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Physical modification of hydroxyapatite: the drastic enhancement of both cation (Cd^{2+}) and anion ($F^{–}$) adsorption and recycling efficiency

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S1. Characterizations

Powder X-ray diffraction (XRD) analysis was performed using a Rigaku Ultima IV X-ray diffractometer equipped with CuKα radiation ($\lambda = 0.154$ nm) in the 2θ range of 10° to 70° scanning step size 0.02°. The average crystallite size (L) of all the samples was calculated from the XRD pattern using the Scherrer formula, $L = k\lambda/\beta\cos\theta$, where, λ is X-ray wavelength (1.5406 Å), θ is the diffraction angle, k is a constant varying with crystal habit and it was chosen as 0.9, and β is the Full Width Half Maximum (FWHM). The crystallinity of all samples was calculated from an empirical relation between X_c and β, i.e., $\beta \times (X_c)^{1/3} = K_a$, where X_c is the degree of crystallinity, and K_a is a constant set at 0.24. The XRDA software was used to index the X-ray diffraction peaks of all the samples, and it was found to be FWHM, lattice parameters, and unit cell volume. The adsorbent functional group was analyzed using a Fourier Transform Infrared Spectrometer (Jasco FTIR-6300) with KBr pellet technique in the range of 4000–400 cm^{-1} in transmission mode. Particle size and morphology were analyzed using a high-resolution scanning electron microscope (HRSEM, FEI Quanta FEG 200) and a high-resolution transmission electron microscope (HR-TEM, JEOL-2100). The surface elemental composition of the adsorbent was determined by X-ray photoelectron spectroscopy (ULVAC-PHI, Inc; Model: PHI5000 version probe III). Further, the colloidal stability and particle size in different pH values were determined from the Dynamic Light Scattering (DLS- Malvern Zetasizer Nano-ZS) technique equipped with a He-Ne diode laser at a wavelength of 633 nm. The specific surface area and pore size of the synthesized nanoparticles were analyzed by the BET analyzer (BELSORP-MR6). The equilibrium Cd^{2+} concentration was measured by an Atomic Adsorption Spectrometer (Thermo iCE 3300) using a specified cadmium source with a wavelength of 228 nm. The quantification of F^{-} ions was measured by a fluoride ion-selective electrode (Ex-Tech model no. FL 700). The elemental composition of Ca, P, Cd, and F present in the VD-HAp and FD-HAp was analyzed before and after adsorption using ICP-OES (Perkin Elmer Optima 5300 DV).

S2. Effect of pH on equilibrium F^- concentration

The equilibrium F^- concentration (2000 mg/L) was fixed with various initial pH to find the equilibrium F^- adsorption capacity (**Fig. S4c).** As previously indicated (**section 3.2.3**), the maximum F^- adsorption capacity of VD-HAp and FD-HAp was highly dependent on the adsorbate pH values. Accordingly, the maximum equilibrium F^- adsorption capacity of VD-HAp and FD-HAp was decreased from 175 to 7 mg/g and 290 to 22 mg/g, by increasing pH values from 3 to 11 respectively. At neutral pH (pH = 7), the maximum equilibrium F^- adsorption capacity of VD-HAp was 75 mg/g and FD-HAp was 200 mg/g.

S3. HR-SEM and EDX analysis

After adsorption of Cd^{2+} ions, there were no changes in VD-Cd and FD-Cd morphology compared with pristine adsorbents; the average particle size of VD-Cd and FD-Cd were 45×25 ± 5 nm and 35×15 ± 5 nm, respectively. (**Fig. S9a-b).** In contrast, the VD-HAp and FD-HAp nanorods transform into spheres on adsorption of F^- at pH 3, due to the change in the crystalline phase of HAp into CaF_2 and FAp phases. The average particle size of VD-F and FD-F was 110 ± 5 nm and 220 ± 5 nm, respectively (**Fig. S9c-d**). The qualitative analysis of EDX spectra of VD-HAp and FD-HAp shows the presence of Ca, P, O, and C (**Fig. S10a-b**). The EDX spectra of VD-Cd and FD-Cd, and VD-F and FD-F confirm the adsorption of Cd^{2+} and F^- ions, respectively (**Fig. S10c-f**).

