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Prospective chemisorption of fluoride utilizing coastal molluscan (*Crassostrea Sp.*) shell from phosphatic fertilizer pond wastewater, Paradeep, Odisha

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The present study explores the utilization of very acidic (pH 1.46) and high fluoride (F-) containing (9290 ppm) phosphatic fertilizer industry (Paradeep, Odisha, India) pond wastewater (PW) generated from phosphogypsum (PG) stacks by using Crassostrea Sp. molluscan shell (MS) as an adsorbent. F- chemisorption batch experiments on molluscan shells (MS) powder (212 - 500 micron) varying 6 different MS (Solid-S) to PW (Liquid-L) i.e. S/L ratios (1: 8 to 1: 30), time (0.08 to 48 hours) and fluoride concentration (4645 – 8361 ppm) as diluted PW. Chemisorption of F- peaked with 1: 20 S/L ratio at 24 hrs and its concentration in the supernatant reduced by 99.9 %. XRF, FTIR and XRD analysis of MS and its chemisorbed residues confirmes the role of relatively high calcium containing MS (72 % CaO) towards formation of Fluorapatite (FA) [Ca5(PO4)3F]. Desorption experiments of FA residue for 24 hrs, highlights the stability of F- chemisorption process on MS, which is confirmed by presence of FA in desorbed residue through XRD analysis. The research findings establish prospects of F- recovery from PW through chemisorption process utilizing selected MS.

Keywords: Chemisorption, Fertilizer industry, Fluorapatite, Fluoride, Molluscan shell, Pond wastewater

Phosphate fertilizer industry pond wastewater (PW) is highly acidic (around *p*H 2) and primarily contains F^- and phosphate along with other trace elements (Ca^+, NaH_4^+, Mg^{2+}, Cl and K^+)[1]. The concentration of F^- in PW showed variation depending on site locations and seasonal time with its value ranged from 3000 to 13000 ppm as reported by Florida Institute of Phosphate Research[2]. Other than phosphate fertilizer industries, aluminum fluoride, semiconductor, electroplating, glass, ceramic and steel producing industries also produces fluoride containing wastewater[3,4]. The wastewater from these industries is an important anthropological source of F^- contamination to the nearby environment, in particular to the groundwater table[5,6].

Till recent, very few studies reported about prospective chemisorption of fluoride from highly concentrated industrial wastewater. Majority of earlier works were focused on synthetic wastewater and low F^- contaminated drinking water. Among several defluoridation procedures like adsorption, precipitation, electro-coagulation, membrane filtration, ion exchange etc. chemisorption was widely explored[7,8]. Calcareous egg shell and related nano-hydroxyapatite powder, activated coconut shell carbon, bone-char, synthetic apatites, zirconium ion impregnated coconut shell carbon, calcite (99 % pure) and acetic acid treated calcite (90 - 97 % $CaCO_3$) were utilized as F^- adsorbents[9-16]. Recent study highlighted the use of naturally occurring mollusc shells alone and its composite (lateritic soil and Gastropod shell) for treatment and defluoridation of synthetic and groundwater[17]. Among molluscan shells (MS), modified bivalve, oyster shells are widely explored for removal of F^- and other pollutant from industrial effluents with initial concentration of 100 ppm[18]. Reaction of bone char (hydroxyapatite) and modified bone char with F^- of wastewater resulted into formation of fluorapatite [$Ca_{10}(PO_4)_6F_2$] and CaF_2 respectively[19] depending on F^- concentration. In present study, worldwide distributed, relatively large, massive and higher calcium oxide (47.49 %) containing *Crassostrea* mollusc dead shells were utilized directly for the prospective single step chemisorption of F^- [20,21]. The phosphogypsum pond wastewater samples utilized in the experiments were collected from Paradeep Phosphate Limited (PPL), Paradeep, Odisha, India. The research work investigated the scope of prospective F^- chemisorption along with fluoroapatite production using selected MS and phosphatic fertilizer industries high F^- containing PW.

