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Synthesis, characterization and application of lanthanum-impregnated activated alumina for F removal†

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Elevated fluoride (F) in groundwater presents an obvious environmental concern. Adsorption using activated alumina (AA) is currently the best available technology for F removal, despite its low efficiency, pH dependence, and aluminium (Al) release. The motivation for our study is to synthesise a new F adsorbent by impregnating commercially available granulated AA with lanthanum oxide (LAA), and to explore its F adsorption mechanism on the molecular scale. Five cycles of lanthanum impregnation on AA followed by calcination at 573 K increased the La content up to 19.1% and the F removal from 18.1% by pristine AA to 92.4% by LAA. The SEM, TEM, XRD, TGA, and EXAFS results demonstrated that the 5–20 nm thin flakes of LaOOH on LAA were in an amorphous form, with 7.6 oxygen atoms around each La. This LaOOH layer was uniformly distributed inside the micropores of the 1–3 mm AA granules. LAA exhibited four fold higher F adsorption capacity than AA in the pH range 3.9 to 9.6, with substantially reduced Al release. The ability to regenerate and reuse LAA makes it an attractive sustainable material. Multiple complementary spectroscopic analyses demonstrated that ligand exchange between F and surface hydroxyl groups is the mechanism for F adsorption on LAA. Our work improves the understanding of F interaction with metal oxides on the molecular scale and presents an alternative solution for elevated F water treatment.

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Introduction

Naturally occurring fluoride (F) in groundwater is causing increasing public concern due to its health effects. About 200 million people drink water with F concentrations exceeding the World Health Organization (WHO) guideline of 1.5 mg L⁻¹.¹ Long-term exposure to F-rich water leads to dental and skeletal fluorosis.²

The F removal from groundwater is still a challenge in rural areas of developing countries such as China and India^{3,4} due to the lack of efficient adsorptive materials. Currently, activated alumina (AA) is a widely used adsorbent, and AA-based

adsorption is the best available technology for defluoridation.^{1,5} However, AA is also recognized to have well-known limitations, including reduced F adsorption capacity at pH > 6⁶ and the release of aluminium (Al), which may lead to secondary Al contamination.⁷ Therefore, the need to improve the existing AA for enhanced F removal with wide pH range applicability and minimal Al leaching ability motivates our study.

Recently, extensive studies have been performed by impregnating AA with alum,⁸ manganese,^{9–11} magnesium,¹² iron,^{13,14} lithium¹⁵ and lanthanum¹⁶ to improve F adsorption. Among these methods, lanthanum (La) impregnation has been proved to be most promising because of its specific affinity for F.^{16,17} Wasay *et al.* were the first to add La on AA by mixing 0.1 mm diameter AA particles with La solution at pH 7.5 for 48 h. The resulting material increased the F adsorption capacity from 3.31 mg g⁻¹ to 6.23 mg g⁻¹.¹⁶ Meanwhile, enhanced F removal was also reported for La impregnation on various supports such as gelatine,¹⁸ amberlite resins,¹⁹ and chitosan.^{20,21}

However, the synthesis procedure for La-doped AA (LAA) was not fully optimized. The La impregnation on AA achieved previously was 3.3%,^{16,22} which could potentially be increased to improve F adsorption. The fabrication of AA with uniformly distributed La is needed. In addition, the F adsorption mechanism on LAA is not well understood on the molecular level.

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† Electronic supplementary information (ESI) available: Fig. S1: photo of LAA; Fig. S2: XRD patterns of various LAAs synthesized at different calcination temperatures; Table S1: pore volume and diameter of AA and LAA; Fig. S3: EDS of flake structures on LAA; Fig. S4: EDS elemental mapping of F, La, and Al on LAA with adsorbed F; Fig. S5: high resolution transmission electron microscope HRTEM of LAA; Table S2: structure parameters derived from La L_{III}-edge EXAFS analysis; Fig. S6: high resolution XPS surveys of F 1s for spent AA (A), LAA (B), and LaOOH (C); Fig. S7: isotherm of LaOOH and the mixture of AA and LaOOH. Fig. S8: mechanical strength of AA and LAA; Fig. S9: La release from LAA as a function of solution pH. See DOI: 10.1039/c3ta12548c

The lack of this crucial knowledge constrains our ability to design, synthesize, and regenerate an effective F adsorbent.

