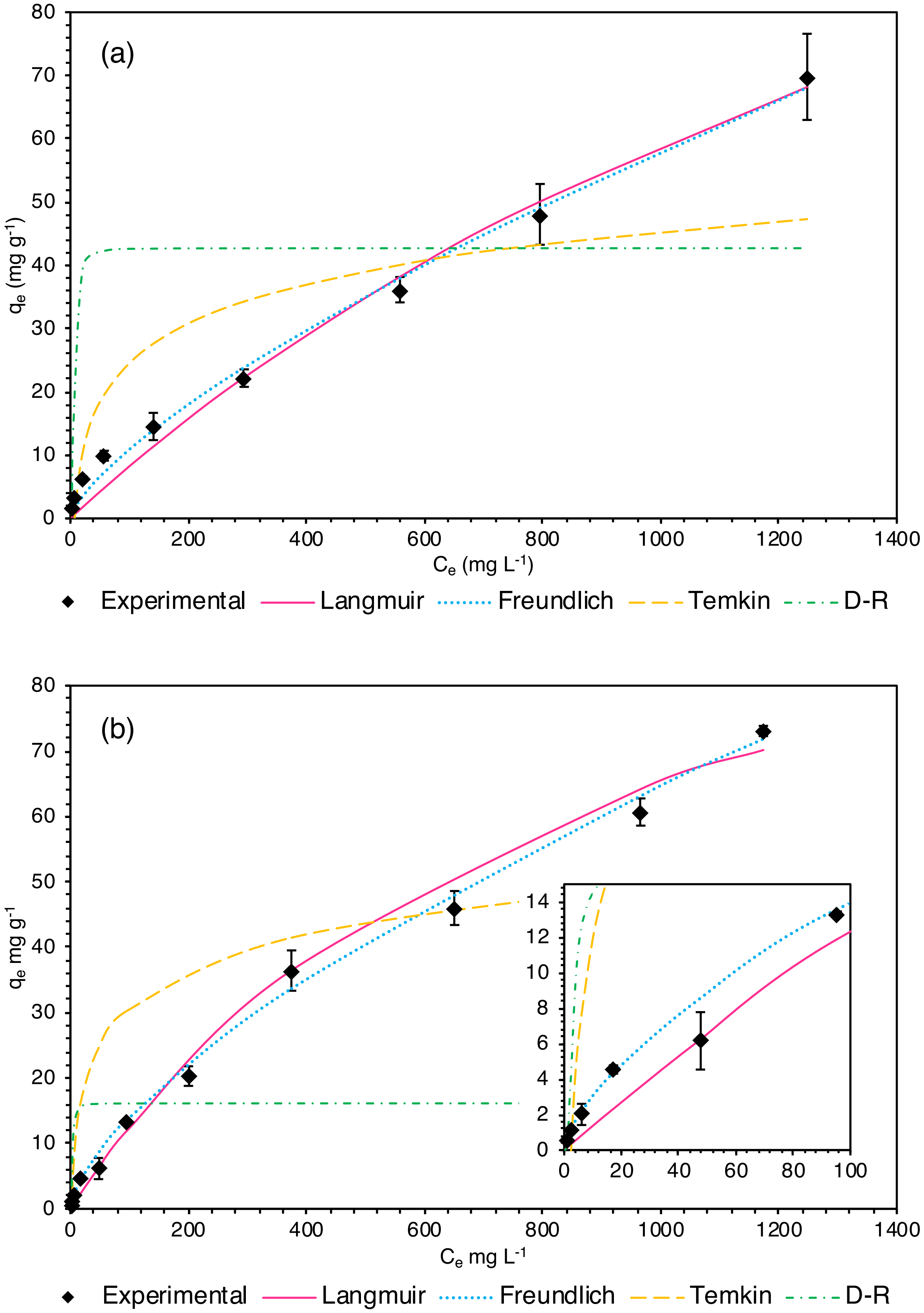

Fig. 5. Fluoride uptake of La S950+ fitted to isotherm models from (a) NaF solution and (b) PLS. F^- C_i range = 10-1500 mg L^{-1}. Enlargement shows 1st 6 data points for clarity.