Experimental Section

Materials

Collection and processing of MS and PW

Coastal molluscan shell (MS) of genus *Crassostrea* collected from intertidal zone of Gangasagar beach, West Bengal (21°31' - 21°53' N latitudes and 88°02' - 88° 15' E)[22]. MS were thoroughly cleaned using tap as well as distilled water, oven dried at 60^o C for 12 hrs and crushed-ground using granitic mortar and pestle. The particle size of powdered shells utilized for F^- chemisorption were 212-500 µm separated by sieving though 500 µ (ASTM 35) to 212 µ (ASTM 70) standard sieves.

PW were randomly collected in a polypropylene jar (50 liters) with the help of plastic bucket from 10 different sites of Paradeep Phosphate Limited (PPL) fertilizer industries (20º16’56” N and 86º38’52” E) in May 2019. The original and diluted PW (variation in F^-concentration) were utilized in chemisorption reaction.

Methods

Chemisorption and desorption batch experiments

Initially to optimize the S/L ratio for maximum chemisorption of F^-, different volumes of PW (8 to 30 ml) were added to 1 g of MS in 100 mL screwed stopper conical flasks and agitated in water bath shaker for 1 hr with 20 rpm at ambient temperature. Thereafter optimized S/L ratio towards maximum F^- chemisorption, the experiments were conducted to assess the influence of contact time (0.08 to 48 hrs) along with varying fluoride concentration (4645 - 8361 ppm) in the form of diluted PW. The experiments were conducted in triplicate and average values were reported.

The fluoride adsorption efficiency was calculated using the following equation

$$E = (C_0 – C_f) / C_0 \times 100$$

where E (%) – efficiency of F^- removal, C_0 – Initial F^- concentration, C_f – Final F^- concentration

The chemisorbed residues (MS-AD) produced at 24 hrs with S/L ratio of 1:20 were desorbed for 0.08 to 24 hrs with distilled water at a fixed ratio. For both chemisorption and desorption experiments, their respective residues (MS-AD and MS-D) and filtrates were separated by centrifugation of chemisorbed MS suspension followed by filtration using Whatman 42 filter paper.

*p*H and F^- in filtrate were measured using OAKION (Model: *p*H/ION 700) *p*H /mV/Ion/°C/°F meter with F^- ion selective electrode following standard method. Phosphate ion estimated by 4500-P E ascorbic acid spectroscopy method (λ 880 nm) using Cary-series UV-Vis-NIR spectrophotometer product no G9825A[23]. Sulphate concentration estimated by turbidity meter HACH (TL2300). Analytical grade chemicals and plastic apparatus were used in analysis. Total C of MS was estimated by SHIMADZU (model: TOC-L-CPH, serial no: H54435602507 CD). The FTIR and XRF of MS, MS-AD and MS-D were recorded by IR spectrometer (model: BRUKER ALPHA II, 4000-500 cm^{-1}) and XRF instrument (Malvern Panalytical Model Zetium 4.0 kW). Minerals phases of samples identified by X-ray diffraction (diffractometer: X’PERT PRO, PANalytical, Netherlands) using Cu Kα radiation source (wavelength 1.54060 nm) at 40 kV and 30 mA with scanning range of 2θ (10 to 80°). Field emission scanning electron microscope (FESEM, model ZEISS SUPRA55) with energy dispersive spectroscope (EDS) utilized for studying surface morphology and proximate elemental composition in the samples.

Results and Discussion

Characterization of MS, MS-AD, MS-D and PW

Crassostrea Sp. MS were larger in length (14 - 21 cm) and breadth (8 - 12 cm) along with massive size (average 324 g/valves). FESEM image with EDS, XRF based elemental chemical composition (Fig. 1), FTIR peaks and XRD of MS, MS-AD and MS-D are given in Table 1, (Fig. 2) and (Fig. 3) respectively. FESEM images of powdered MS appeared as small sheet with beads like structures and EDS analysis pointed about C (13.26%), O (62.95%) and Ca (23.79%) as major elemental composition. The XRF estimate of percentage of Calcium oxide (CaO) was 72 % in solid matrix of MS. In different species of *Crassostrea,* the value of Calcium (as CaO) as the primary elemental component constituted 47.49 % and as Calcium carbonate ranged from 91 to 95 %[20, 24]. The broad FTIR spectra at 3441 cm^{-1} in MS-AD and 3457 cm^{-1} in MS-D were recorded and it relates to stretching vibrations of –OH groups[25]. Strong IR bands at 713 and 1447 cm^{-1} in MS reflected about C-O groups of calcite[26.]. In MS-AD a