The objectives of this study were (1) to synthesize highly efficient LAA for elevated F removal, and (2) to explore the adsorption mechanism on the molecular level. La was uniformly loaded on AA repeatedly using ultrasonic irradiation and calcination. Batch adsorption experiments and multiple complementary characterization techniques including BET, TGA, FESEM/EDS, HRTEM, XRD, EXAFS, Raman, and XPS were used to study the interactions of F and LAA. The insights gained from this study should shed light on F adsorption using the composite material LAA.

Experimental section

Materials

Commercial granular AA optimized for F removal with a diameter of 1–3 mm (Keyuan, China, Fig. S1†) was used without further purification. NaF was heated at 393 K for 2 h before use.

A stock solution of 1000 mg L⁻¹ F was prepared by dissolving 2.210 g NaF in 1 L deionized (DI) water (18.2 MΩ, Milli-Q), and stored in a refrigerator at 277 K. The La solution was prepared by dissolving 19.485 g analytical grade La(NO₃)₃·6H₂O in 50 mL DI water, and the pH was adjusted to 6.0 using NH₃·H₂O. A background electrolyte of 0.01 mol L⁻¹ NaClO₄ was used in the experiment. 0.1 mol L⁻¹ HClO₄ and NaOH were used to adjust the solution pH. All reagents were obtained from Sinopharm, China.

Preparation of LAA and LaOOH

LAA was prepared by impregnating AA with La oxides. Briefly, AA was washed with DI water, and then dried at 328 K. To impregnate La on AA, a mixture of 10 mL La solution and 14.5 g AA was sonicated for 4 h, then the solid was separated and dried at 328 K. The solid was then calcined for 4 h at various temperatures. After the obtained material was cooled down, it was washed with DI water until the conductivity was below 100 μS cm⁻¹. The impregnation process was repeated and the amount of La loaded on AA was calculated based on mass balance. Lanthanum oxyhydroxide (LaOOH) was also synthesized using the same process in the absence of AA.

Characterization

The Brunauer–Emmett–Teller (BET) surface area of the granules was determined using an automated surface area analyzer (AutosorbIQ, US).

To investigate the surface morphology, spent granular adsorbents were cut into hemispheres. Then, the cross-section of the hemisphere was examined using field emission scanning electron microscopy (FESEM) with an Oxford energy dispersive X-ray spectroscopy (EDS) analyzer (SU 8020, Hitachi, Japan).

The solid sample was ground and passed through a 200-mesh sieve for characterization. The crystal morphology was characterized using high resolution transmission electron

microscopy (HRTEM, JEM2010, JEOL, Japan). X-ray powder diffraction (XRD, X'Pert PRO MPD, PANalytical, The Netherlands) data were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA using a Cu-target tube ($\lambda = 1.5418$) and a graphite monochromator. Scans were made in the 2θ range of 5° to 90° with a step size of 0.01° and a count time of 2 s per step. Analysis of the XRD patterns was performed using the PDF-2 reference database from the International Center for Diffraction Data (ICDD) database. X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Fisher Sci., US) was used to investigate the chemical properties of adsorbents before and after F adsorption. The binding energies obtained in the XPS analysis were calibrated against the C 1s peak at 284.8 eV. The XPS data processing and peak fitting were performed using the XPSPeak software package. Raman spectra were obtained using a portable Raman spectrometer (Enwave Optronics, Inc. USA) with a 4 cm⁻¹ resolution at 785 nm excitation energy.

The samples for extended X-ray absorption fine structure (EXAFS) spectroscopy were sealed between two layers of Kapton tape, and La L_{III}-edge data were collected on beamline 14W1 at the Shanghai Synchrotron Radiation Facility (SSRF), China. The detailed information on sample collection and data processing are shown in the ESI.†

In the thermogravimetric analysis (TGA), AA powder was evaluated on a TA SDTQ600 (TA instruments, US) in the temperature range of 298 K to 1283 K with a nitrogen flow rate of 100 mL min⁻¹ and a heating rate of 10 K min⁻¹. The LAA and LaOOH powder samples subjected to TGA analysis were synthesized without the calcination step.