Table 2. Isotherm fitting parameters calculated using all models over C_i range of 1.5-50 mg L^{-1}.

Model	**Parameter**	**NaF**	**PLS**
Langmuir	K_L	0.354 ± 0.033	0.0691 ± 0.0153
	q_{max} (mg g^{-1})	3.38 ± 0.06	8.08 ± 0.74
	R_L (when C_i = 50 mg L^{-1})	0.0507 ± 0.0047	0.183 ± 0.030
	R^2	0.999	0.980
Freundlich	K_f (mg g^{-1})	1.26 ± 0.17	0.848 ± 0.073
	n	3.88 ± 0.72	1.90 ± 0.12
	R^2	0.786	0.985
Temkin	A_T	5.05 ± 0.7	1.74 ± 0.28
	B (J mol^{-1})	0.635 ± 0.054	1.26 ± 0.20
	R^2	0.953	0.908
D-R	B_D	6.01 ± 0.66 x 10^{-7}	1.49 ± 0.49 x 10^{-7}
	q_{max} (mg g^{-1})	2.82 ± 0.30	1.43 ± 0.84
	E_{des} (kJ mol^{-1})	48.0 ± 5.3	96.4 ± 31.6
	R^2	0.933	0.756

Table 3. Isotherm fitting parameters calculated using Langmuir and Freundlich models over C_i range of 10-1500 mg L^{-1}.

Model	**Parameter (with units where applicable)**	**NaF**	**PLS**
Langmuir	K_L	4.59 ± 1.67 x 10^{-4}	1.08 ± 0.14 x 10^{-3}
	q_{max} (mg g^{-1})	187 ± 15	126 ± 10
	R_L (when C_i = 1500 mg L^{-1})	0.372 ± 0.135	0.276 ± 0.033
	R^2	0.982	0.976
Freundlich	K_f (mg g^{-1})	0.384 ± 0.042	0.661 ± 0.042
	n	1.38 ± 0.05	1.51 ± 0.03
	R^2	0.993	0.997

The uptake of fluoride from NaF solution was very well described by the Langmuir equation up to a C_i of ~ 50 mg L^{-1}, but at higher C_i, the Freundlich model provided better description. Uptake from the PLS also fit the Freundlich model well over higher C_i, but at low C_i, the fit for both models was similar. The other 2 monolayer-based models generally provided inaccurate descriptions of behaviour in comparison, but were fit much better by NaF than PLS data. The E_{des} values of > 16 kJ mol^{-1}, although imprecise, indicate a chemisorption uptake process dominates at low C_i [50], but given the poor agreement with the D-R model, at higher C_i this likely changes to a physisorption-dominated process.

The data suggest that at low C_i, fluoride uptake from NaF solution is controlled by monolayer formation, via the expected aqua/fluoride ligand-exchange process, but at higher C_i, an unexpected multilayer physisorption interaction takes over, causing the greatly enhanced q_{max} values reported. Uptake from the PLS also seems to involve multilayer adsorption and moreover, the mechanism appears to dominate the uptake behaviour at lower C_i. In support of this, the Langmuir-derived R_L values (a measure of favourability of adsorption), did not significantly change, depending on C_i, for the PLS matrix, but was much greater at low C_i than at high C_i for the NaF matrix.

For both matrices, the Freundlich n values of > 1 indicated a degree of heterogeneity of binding sites on the resin surface [52]. This again suggested more than 1 uptake process was operating and also that uptake was more favourable at higher C_i [53].