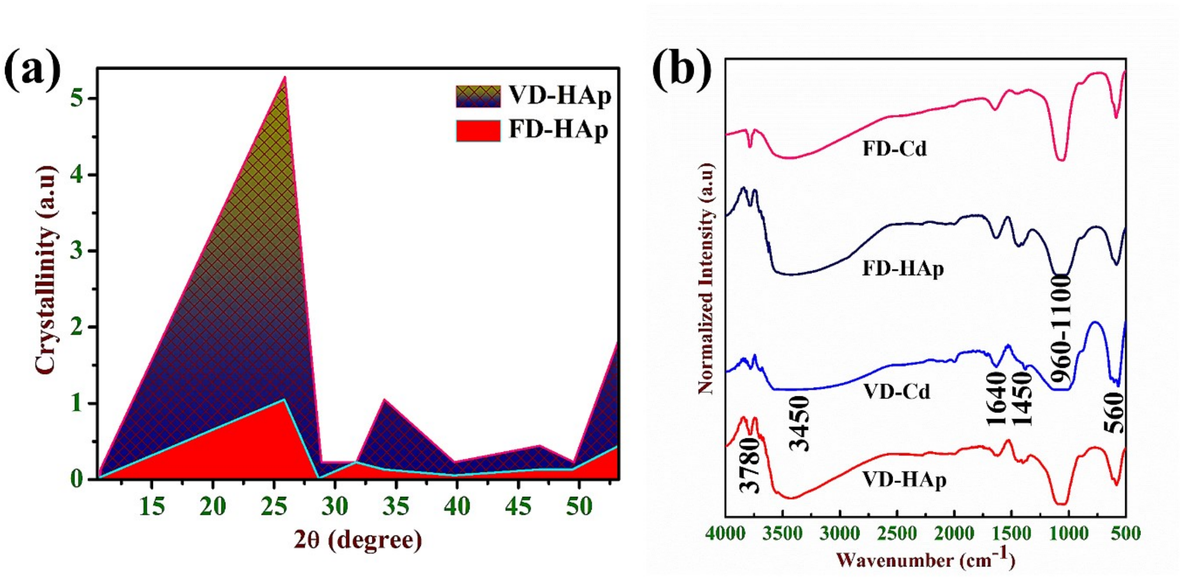

Fig. S1 (a) Crystallinity of VD-HAp and FD-HAp, and (b) FTIR spectra of before and after Cd^{2+} adsorbed VD-HAp and FD-HAp

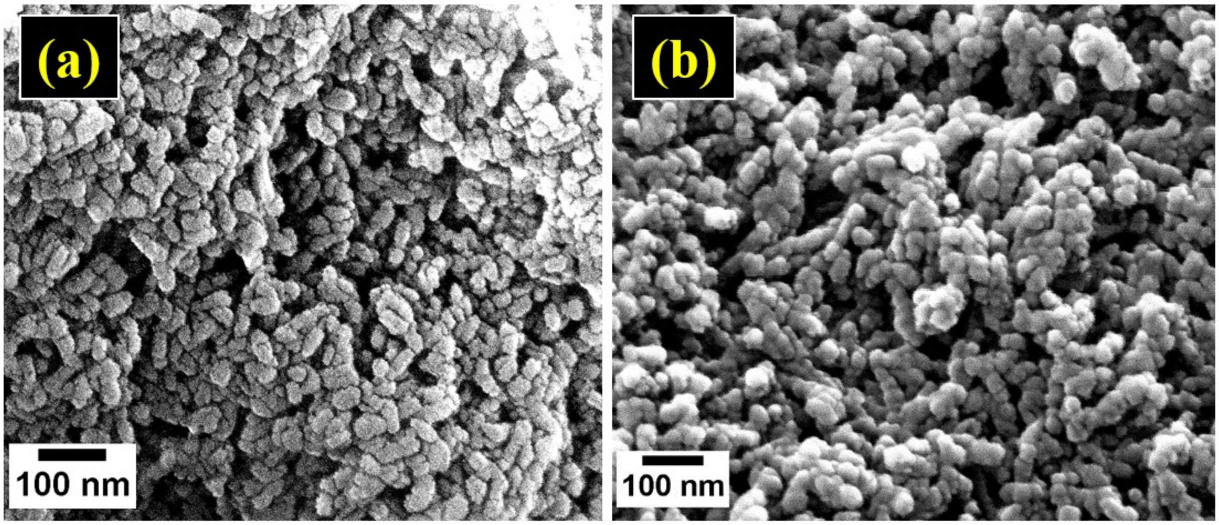

Fig. S2 HR-SEM analysis: (a) VD-HAp and (b) FD-HAp.