Adsorption experiments

Batch adsorption experiments were conducted to compare the effectiveness of the adsorbents. In a typical experiment, 0.1 g adsorbent was mixed with 100 mL F solution at the desired pH value. The samples were mixed on a rotary shaker at 200 rpm at 298 K for 24 h. The solution pH was adjusted with HClO₄ and NaOH.

The pH edge adsorption experiments of 10 mg L⁻¹ F on 1 g L⁻¹ AA were conducted as a function of solution pH. Suspension samples in 0.01 mol L⁻¹ NaClO₄ were adjusted to desired pH values with NaOH and HClO₄. The adsorption isotherms of AA and LAA were investigated at pH 7 in 0.01 mol L⁻¹ NaClO₄ solution. The adsorbent concentration was fixed at 1 g L⁻¹, and the F concentration was increased up to 100 mg L⁻¹. After being mixed on a rotary shaker at 200 rpm for 24 h at 298 K, samples were centrifuged and passed through a 0.45 μm membrane filter for analysis.

To explore the regeneration and reuse, LAA was mixed with 100 mg L⁻¹ F and 0.01 mol L⁻¹ NaClO₄. Then, the spent LAA was regenerated using 1 mol L⁻¹ NaOH for 3 h before the next adsorption or re-use cycle.

The F concentration was measured using an F ion-selective electrode (Orion, Thermo Fisher Sci., US). Concentrations of Al and La were determined using an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7500a, US).

Results and discussion

The calcination temperature for LAA synthesis played a critical role in its subsequent F removal (Fig. 1). F removal increased from 31.2% for calcination at 373 K to a maximum of 42% at 573 K, and then decreased to 13.25% at 1273 K. However, the percentage of La loaded on AA increased from 2.4% for calcination at 373 K to 8.6% at 673 K and remained constant thereafter. Because the maximum F removal was found for LAA synthesized at 573 K and the maximum La loading at 673 K, we therefore investigated the effect of multiple La impregnations at 573 K and 673 K.

F removal increased from 18.1% using pristine AA to 92.4% upon five cycles of La impregnation with calcination at 573 K (Fig. 2). Meanwhile, F removal reached the maximum of 51.3% after three cycles of impregnation with calcination at 673 K, and decreased substantially with further increasing impregnation–calcination cycles. The results showed that the maximum F removal can be achieved by stepwise La impregnation and 573 K calcination for five cycles.

The calcination temperature usually determines the crystal structure of La oxides,^{23,24} which is critical in F adsorption. To investigate the structure of the La-oxide coatings, XRD analysis was used for LAA calcined at various temperatures, but no crystalline La oxide was found (Fig. S2†). Therefore, the change in F adsorption (Fig. 2) was not due a change in the crystal structure of La oxides, prompting further investigation using TGA and BET.

Our TGA results in Fig. 3 show the transformation of LaOOH to La₂O₃ over 573 K. The weight losses from 495 to 565 K of AA (1.18%, Fig. 3a) and from 498 to 564 K of LAA (2.59%, Fig. 3b) were attributed to the adsorbed water. The weight loss from 502 to 646 K of LaOOH (8.15%, Fig. 3c) was due to the adsorbed water and formation of LaOOH.²⁵ Moreover, the change of LaOOH to La₂O₃ induced the weight loss from 561 to 858 K of LAA (9.92%, Fig. 3b) and from 646 to 892 K (16.28%, Fig. 3c) of LaOOH.^{25,26} The F affinity of crystalline La₂O₃ was lower than that of amorphous LaOOH,²⁷ as evidenced by the

Fig. 1 Evaluation of LAA synthesized at different calcination temperatures for F removal (□) and La content (Δ). The dashed line represents F removal using AA. Adsorbent = 1 g L⁻¹, initial F concentration = 10 mg L⁻¹, pH = 7, temperature = 298 ± 2 K.