Langmuir-calculated q_{max} values in this instance were not as great as the largest reported in the literature for metal-loaded resins over similar C_i ranges (Supporting Information, Table S1). However, over the higher C_i range, not previously investigated, q_{max} values were > 4 times greater than has yet been reported. The data overall suggested that such resins could operate successfully in more concentrated waste-streams than have previously been considered.

3.5. Co-uptake of other ions and leaching of La from PLS

Ion chromatography and ICP-OES results showing uptake of the major coexisting anions and cations in the PLS are presented in Table 4.

Table 4. Uptake of co-ions by La-S950+ from PLS under standard experimental conditions.

Species	**Undiluted PLS**		**1/10 diluted PLS**	
	q_e (mg g^{-1})	**q_e (mmol g^{-1})**	**q_e (mg g^{-1})**	**q_e (mmol g^{-1})**
F^-	73.1 ± 0.8	3.85 ± 0.02	13.3 ± 0.2	0.700 ± 0.001
Cl^-	< 0.1	<0.01	<0.1	<0.01
NO_3^-	43.9 ± 1.6	0.707 ± 0.026	6.88 ± 0.28	0.111 ± 0.005
SO_4^{2-}	5.88 ± 0.04	0.0612 ± 0.0004	0.430 ± 0.032	$4.48 \pm 0.17 \times 10^{-3}$
Al^{3+}	17.4 ± 0.2	0.645 ± 0.006	7.56 ± 0.08	0.280 ± 0.003
Ca^{2+}	0.429 ± 0.042	0.0107 ± 0.0010	0.0979 ± 0.0101	$2.44 \pm 0.23 \times 10^{-3}$
Fe^{2+} (as $[Fe(CN)_6]^{4-}$)	1.47 ± 0.08	0.0263 ± 0.002	0.224 ± 0.082	$4.01 \pm 1.45 \times 10^{-3}$
La^{3+}	-0.959 ± 0.040	$-6.90 \pm 0.02 \times 10^{-3}$	-0.199 ± 0.008	$-1.44 \pm 0.06 \times 10^{-3}$

The only cation taken up in appreciable amounts was Al^{3+}. This suggested that a possible uptake mechanism was chelation of Al^{3+} complexes with coordinated fluoride ligands to vacant aminophosphonic acid sites. However, this is unlikely, since the metal-loading data suggested the resin was fully-saturated with La. Another considered possibility was precipitation of aluminium hydroxyfluorides (AHFs) on to the resin surface. AHFs have the general formula $AlF_n(OH)_{3-n}.xH_2O$ and precipitate over a pH range (4.5-5.5) similar to our observed optimum for fluoride removal (Fig. 3) [54]. They are a possible precursor to AlF_3 [55], which is consumed in large quantities via the aluminium smelting electrolysis process. The small amount of La^{3+} leaching was thought to be due to displacement by Al^{3+} or Ca^{2+} [56]. The effect is not sufficiently severe that the performance of the resin would be notably affected over several cycles, since it is well-known that fluoride can be eluted via hydroxide treatment without significant metal leaching [25].

It was discovered that co-anions NO_3^-, SO_4^{2-} and $[Fe(CN)_6]^{4-}$ were bound very weakly, probably through electrostatic interactions with the positively-charged resin surface [48], and were easily eluted with deionised water. XPS spectra of well-washed resin, post-PLS-contact, found no evidence of these species (Supporting Information, Figs. S1-S2).