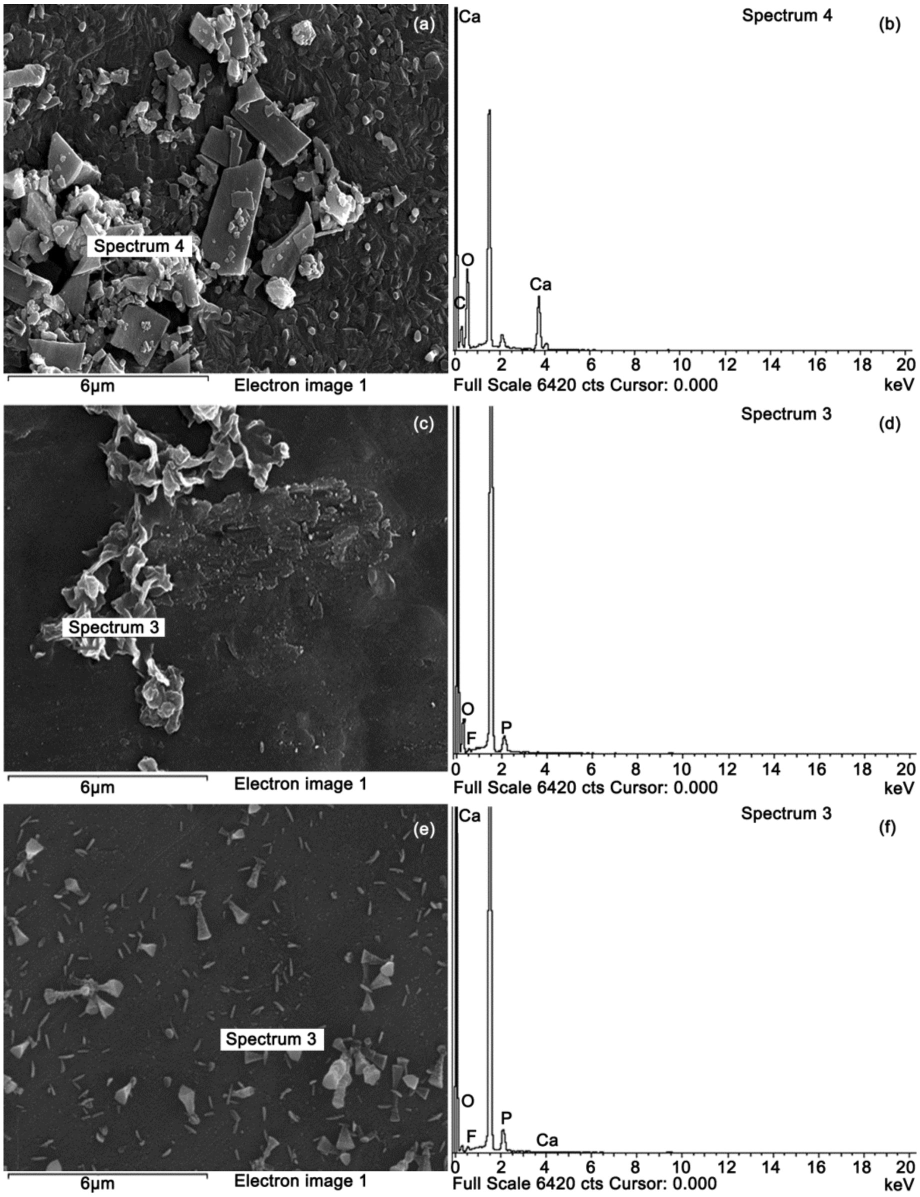

Fig. 1 — [a], [c], [e] FESEM images and [b], [d], [f] EDS of MS, MS-AD and MS-D

Table 1 — XRF elemental composition (% oxides) of MS, MS-AD and MS-D

Samples	CaO	SO_3	SiO_2	P_2O_5	F^-	Others (Na_2O,MgO, Fe_2O_3)
MS	72	0.6	0.35	0.11	NIL	26.94
MS-AD	51	2.8	2.43	21.79	18.74	3.24
MS-D	53	2.3	2.17	21.79	17.56	3.18

weak IR band (1431 cm^{-1}) and strong IR band (1057 cm^{-1}) highlighted about C-O and P-O functional groups respectively. In MS-D also IR band at 1057 cm^{-1} was recorded. The major XRD peaks (2θ) at 29.43 were identified in MS and it confirmed about dominant calcite minerals. Whereas, in MS-AD and MS-D (2θ) peaks related to fluorapatite at 31.99 and 31.76 respectively were measured (JCPDS reference data files 01-087-2462 and 01-082-1109).