Fig. 2 Comparison of LAA synthesized with calcination at 573 K (a) and 673 K (b) for F removal (□) and La content (Δ). Adsorbent = 1 g L⁻¹, initial F concentration = 10 mg L⁻¹, pH = 7, temperature = 298 ± 2 K.

significant decrease in F adsorption after calcination over 573 K (Fig. 1). In agreement with our observation, Rosynek and Yang also found that LaOOH was transformed to La₂O₃ from 564 to 858 K.^{25,28}

The BET results showed that the surface area decreased from 235 m² g⁻¹ to 192 and 140 m² g⁻¹ upon five and seven cycles of La loading, respectively (Fig. 4). The observation confirmed that the optimum number of La loading cycles was five. When the number of impregnation–calcination cycles was less than five, the decrease in BET area was balanced by the increase in active LaOOH sites. Additional impregnation beyond five times could not improve the amount of effective LaOOH, resulting in relatively constant F adsorption (Fig. 2). The phenomenon of decreased surface area after impregnation was in accordance with previous observations.^{10,12,29,30}

To investigate the surface morphology, FESEM analyses were performed on the hemispherical cross-sections of AA and LAA synthesized with different numbers of loading cycles (Fig. 5). Compared with AA (Fig. 5a), thin flakes (5–20 nm thickness) appeared on the surface of LAA (Fig. 5b, c and d). Moreover, with the increase in La loading, the amount of thin flakes increased. The primary element of the flake was La (wt. 86.53%, Fig. S3†), while no flakes were observed on AA (Fig. 5a). In addition, the results of elemental mapping for the F-adsorbed LAA (LAA-F) sample showed that LaOOH and fluoride were uniformly distributed on the cross-section (Fig. S4†).

Though thin flakes were formed, no new crystalline phase other than that from Al₂O₃ was detected using XRD (Fig. S2†). The XRD results implied that LaOOH on LAA was in an amorphous phase. To confirm the XRD conclusion, we further measured the interplanar distance using HRTEM (Fig. S5†). The observed distance was 1.98 Å, corresponding to the (104) diffraction line of χ -Al₂O₃ (PDF no. 13-0373). Both XRD and HRTEM results showed that the impregnated LaOOH was in an amorphous form.

To obtain the LAA structure on the molecular level, EXAFS was used to determine the La local coordination environment in LaOOH and LAA (Fig. 6). The k^2 -weighted La L_{III}-edge EXAFS spectra and the corresponding radial structure functions (RSF) as magnitude and real part of the Fourier transformation (FT) vs. radial distance are shown in Fig. 6. The structure parameters listed in Table S2† were obtained by fitting the theoretical curves to the experimental spectra.

Fig. 3 TGA of AA (a), LAA (b), and LaOOH (c).

Fig. 4 Surface area of LAA at different La loading times.

Fig. 5 FESEM images of AA (a), one cycle La loading (b), two cycles La loading (c), and five cycles La loading (d). (Inset in d: high-magnification FESEM image).

Based on the fit of the theoretical to the experimental spectra, the first and strongest peak in the FT curve indicated there was 7.6 oxygen atoms at an average distance of 2.58 Å for the LaOOH sample. An additional oxygen atom was found at 3.56 Å. The third peak in the FT spectra was due to 3.3 La at 4.22 Å. The distances and coordination numbers (CNs) of La–O and La–La were in good agreement with previously published

Fig. 6 Normalized k^2 -weighted observed (dotted line) and model calculated (solid line) La L_{III} -edge EXAFS spectra (a), the corresponding Fourier transformed magnitude (b) and real parts of Fourier transform (c) for LAA (A) and LaOOH (B) samples.

data.^{31,32} When La was coated on AA, the first La–O shell remained unchanged. Al atoms were detected at 3.19 Å with a CN of 3.7. This structure change from LaOOH demonstrated that La was adsorbed on the surface of AA. The La L_{II} -edge at 410 eV beyond the L_{III} -edge complicated the data analysis because truncation led to a limited data range in k -space. Therefore, the FT peaks higher than 4.5 Å were unresolved.

XPS surveys of O 1s for pristine and spent adsorbents were used to elucidate the F adsorption mechanism. The O 1s spectra were simulated by considering Al–O^{2−}, Al–OH, La–O^{2−}, and La–OH.^{24,33} The XPS peaks of Al–O^{2−} at 530.9 eV and Al–OH at 532.5 eV were observed in AA (Fig. 7a). Similarly, the peak positions of La–O^{2−} at 530.7 eV and La–OH at 532.1 eV were resolved in LaOOH (Fig. 7c). These four peaks were all detected