3.6. XRD analysis

XRD spectra of La-S950+ samples are shown in Fig. 6. Whilst most samples exhibited no crystalline character, the post-NaF contact sample, where C_i = 1500 mg g^{-1}, clearly produced peaks corresponding to the LaF_3, lattice [43], indicating precipitation of this species. This has been previously reported for mineral-based sorbents [53], but not in the case of metal-loaded ion-exchange resins. Crystalline NaF was also unexpectedly present, suggesting that, in addition to the surface La^{3+}/F^- interaction, fluoride was also taken up by the diffusion and precipitation of Na^+ and F^- into the pores of the resin beads. No similar examples were found in the literature, but the uptake from NaF solution definitively cannot be explained by LaF_3 precipitation alone, since the F:La molar ratio on the resin following uptake experiments at high C_i was << 3:1. It must be assumed that the hydrophobic pore environment reduces NaF solubility. This partially explains the observed change to multi-layer adsorption when C_i > 50 mg L^{-1}. The lack of crystalline NaF in the post-PLS-contact sample supported the hypothesis that the dominant mechanism of fluoride uptake in this matrix did not involve free aqueous fluoride. Crystalline AHFs [54] were also not observed.

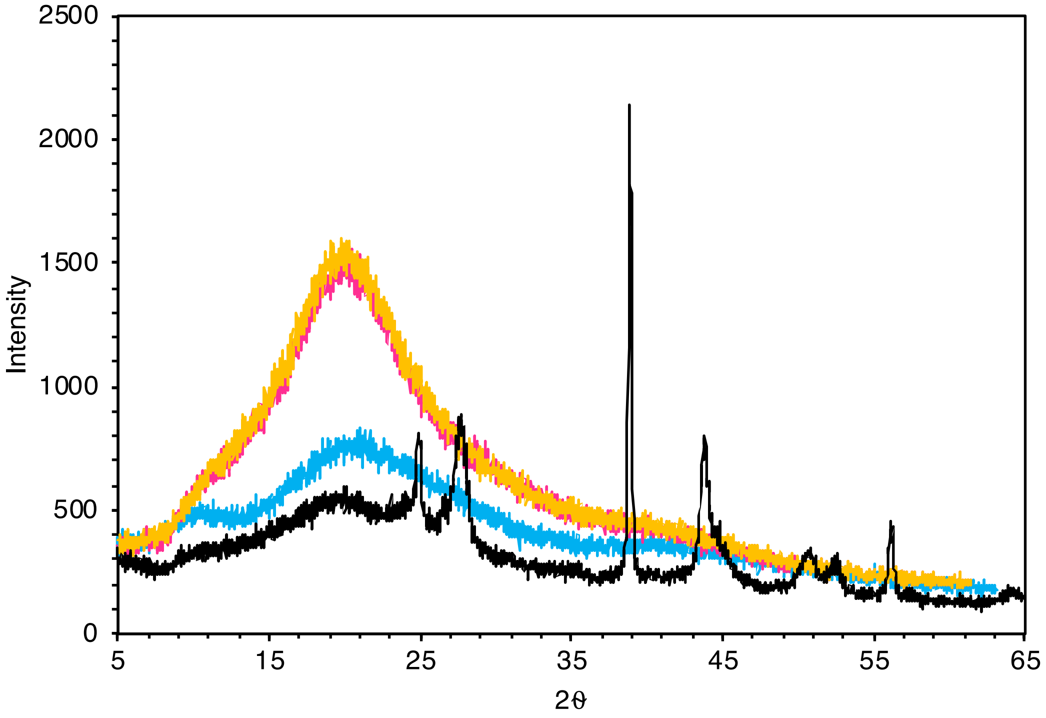

Fig. 6. XRD spectra of La-S950+ resin at various process stages. Post-contact samples were derived from 0.1 g resin, contacted with 25 ml NaF solution or PLS. | = pre-fluoride contact. | = post-PLS contact, C_i = 1500 mg L^{-1}. | = post-NaF contact, C_i = 50 mg L^{-1}. | = post-NaF contact, C_i = 1500 mg L^{-1}. ◆ = NaF crystal lattice. ☐ = LaF_3 crystal lattice.