The *p*H of PW was estimated 1.46 and was highly acidic. It was analyzed and found presence of high fluoride content (9290 ppm) along with other acidic constituents viz phosphate (8600 ppm), sulphate (760 ppm) etc. in PW. The acidic pH of composite

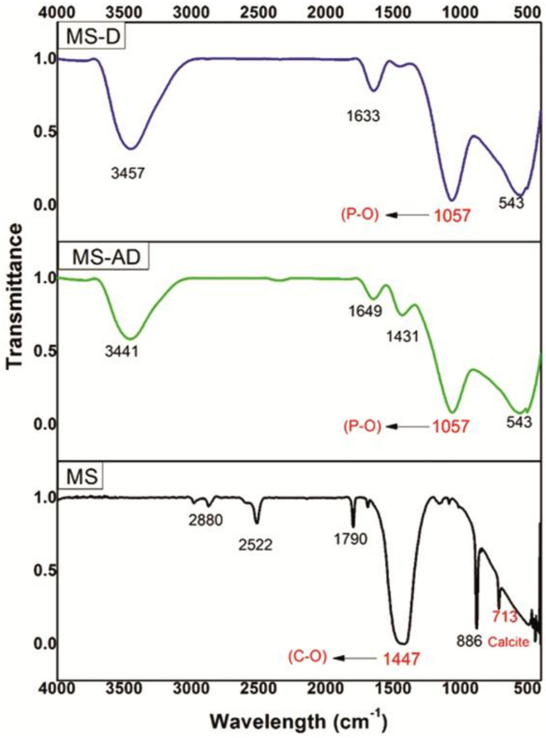

Fig. 2 — FTIR peaks of MS, MS-AD and MS-D

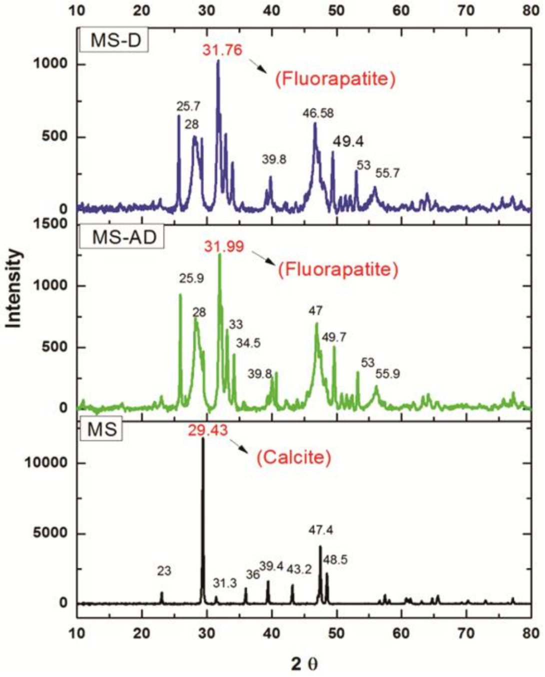

Fig. 3 — XRD of MS, MS-AD and MS-D

PW from phosphate industry was due to the same anions F^- (7600 ppm), P (6600 ppm), S (1695 ppm) and Cl (10-300 ppm) [27]. In PW the dominant forms of fluoride were HF (free) and H_2SiF_6 (bound) [28].