Fig. 7 High resolution XPS surveys of O 1s for pristine (A) and spent (B) AA (a), LAA (b), and LaOOH (c). Vertical lines indicate binding energies of Al–O^{2−} (cyan) at 530.9 ± 0.1 eV, Al–OH (blue) at 532.5 ± 0.1 eV, La–O^{2−} (wine) at 530.7 ± 0.1 eV, and La–OH (red) at 532.1 ± 0.1 eV.

in LAA (Fig. 7b). The lower binding energies of La-O²⁻ and La-OH, compared with those of Al-O²⁻ and Al-OH, were in agreement with previous publications.^{24,33} The difference in binding energies of La and Al can be attributed to the higher CN of O atoms with La (7.6, Table S2†) than that with Al (4–6 (ref. 34)), and the longer interatomic distance of La-O (0.25 nm, Table S2†) than that of Al-O (0.17–0.19 nm).³⁴

Similar results were observed in the high resolution XPS surveys of F 1s for spent adsorbents (Fig. S6†). The peaks of F 1s were resolved into 685.7 and 684.4 eV for Al-F and La-F,^{35,36} respectively. Al-F was obtained in AA and LAA, whereas La-F was obtained in LAA and LaOOH. The observed Al-F in LAA may be due to the exposure of alumina in LAA when polishing the sample for XPS analysis.

Upon F adsorption, the XPS peak intensities of Al-OH on AA and La-OH on LAA and LaOOH decreased substantially (Fig. 7), indicating the reduction in hydroxyl group concentrations. However, the peak intensity of Al-OH on LAA decreased only slightly, suggesting that La-OH played a dominant role in F adsorption compared to Al-OH.

Raman analysis was used to study the interactions between La-OH and F (Fig. 8). The peak at 1162 cm⁻¹ was observed in the spectra of spent LAA and LaOOH but not in that of AA, suggesting the formation of La-F bonds. The loss of La-OH content (Fig. 7) and the occurrence of La-F bonds (Fig. 8) indicated the ligand exchange between F and hydroxyl groups on La-OH. Although the ligand exchange mechanism has been proposed by previous researchers,³⁷ our results provided direct experimental evidence and showed how the process occurred.

To investigate the performance of LAA for F removal, isotherms were measured to determine the maximum F adsorption capacity of AA and LAA (Fig. 9a). Adsorption isotherms of F followed the Langmuir equation: $C_e/q_e = 1/q_m b + C_e/q_e$, where C_e (mg L⁻¹) is the equilibrium concentration of F, and q_e (mg g⁻¹, adsorbent) is the amount of F adsorbed; q_m (mg g⁻¹) and b (L mg⁻¹) are fitting parameters representing the maximum adsorption capacity and the adsorption affinity constant, respectively. The F adsorption on LAA (16.9 mg g⁻¹) was 5.6 times higher than that of AA (Fig. 9a). Accordingly, the estimated density of functional surface sites on LAA (2.8 sites

Fig. 8 Raman spectra of AA (A), AA-F (B), LAA (C), LAA-F (D), LaOOH (E), and LaOOH-F (F).

Fig. 9 Isotherm (a) and Al release (b) using AA and LAA for F removal. Dashed line is the drinking water standard for Al (0.2 mg L⁻¹). Adsorbent = 1 g L⁻¹, pH = 7, temperature = 298 ± 2 K. Inset table in (a) Langmuir parameters: Q_m is the maximum adsorption amount (mg g⁻¹), b is Langmuir constant (L mol⁻¹), and r^2 is the correlation coefficient.

nm⁻²) was 6.9 times more than that on AA (0.4 sites nm⁻²). Our work improved considerably on the F adsorption capacity of La(III)-AA reported by Wasay (6.23 mg g⁻¹).¹⁶

The Al release is a major consideration in F removal using AA. When F adsorption on AA was higher than 2 mg g⁻¹ (Fig. 9b), the dissolved Al concentration exceeded 0.2 mg L⁻¹, the WHO drinking water standard. The elevation of Al leaching with increasing F content can be ascribed to the F-promoted dissolution of Al₂O₃.³⁸ Conversely, the La impregnation suppressed the release of Al from LAA. The Al concentration in water treated with LAA was under 0.2 mg L⁻¹ until the mass of F adsorbed reached 12 mg g⁻¹. Meanwhile, the La concentration was in the range 8 to 146 µg L⁻¹, which was an order of magnitude lower than the lowest commonly accepted concentration having adverse health effects.³⁹

Another main limitation in using AA to remove F is its narrow pH range (<6).⁶ However, the pH of natural groundwater with high

Fig. 10 F removal (open) and Al concentration (filled) of AA (squares) and LAA (triangles) as a function of pH. Dashed line represents the Al drinking water standard. Adsorbent = 1 g L^{-1} , initial F concentration = 10 mg L^{-1} , temperature = $298 \pm 2 \text{ K}$.