3.7. XPS analysis

The Al 2p spectrum of PLS-treated resin (Fig. 7a) showed a single peak, of binding energy consistent with spectra reported by Stosiek *et al.* [57] for amorphous $AlF(OH)_2$. There was no evidence of chelated Al. This was supported by the O 1s spectra (Figs. 7b-d), which revealed 2 different O environments for untreated and NaF-treated La-S950+, corresponding to P=O and P-O-H/La. For PLS-treated La-S950+, the spectrum was instead dominated by a single O environment, indicating an O-rich surface precipitate and again consistent with $AlF(OH)_2$ formation [57], suggesting that this is the dominant precipitate species. Although a crystalline precipitate might be predicted [55, 58], it is known that gelatinous hydrated $Al(OH)_3$ will precipitate favourably, over crystalline species at lower solution pH [59].

The La 3d spectra (Figs. 8a-c) showed the expected 2 separated spin orbit components, each with multiplet splitting. The spectrum for the sample contacted with 1500 mg L^{-1} fluoride as NaF demonstrated a new La environment at a binding energy of 837.4 eV, corresponding to LaF_3 [60] and in agreement with XRD data. However, the PLS-treated sample exhibited 2 unique La environments (831.9 and 836.2 eV), which could not be matched in the literature and likely represent chelated La centres with 1 and 2 fluoride ligands. This suggested that $AlF(OH)_2$ precipitation was not the only uptake mechanism from the PLS and that direct aqua/fluoride ligand exchange did still occur. This is supported by the relative molar ratios of Al^{3+} and F^- uptake (Table 4). Full curve-fitting and characterisation is found in the Supporting Information, Table S5.

3.8. Proposed Uptake mechanism

Taking into account all uptake and spectral data, the likely fluoride removal mechanisms for the 2 matrices are presented in Fig. 9. For the NaF solution matrix at low C_i, La-S950+ uptake appears to operate via the ligand-exchange process widely reported in the literature [26-29], hence the good agreement with the classical Langmuir model. For the same matrix at high C_i, a combination of LaF_3 precipitation and NaF physisorption appears to be prevalent, resulting in better agreement with the Freundlich isotherm. This may be of interest for recovery of fluoride from concentrated aqueous waste-streams without high levels of complexing and hard acid cations. For the PLS matrix, uptake appears to proceed via a combination of ligand-exchange and $AlF(OH)_2$ precipitation, with the latter becoming more prevalent at higher C_i and hence better suiting description by the Freundlich model. Such behaviour would certainly complicate potential fluoride recovery. However, recovered AlF_3 precursor chemicals would be more economically desirable, from an industry point of view, than CaF_2 as there is a direct pathway to recycling back into the Al electrolysis process.