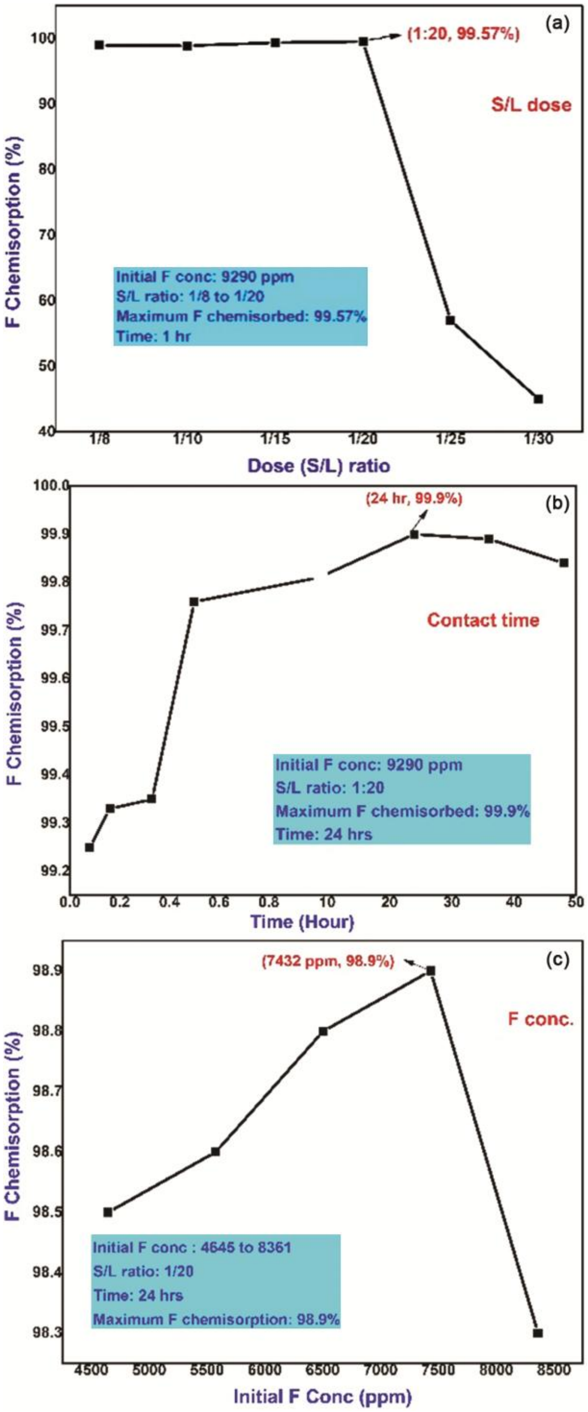

Fig. 4 — F^- Chemisorption by MS as a function of [a] S/L dose [b] Contact time and [c] F^-concentration in PW

Effect of S/L ratio, Contact time and F^- concentration on chemisorption

F^- chemisorption by MS from PW was very high and ranged 98.96 to 99.57 % with varying S/L ratios 1: 8 to 1: 20 for one hour reaction time [Fig. 4(a)]. Subsequently the Percentage of F^- chemisorption was decreased sharply to 57 % and 45 % with S/L ratios of 1: 25 and 1: 30 respectively. Decrease in F^- chemisorption was mainly due to complete exhaustion of active calcite surface at 1:20 S/L ratio. Although similar trend of F^- adsorption was highlighted by graphite with dose 250 mg/50ml in 60 min with initial F^- concentration 4 mg/L[29], but studies on natural wastewater (with high F^- concentration) is scarce.