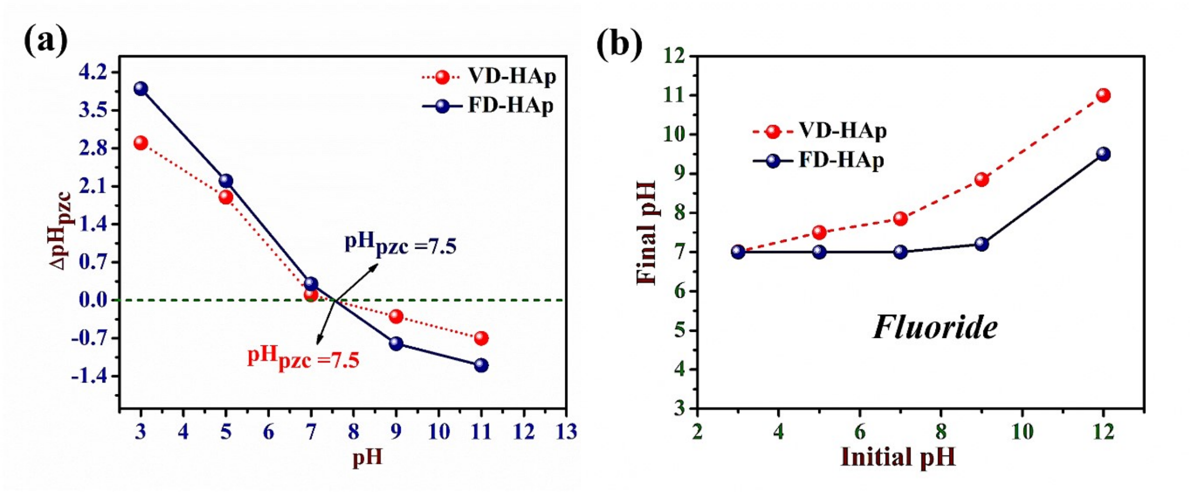

Fig. S3 (a) Point zero charge (pH_{pzc}) of VD-HAp and FD-HAp, and (b) Initial and final pH of after F^{-} adsorption.

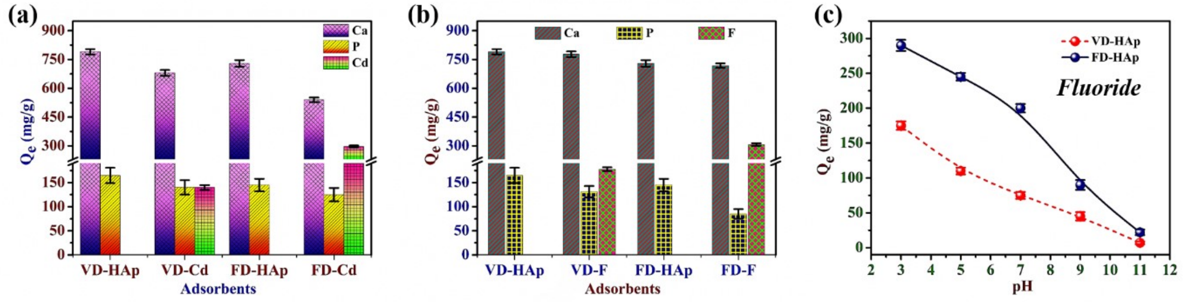

Fig. S4 Quantification of elemental composition of VD-HAp and FD-HAp: (a) prior to and after Cd^{2+} adsorption, (b) prior to and after F^{-} adsorption; and (c) pH effect of F^{-} adsorption with an equilibrium F^{-} concentration (2000 mg/L).