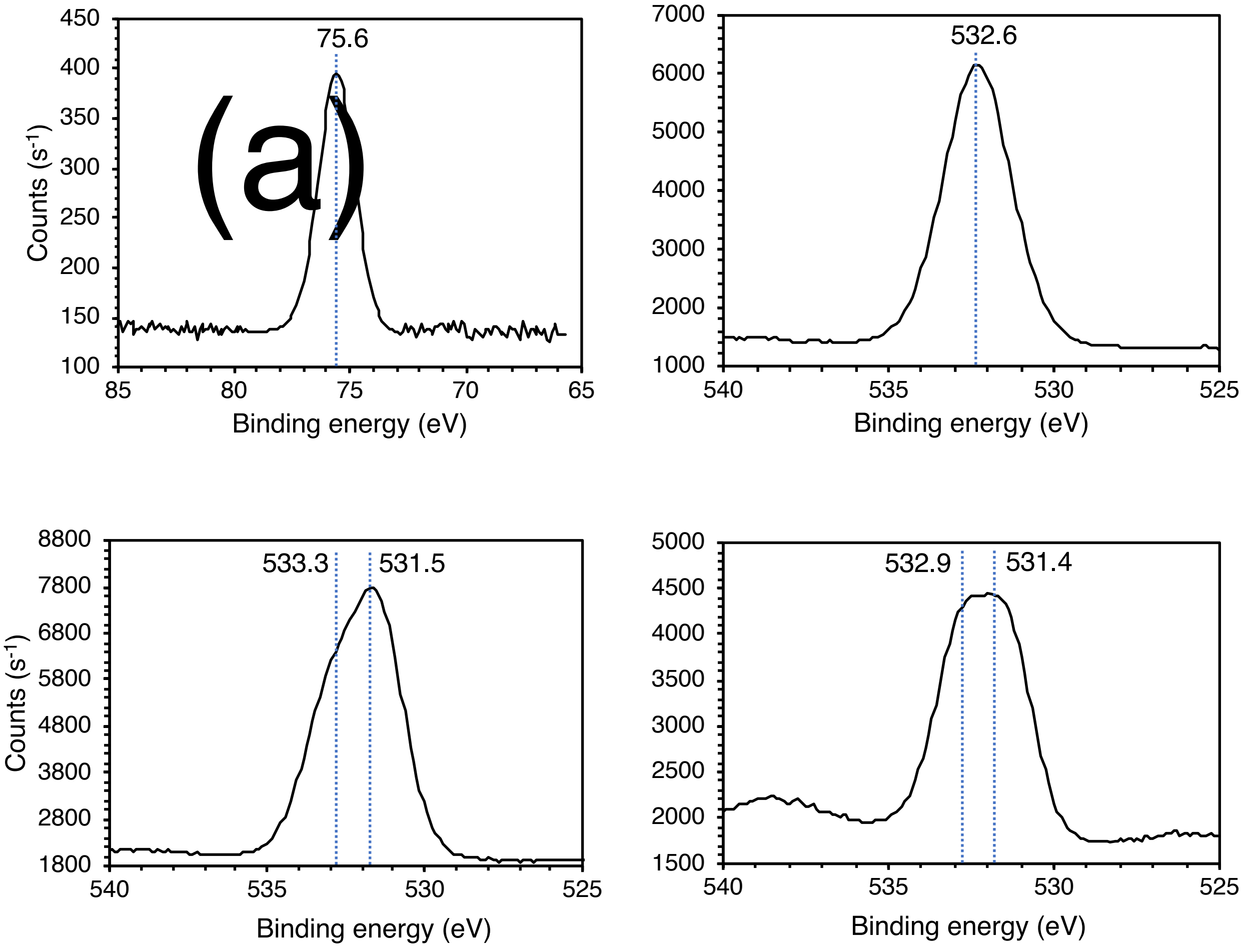

Fig. 7. XPS spectra of La-S950+ (a) Al 2p, post-PLS-contact, (b) O 1s, post-PLS-contact, (c) O 1s, untreated resin, (d) O 1s, post-NaF solution-contact.