Maintaining the optimum S/L (1: 20) ratio for higher F^- chemisorption, experiments were repeated with different contact times from 0.08 to 48 hrs. Fig .4[b] depicts immediate increase in F^- chemisorption Percentage in first 0.08 hrs (99.25%) and thereafter gradual increase up to 24 hrs (99.9%) and beyond, it decreased but very slowly up to 48 hrs[30]. It confirms the reaction of F^- and phosphate with calcite surface is very fast.

Based on optimum S/L ratio (1 : 20) and contact time (24 hrs) for maximum F^- chemisorption, experiments with variable F^- concentrations (4645 - 8361 ppm) by diluting PW were undertaken to determine the role of F^- concentration on chemisorption. Rate of F^- chemisorption increased slightly with increasing F^- concentrations[31] from 4645 to 7432 ppm i.e. 98.5 to 98.9% (Fig 4. [c]) this could be due to high Ca content and F^- binding capacity of calcite. Thereafter, chemisorption of F^- showed slight decrease to 98.3% at 8361 ppm, which may be due to unavailability of effective chemisorption area. Similar findings were reported for Bivalve and Oyster shell powder which showed 98% to 99% removal of F^- along with other metals[32]. Contrasting results were reported by egg shell as well as hydrated cement where decrease in F^- removal percentage linked with increasing initial F^- concentration due to unavailability of active sites[8, 33].

Chemisorption of F^- from PW by MS resulting MS-AD (Fluorapatite) production and desorption

F^- ions have a tendency to react with calcium bearing adsorbents like calcite and leads to formation of different calcium-fluoride bearing minerals like fluorite or apatite (if PO_4^{3-} as a component of adsorbate). Product synthesis in this reaction dominantly depends upon *p*H along with co-ions present in reaction mixture. At *p*H < 2 removal of F^- was maximum by powdered and granular $Ca_3(PO_4)_2$ and abruptly reduced with alkaline *p*H[34]. As earlier reported, Presence of F^- ions in solution facilitates binding of PO_4^{3-} ions with calcite and results into synthesis of apatite but opposite is hindered[35]. According to PHREEQ model F^- precipitates on calcite surface as CaF_2 even in presence of PO_4^{3-} only at *p*H < 1.6[36]. In the present study the role of pH is prominent i.e. at *p*H 4.54 maximum chemisorption (99.57 %) of F^- takes place in presence of high PO_4^{3-} and resulted into fluorapatite (MS-AD) synthesis, as in equation 1. Synthesis of fluorapatite also reported earlier where chemisorption of F^- from PG by ($CaHPO_4 \cdot 2H_2O$) of reagent grade in aqueous medium[37].

$$5CaCO_3 + 3H_3PO_4 + HF \rightarrow Ca_5(PO_4)_3F + 5H_2O + 5CO_2 \quad \ldots (1)$$

(Calcite) (Fluorapatite)

Desorption of MS-AD in distilled water at 1:20 ratio for 0.08 to 24 hrs (Fig. 5) highlighted the strength and solubility of fluorapatite mineral. Very less amount of F^- ions were leached out from MS-AD i.e. 15 ppm in first 0.08 hour and maximum 35 ppm detected in 24 hrs.

FESEM (Rod like structure) and EDS in Fig. 2 [c], [d] of MS-AD gave the clue about appearance of Ca, P and F^- elements in chemisorbed residue. XRF data in Table.2 clarified the appearance of F^- and PO_4^{3-} in MS-AD which was initially absent in MS and remained in MS-D after desorption. Later FTIR peaks analyzed to determine the nature of functional groups present in MS-AD and MS-D. The strong IR peaks at 1057 cm^{-1} in both MS-AD and MS-D (in the range of 1037.75 -1093.69 cm^{-1}) is due to the stretching and bending modes of phosphate in the fluorapatite spectrum[38,39]. This peak conformed formation of chemically strong bond by chemisorption of F^- and