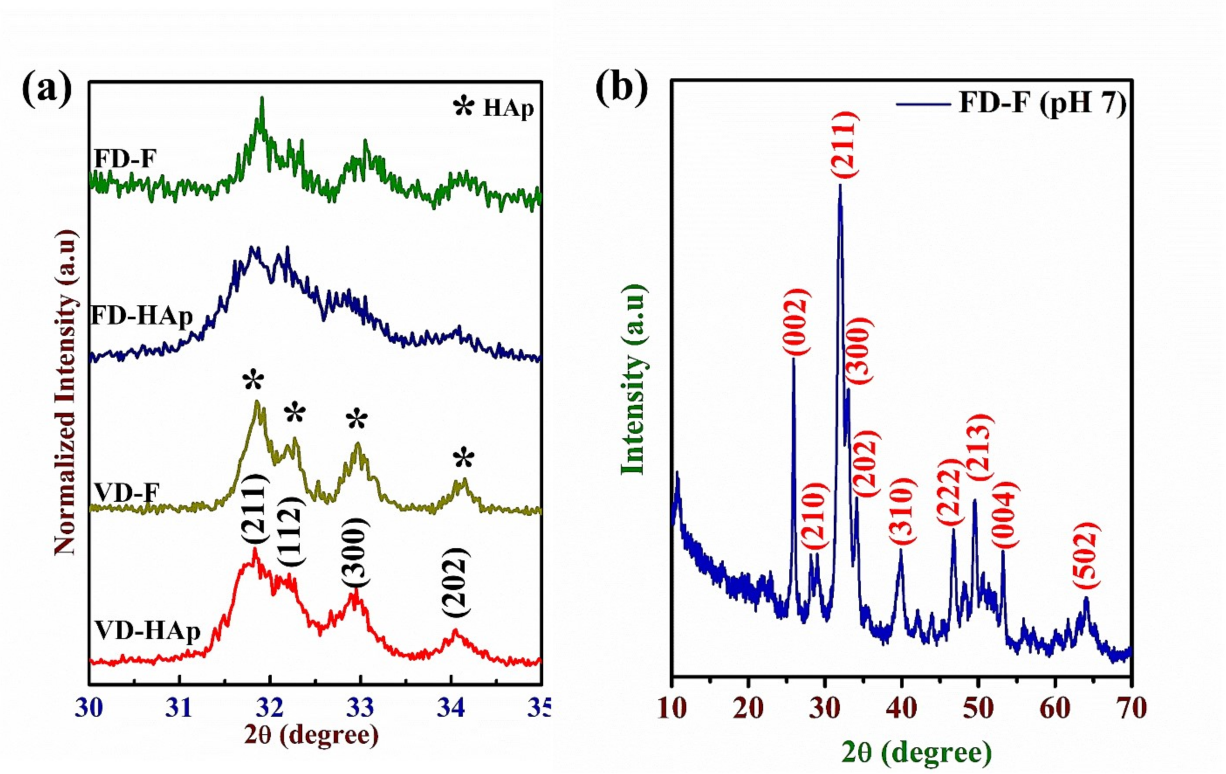

Fig. S5 (a) Magnified XRD pattern of prior to and after F⁻ adsorbed VD-HAp and FD-HAp, and (b) XRD pattern of F⁻ adsorbed FD-HAp at neutral pH