Fig. 11 Regeneration of LAA and F desorption.

fluoride is usually in the range of 7.6–8.6.^{1,40,41} Within this pH range, F removal using LAA reached 70.5–77.2%, four times higher than that achieved using AA (Fig. 10). Meanwhile, Al leached from LAA was lower than 0.2 mg L^{-1} within the pH range 5.5–8. In contrast, the amount of Al released from AA cannot meet the WHO standard. Furthermore, the Al concentration increased significantly at $\text{pH} < 6$ and $\text{pH} > 8$ because of the amphoteric characteristics of Al. In addition, the decreasing F removal at $\text{pH} < 6$ using LAA may be ascribed to La dissolution (Fig. S9†).

Regeneration is a critical factor of an adsorbent. The results in Fig. 11 show that the F desorption in the regeneration process was in the range 84–98%. After 5 adsorption–regeneration cycles, the F adsorption capacity of LAA remained as high as 11.8 mg g^{-1} which is about four times higher than that of AA (3.02 mg g^{-1}).

Conclusions

In summary, we have successfully synthesized and characterized LAA for effective F removal and investigated its ligand exchange mechanism. Five cycles of La impregnation on AA and

calcination at 573 K improved the La content to 19.1%, and achieved the maximum F adsorption at 16.9 mg g^{-1} . The thin flake LaOOH on LAA was in an amorphous form with approximately 7.6 oxygen atoms around each La. LAA could adsorb 70.5–77.2% F in the pH range of the actual groundwater, about four times higher than AA. Meanwhile, the Al release can be substantially reduced due to LaOOH formation. In addition, LAA can be regenerated and reused. XPS, Raman, and FTIR results show that ligand exchange between F and surface hydroxyl groups is the mechanism for F adsorption on LAA. Our work presents an alternative solution for elevated F water treatment.

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Notes and references

- 1 S. Ayoob, A. K. Gupta and V. T. Bhat, *Crit. Rev. Environ. Sci. Technol.*, 2008, **38**, 401–470.
- 2 S. Hillier, C. Cooper, S. Kellingray, G. Russell, H. Hughes and D. Coggon, *Lancet*, 2000, **355**, 265–269.
- 3 M. Agarwal, K. Rai, R. Shrivastav and S. Dass, *J. Clean. Prod.*, 2003, **11**, 439–444.
- 4 Y. Ku, H. M. Chiou and W. Wang, *Sep. Sci. Technol.*, 2002, **37**, 89–103.
- 5 V. S. Chauhan, P. K. Dwivedi and L. Iyengar, *J. Hazard. Mater.*, 2007, **139**, 103–107.
- 6 S. Jagtap, M. K. Yenkie, N. Labhsetwar and S. Rayalus, *Chem. Rev.*, 2012, **112**, 2454–2466.
- 7 B. D. Turner, P. Binning and S. L. S. Stipp, *Environ. Sci. Technol.*, 2005, **39**, 9561–9568.
- 8 S. S. Tripathy, J. L. Bersillon and K. Gopal, *Sep. Purif. Technol.*, 2006, **50**, 310–317.
- 9 S. S. Tripathy and A. M. Raichur, *J. Hazard. Mater.*, 2008, **153**, 1043–1051.
- 10 S. M. Maliyekkal, A. K. Sharma and L. Philip, *Water Res.*, 2006, **40**, 3497–3506.
- 11 S. X. Teng, S. G. Wang, W. X. Gong, X. W. Liu and B. Y. Gao, *J. Hazard. Mater.*, 2009, **168**, 1004–1011.
- 12 S. M. Maliyekkal, S. Shukla, L. Philip and I. M. Nambi, *Chem. Eng. J.*, 2008, **140**, 183–192.
- 13 K. Biswas, S. K. Saha and U. C. Ghosh, *Ind. Eng. Chem. Res.*, 2007, **46**, 5346–5356.
- 14 M. G. Sujana, G. Soma, N. Vasumathi and S. Anand, *J. Fluorine Chem.*, 2009, **130**, 749–754.
- 15 J. B. Zhou, Y. Cheng, J. G. Yu and G. Liu, *J. Mater. Chem.*, 2011, **21**, 19353–19361.
- 16 S. A. Wasay, S. Tokunaga and S. W. Park, *Sep. Sci. Technol.*, 1996, **31**, 1501–1514.
- 17 S. A. Wasay, J. Haron and S. Tokunaga, *Water Environ. Res.*, 1996, **68**, 295–300.
- 18 F. Luo and K. Inoue, *Solvent Extr. Ion Exch.*, 2004, **22**, 305–322.