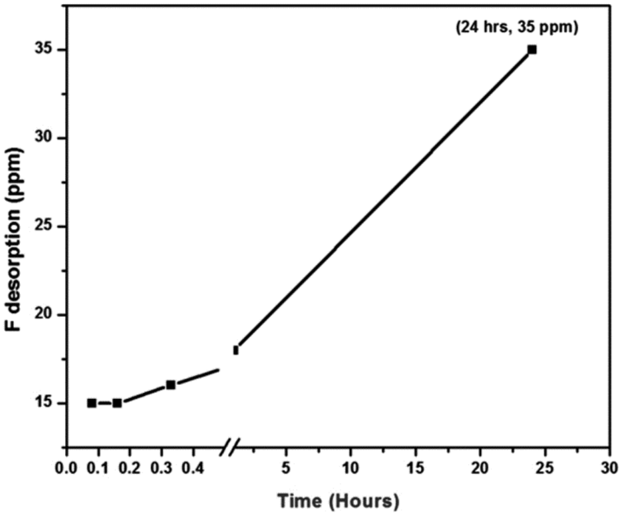

Fig. 5 — Desorption curve of MS-AD (MS-AD: DW ratio 1: 20, time 0.08 to 24 hrs)

phosphate of PW by calcite of MS. Further the process of chemisorptions was supported by XRD patterns of MS, MS-AD and MS-D (Fig. 3). Comparing the 2θ and d-spacing values of MS with MS-AD, the shifting of calcite peak from 29.436 (3.03188) to 31.991 (2.79532) suggested chemisorptions of fluoride and PO_4^{3-} by calcium on calcite surface. Further appearance of similar peaks with 2θ value of 31.99 and 31.764 in MS-AD and MS-D respectively confirmed the presence of stable compound fluorapatite in both. Similarity in the 2θ and d-spacing value of all residues with registered patterns of JCPDS reference data files, it was concluded that fluorapatite [$Ca_5(PO_4)_3F$] was formed in MS-AD (01-087-2462) which remained in MS-D (01-082-1109) with slight differences in crystal structures. The crystalline structure of fluorapatite is hexagonal with space group P 63/m and unit cell dimensions of a = b =9.364 ˚A, c =6.881 ˚A.

Conclusion

The present research work highlight the scope of recovering F^- from phosphate industries pond wastewater by chemisorption process utilizing selected *Crassostrea* coastal molluscan shell. The experimental results confirmed the role of relatively high proportion of calcium towards their chemical reaction with F^- present in highly acidic pond wastewater of phosphatic fertilizer industry. Also, the maximum F^- chemisorption was achieved at about 24 hours with S/L ratio of 1: 20. The research outcome also highlights the feasibility of fluorapatite formation due to chemisorption on molluscan shell. The present research work not only deciphered an alternative method of F^- recovery from pond wastewater, but also has prospects towards minimization the pollution risks.