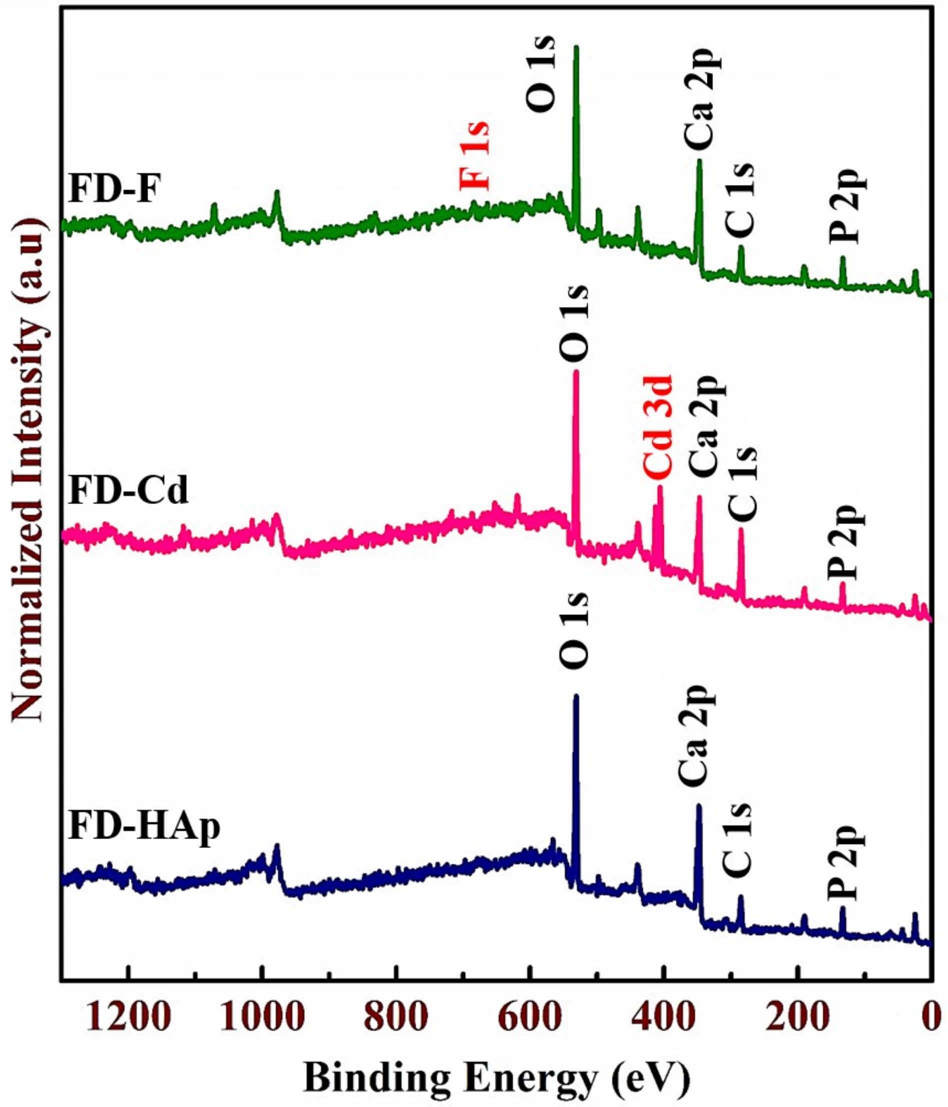

Fig. S6 XPS survey spectra of prior to and after Cd^{2+} and F^{-} adsorption of VD-HAp and FD-HAp.

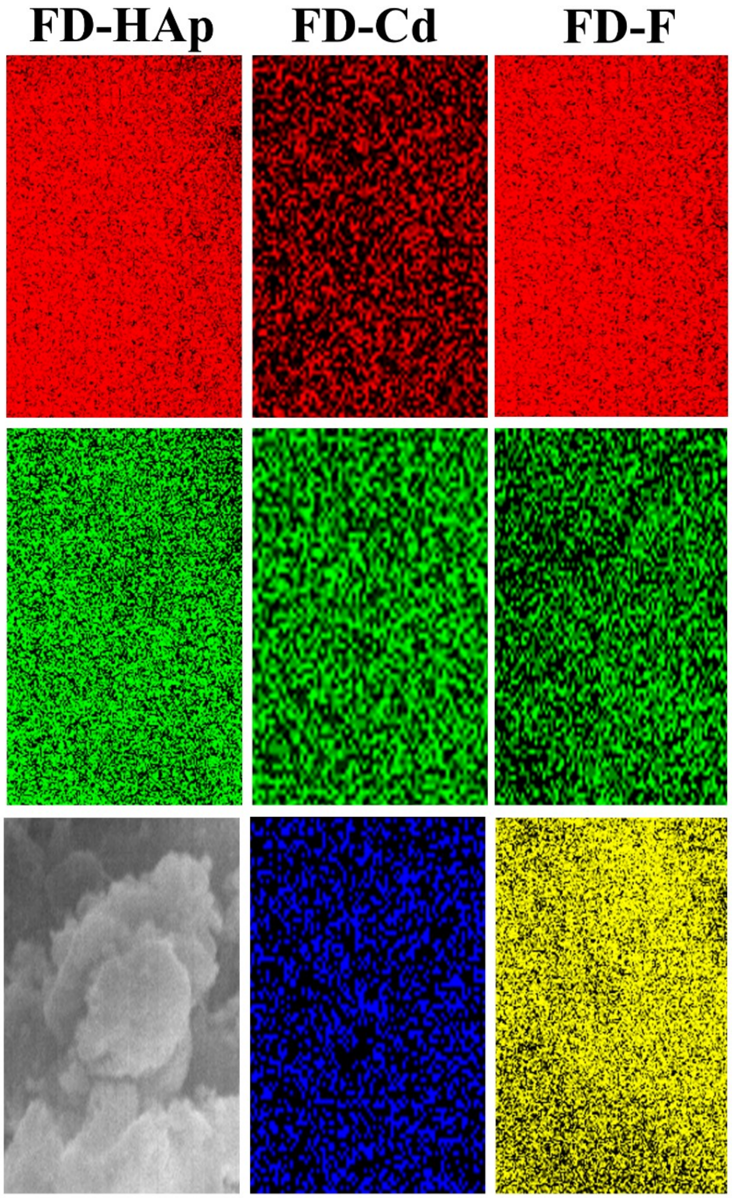

Fig. S7 Elemental mapping prior to and after Cd^{2+} and F^{-} adsorption on FD-HAp (Ca-Red, P-Green, Cd-Blue, and F-Yellow)