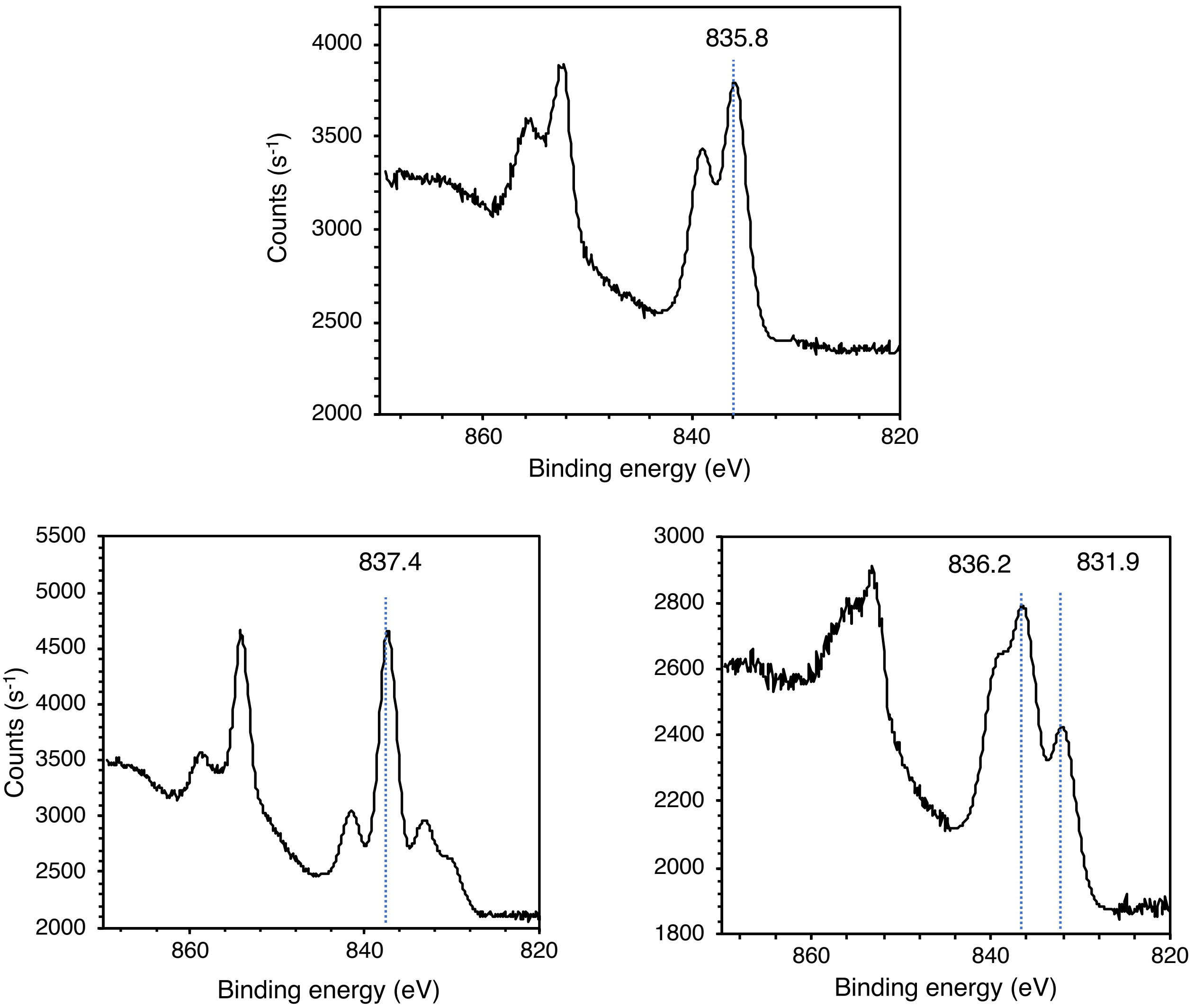

Fig. 8. La 3d5/2 XPS spectra of La-S950+ (a) Untreated resin, (b) Post-NaF solution-contact (C_i – 1500 mg g^{-1}), (c) Post-PLS-contact (C_i – 1500 mg g^{-1}).