- 19 Y. M. Zhou, C. X. Yu and Y. Shan, *Sep. Purif. Technol.*, 2004, **36**, 89–94.
- 20 A. Bansawal, D. Thakre, N. Labhshetwar, S. Meshram and S. Rayalu, *Colloids Surf., B*, 2009, **74**, 216–224.
- 21 N. Viswanathan and S. Meenakshi, *J. Colloid Interface Sci.*, 2008, **322**, 375–383.
- 22 B. K. Puri and S. Balani, *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.*, 2000, **35**, 109–121.
- 23 M. Bettman, R. E. Chase, K. Otto and W. H. Weber, *J. Catal.*, 1989, **117**, 447–454.
- 24 L. P. Haack, J. E. Devries, K. Otto and M. S. Chattha, *Appl. Catal., A*, 1992, **82**, 199–214.
- 25 M. P. Rosynek and D. T. Magnuson, *J. Catal.*, 1977, **46**, 402–413.
- 26 S. L. Zhong, B. Deng, A. W. Xu and S. P. Wang, *Curr. Nanosci.*, 2011, **7**, 407–414.
- 27 C. Y. Jing, J. L. Cui, Y. Y. Huang and A. G. Li, *ACS Appl. Mater. Interfaces*, 2012, **4**, 714–720.
- 28 J. Yang, L. Zhou, L. Z. Zhao, H. W. Zhang, J. N. Yin, G. F. Wei, K. Qian, Y. H. Wang and C. Z. Yu, *J. Mater. Chem.*, 2011, **21**, 2489–2494.
- 29 L. M. Camacho, A. Torres, D. Saha and S. G. Deng, *J. Colloid Interface Sci.*, 2010, **349**, 307–313.
- 30 M. Jang, J. K. Park and E. W. Shin, *Microporous Mesoporous Mater.*, 2004, **75**, 159–168.
- 31 P. Malet, M. J. Capitan, M. A. Centeno, J. A. Odriozola and I. Carrizosa, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2783–2790.
- 32 F. Ali, A. V. Chadwick and M. E. Smith, *J. Mater. Chem.*, 1997, **7**, 285–291.
- 33 L. Katta, T. V. Kumar, D. N. Durgasri and B. M. Reddy, *Catal. Today*, 2012, **198**, 133–139.
- 34 G. Gutierrez and B. Johansson, *Phys. Rev. B: Condens. Matter*, 2002, **65**, 104202.
- 35 S. D. Yao, Y. Zheng, L. H. Ding, S. Ng and H. Yang, *Catal. Sci. Technol.*, 2012, **2**, 1925–1932.
- 36 L. Armelao, G. Bottaro, G. Bruno, M. Losurdo, M. Pascolini, E. Soini and E. Tondello, *J. Phys. Chem. C*, 2008, **112**, 14508–14512.
- 37 B. Kasprzyk-Hordern, *Adv. Colloid Interface Sci.*, 2004, **110**, 19–48.
- 38 W. Stumm, *Chemistry of the solid-water interface: processes at the mineral-water and particle-water interface in natural systems*, John Wiley & Sons Inc., USA, 1992. pp. 165–169.
- 39 S. Hirano and K. T. Suzuki, *Environ. Health Perspect.*, 1996, **104**, 85–95.
- 40 S. Hu, T. Luo and C. Jing, *J. Geochem. Explor.*, 2012, DOI: 10.1016/j.gexplo.2012.08.013.
- 41 V. K. Saxena and S. Ahmed, *Environ. Geol.*, 2001, **40**, 1084–1087.