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References

1 Mbarka G, Mongi F & Sami S, *Environ Prog Sustainable Energy*, 33 (2013) 463.
2 George A. K, Myra M S, Sandra J M, Jerry D C & Jon L D, *FIPR* (1992) 1.
3 Abdessalem E, Ahmed B, Ahmed H & Nasr B, *Desalin Water Treat*, 54 (2014) 1.
4 Vahid K, Ali T, Fatemeh J & Gholamali H, *J Hazard Mater*, 179 (2010) 276.
5 Kumar S, Gupta A & Yadav J D, *Indian J Chem Technol*, 14 (2007) 355.
6 Chowdhury A, Adak M K, Mukherjee A, Dhak P, Khatun J & Dhak D, *J Hydrol*, 574 (2019) 333.
7 Essadki A H, Gourich B, Vial C , Delmas H & Bennajah M, *J Hazard Mater*, 168 (2009) 1325.
8 Habuda-Stanić Mirna, Ravančić Maja Ergović & Flanagan Andrew, *Mater*, 7 (2014) 6317.
9 Bhaumik R, Mondal N K, Das B, Roy P, Pal K C, Das C, Banerjee A & Datta J K, *E J Chem*, 9 (2012) 1457.
10 Kiley Workeneh, Enyew Amare Zereffa , Toshome Abdo Segne, & Rajalakshmanan Eswaramoorthy, *J Nanomater*, 2019 (2019) 1.
11 Mateso Said & Revocatus L Machunda, *IJSR*, 3 (2014) 2327.
12 Naohito Kawasaki, Fumihiko Ogata, Hisata Tominaga & Isao Yamaguchi, *J Oleo Sci*, 58 (2009) 529.
13 Ahmed Yehia & Khaled Ezza, *Adscript Sci Technol*, 27 (2009) 337.
14 Sai Sathish R, Raju N S R, Raju G S, Nageswara Rao G, Kumar A K & Janardhana C, *Sep Sci Techno*, 42 (2007) 769.
15 Turner B D, Binning P & Stipp S L S, *Environ Sci Technol*, 39 (2005) 9561.
16 Mondal P, George S & Mehta D, *Res J Chem Sci*, 4 (2014) 62.
17 Oladoja N A, Bello G A, Helmreich B, Obisesan, S V, Ogunniyi J A, Anthony E T & Saliu T D, *Sustain Chem Pharm*, 12 (2019) 1.
18 Naik S, Megha B S, Aishwarya J & Shwetha, *Res J Chem Environ Sci*, 4 (2016) 123.
19 Susan S A Alkurdi, Rued A Al-Juboori, Jochen Bundschuh & Insane Hamawand, *Environ Int*, 127 (2019) 704.
20 Geographic distribution of oysters and study area. Sodhganga, 10603/90946/9/09 - chapter4.
21 John A T & Mary J, *J Mar Biol Aqua*, 2 (2016) 1.
22 Dey M, Jamadar Y A & Mitta A, Rec Zool. Surv India, 105 (2005) 25.
23 Standard Methods For the examination of water and wastewater 4500-P-E, American Public Health Association (APHA), New Yoyk 1992.
24 Hamester M R R, Balzer P S & Becker D, *Mater Res*, 15 (2012) 204.
25 Claoston N, Samsuri A W, Ahmad Husni M H & Mohd Amran M S, *Waste Manag Res*, 32 (2014) 331.
26 Onward R, Chainmail R, & Baruah G D, *Indian J Pure Appl Phys*, 42 (2004) 812.
27 Ostara Nutrient Recovery Technology, US pat 2019/0106348 A1, 11 Apr 2019.
28 Gouider M, Feki M & Sayadi S, *J Hazard Mater*, 170 (2009) 962.
29 Karthikeyan M & Elango K P, *Indian J Chem Technol*, 15 (2008) 525.
30 Sivasankari C & Arulanantham A, *Indian J Chem Technol*, 21 (2014) 70.

31 Kitano Y, Okumura M & Idogaki M, *Geochem J*, 12 (1978) 29.
32 Turner B D, Binning P J & Sloan S W, *Environ Eng Sci*, 27 (2010) 643.
33 Tafu M & Chohji T, *J Eur Ceram Soc*, 26 (2006) 767.
34 Karthikeyan M & Elango K P, *J Environ Sci,* 21 (2009) 1513.
35 Dobaradaran S, Nabipour I, Mahvi A H, Keshtkar M, Elmi F, Amanollahzade F & Khorsand M, *Fluoride*, 47 (2014) 253.
36 Weerasooriyagedra M S & Kumar S A, *Int J Sci Res Publ*, 8 (2018) 282.
37 Kagne S, Jagtap S, Dhawade P, Kamble S P, Devotta S & Rayalu S S, *J Hazard Mater*, 154 (2008) 88.
38 Mobasherpour I, Heshajin M S, Kazemzadeh A & Zakeri M, *J Alloys Compd*, 430 (2007) 330.
39 Eisa M Y, Dabbas M A & Abdulla F H, *Int J Curr Microbiol App Sci*, 4 (2015) 270.