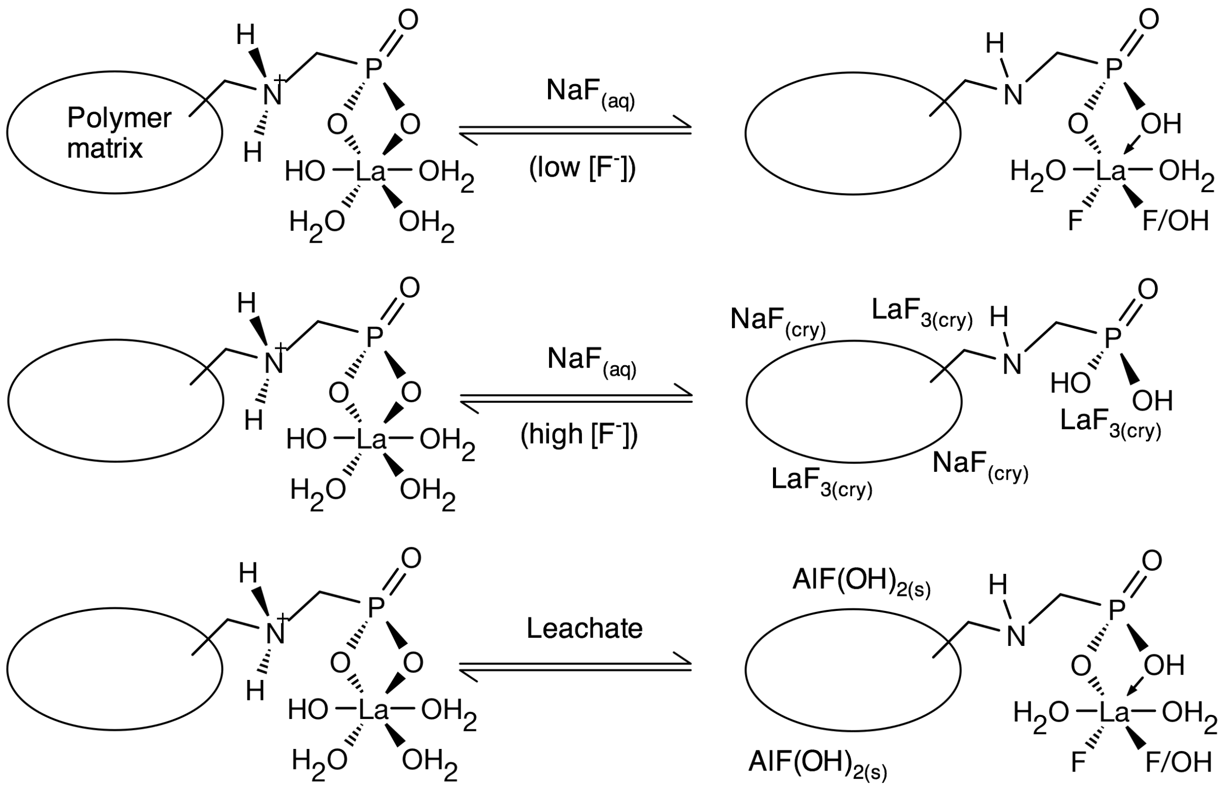

Fig. 9. Proposed fluoride uptake mechanisms for the 2 matrices. “cry” = crystalline.

4. Conclusions

The aminophosphonic acid chelating resin Purolite® S950+ has been chemically modified with La^{3+} ions to produce a novel sorbent for fluoride uptake from aqueous media. In batch extraction studies from NaF solutions and simulant Al industry leachate of high ionic strength, the resin has shown a greater uptake capacity that has previously been reported for similar sorbents. At low C_i ranges, uptake is dominated by a chemisorption ligand-exchange process. At higher C_i ranges, uptake is apparently enhanced by precipitation of LaF_3 and NaF in the first case and by amorphous $AlF(OH)_2$ precipitation in the second. This may complicate the elution of fluoride as analytically pure solutions, but also allow recovery of AlF_3 for Al smelting, which would be a desirable recycling outcome. Proposed uptake mechanisms are supported by isotherm and spectral data.

Purolite® S950+ is an inexpensive sorbent (retail price = £120 L^{-1}) and this, coupled with the relative cheapness of La_2O_3 means that La-S950+ compares favourably with traditional fluoride sorbents such as alumina (typical retail price = £540 kg^{-1}). Overall, La-S950+ is a highly effective fluoride sorbent and a promising potential industrial use for La metal. To move this work towards industrial implementation, the kinetics of the $AlF(OH)_2$ precipitation require further investigation. Dynamic studies, regeneration and performance over repeated cycles are furthermore important parameters for the suitability of an ion-exchange resin for industrial use and are the object of our current research.

Declarations of interest

None.

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