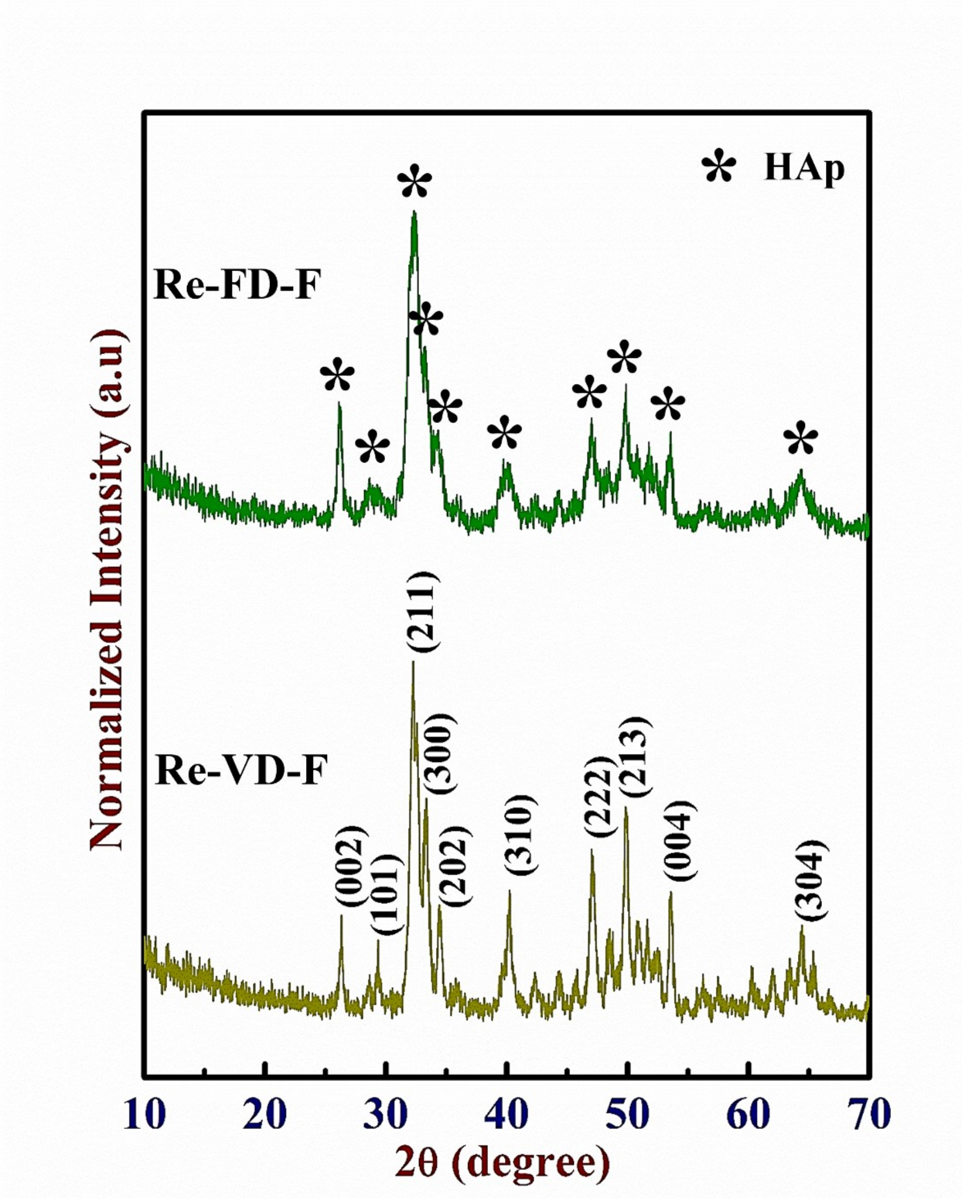

Fig. S8 NaOH treated VD-F and FD-F XRD pattern.

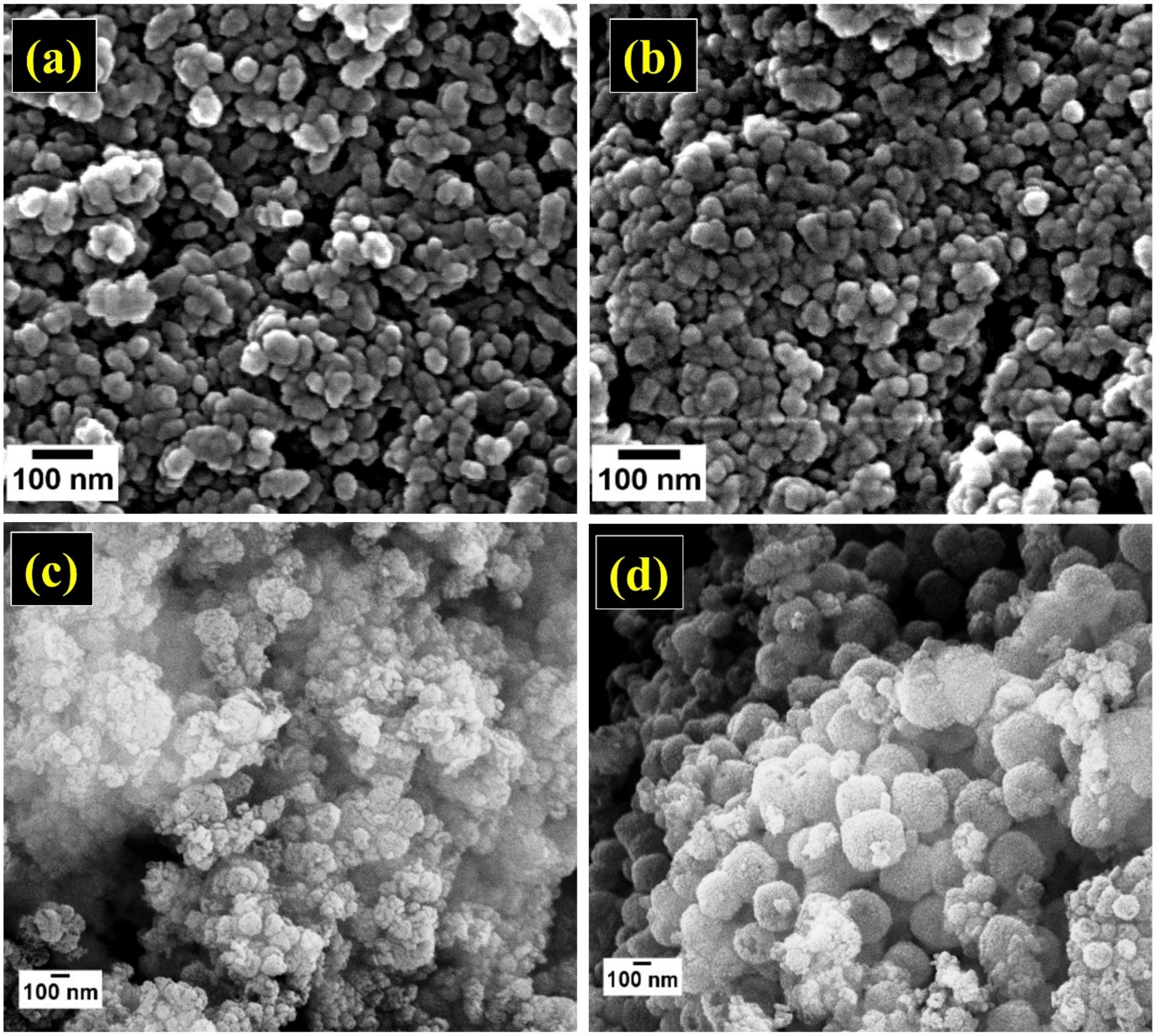

Fig. S9 HR-SEM analysis: (a) VD-Cd, (b) FD-Cd, (c) VD-F, and (d) FD-F

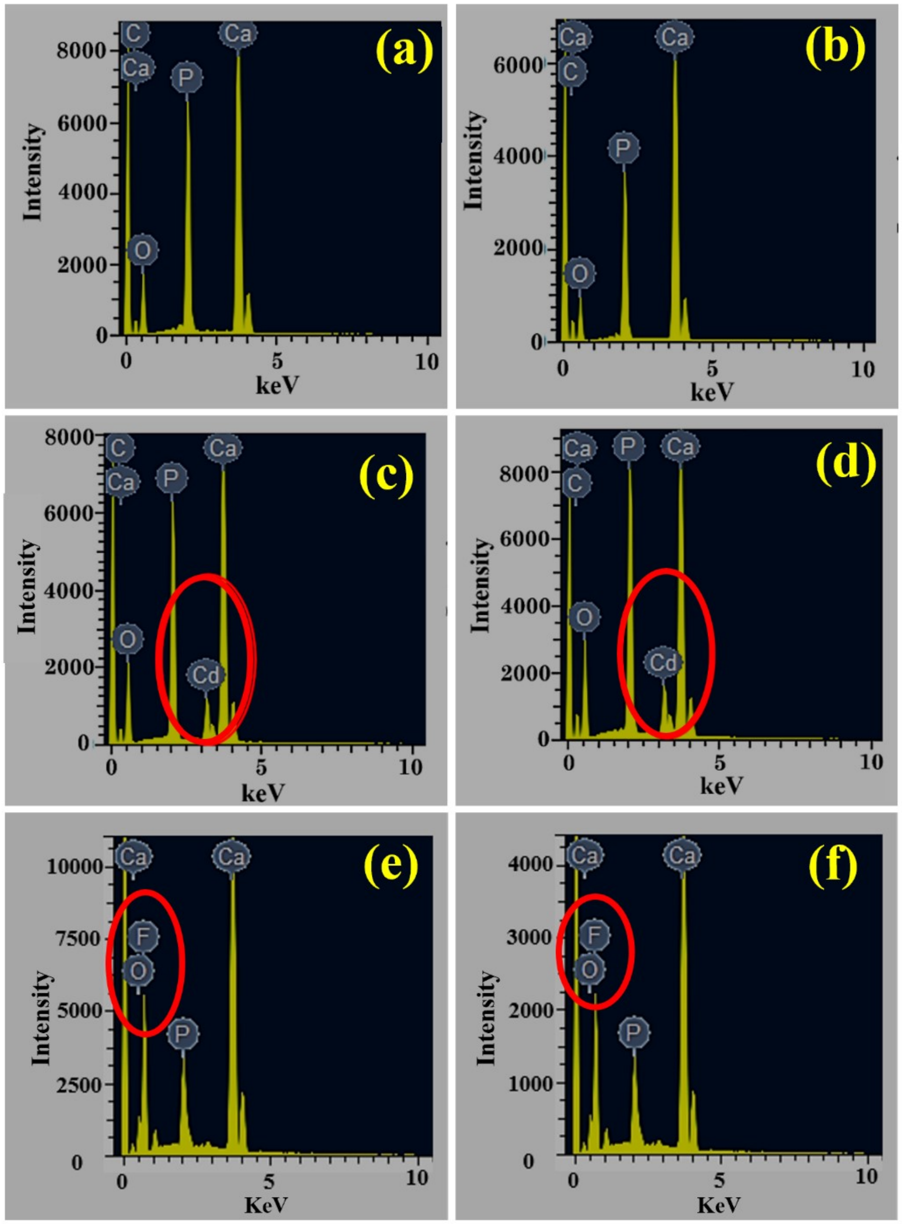

Fig. S10 EDX analysis of prior to and after Cd^{2+} and F^{-} adsorption spectrum: (a) VD-HAp, (b) FD-HAp, (c) VD-Cd, (d) FD-Cd, (e) VD-F, and (f) FD-F.

Table S1. Structural parameter of before and after Cd^{2+} adsorbed VD-HAp and FD-HAp

Adsorbents	Lattice parameter (± 0.01 Å)		Unit cell volume (± 1 cm^3)	Crystallite size (± 1 nm)
	a=b	**c**		
VD-HAp	9.35	6.81	519.85	13
VD-Cd	9.30	6.76	513.25	12
FD-HAp	9.41	6.86	517.69	9
FD-Cd	9.33	6.75	508.56	7

Table S2. BET analysis

Adsorbents	Pore volume (± 0.03 cc/g)	Pore size (± 0.5 nm)	Specific surface area (± 1 m^2/g)
VD-HAp	0.234	9.3	130
FD-HAp	0.264	5.5	150

Table S3. Structural parameter of before and after F^- adsorbed VD-HAp and FD-HAp

Adsorbents	Lattice parameter (± 0.02 Å) of FAp		Lattice parameter (± 0.02 Å) of CaF_2	Volume of the unit cell of FAp (± 1 cm^3)	Volume of the unit cell of CaF_2 (± 1 cm^3)	Crystallite size (± 1 nm)
	a=b	c	a=b=c			
VD-F	9.35	6.87	5.41	521.46	158.59	45
FD- F	9.17	6.89	5.48	526.58	165.31	30