SYNTHESIS AND CHARACTERIZATION OF LAYERED DOUBLE HYDROXIDE NANOSTRUCTURES AND THEIR APPLICATION IN THE REMOVAL OF Fe^{2+} AND Ca^{2+} IONS FROM OIL WELLS

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ABSTRACT

Four new metal-aluminum layered double hydroxides (LDHs): Mg-Al$(OH)_2PO_4$ **1**, *Mg-Al$(OH)_2PO_4PF_6$* **2**, *Ca-Al$(OH)_2SO_4$,* **3** *and Ca-Al$(OH)_2PO_4PF_6$* **4**, *were prepared by co-precipitation method followed by mild hydrothermal processing at 60 ° C. Mg^{2+} and Ca^{2+} in solution with Al^{3+} was titrated with NaOH over 3-5 h to yield Mg-Al and Ca-Al layered double hydroxides, respectively, incorporating PO_4^{3-}, $PO_4^{3-}PF_6^-$ and SO_4^{2-} anions in the inter-lamellar spaces. The isolated compounds were characterized with the help of XRD, IR, SEM/EDAX and their ability to remove scale forming ions from aqueous system was studied with the help of Atomic Absorption Spectroscopy (AAS). The SEM micrographs of Mg-O-Al-OH and Ca-O-Al-OH layers intercalated with PO_4^{3-} and / or $[PO_4PF_6]^{4-}$ anions are similar consisting of uniform nano- spheres with average size of 100 nm, while the M-O-Al-OH layer of compound* **3**, *intercalated with SO_4^{2-} anions consists of hexagonal nano-plate crystals. In the infrared spectra, the characteristic absorption band for water molecules was observed in all the compounds. The XRD pattern showed that d_{012} and d_{104} peaks of M-Al-PO_4 LDHs corresponding to interplanar spacing of 3.4804 and 2.5504 Å respectively, shifted to higher 2θ values for M-Al-PO_4PF_6 system, which indicates a decrease in the interlamellar spacing as PF_6^- was incorporated along with PO_4^{3-} anion. The XRD pattern for Ca-Al-SO_4 LDHs was quite different, showing the presence of low angle peaks at $2\theta = 11.68$ and 14.72°. The results of the column adsorption studies showed that there was a significant removal of Ca^{2+} by all the compounds under investigation with efficiency of 84 -99 %. Whereas compounds 1 and 2 removes Fe^{2+} effectively with efficiency of 98.73 and 99.77 %, respectively, compounds 3 and 4 were shown to have little or no effect.*

Keywords: *Layered double hydroxides, nanospheres, nanoplates, adsorption, nanostructures*

INTRODUCTION

Recently, it has been reported that as gas and oil production progresses, in many oil fields, the ratio of produced brine water to hydrocarbon often increases. These brines are corrosive and tend to produce calcite or sulfate scales [1, 2]. Scaling, which stems from supersaturation of mineral ions in the process fluid, is the deposition of a mineral salt on processing equipment. A natural gas well will, besides producing natural gas, also produce water and carbon dioxide (CO_2). The produced water can come from two sources: water vapor in the gas that condenses into liquid water and formation water containing salts [3]. This water is the source of hydrate formation and in combination with CO_2, forms a weak carbonic acid (H_2CO_3), as shown in equation 1. Scaling is caused by salts and can occur when the produced water contains formation water [4].

$$CO_2\ (g) + H_2O\ (l) = H_2CO_3\ (aq) \tag{1}$$

This carbonic acid will continue to dissociate hydrogen, creating new deprotonated species of carbonic acid, as seen in equations 2 and 3.

$$H_2CO_3\ (aq) + H_2O\ (l) = H_3O^+\ (aq) + HCO_3^-\ (aq) \tag{2}$$
$$HCO_3^-\ (aq) + H_2O\ (l) = H_3O^+\ (aq) + CO_3^{2-}\ (aq) \tag{3}$$

In the water mixture there will be a mixture of H_2CO_3, HCO_3^- and CO_3^{2-}. Finally, in the presence of calcium and carbonic acid, calcium carbonate will precipitate out [5, 6].

$$CO_3^{2-}\ (aq) + Ca^{2+}\ (aq) = CaCO_3\ (s) \tag{4}$$

The Composition of the formation water varies greatly with the reservoirs, but the usual constituents are Na^+, Ca^{2+}, K^+, Mg^{2+}, Fe^{2+}, Cl^-, SO_4^{2-} and HCO_3^-. Long pipelines are constructed of carbon steel [6]. Carbonic acid will corrode the iron in the pipeline wall, producing iron carbonate. This iron carbonate can precipitate in the production fluid and follow the gas and liquid flow, causing problems downstream.

$$Fe\ (s) + H_2CO_3(aq) = FeCO_3(s) + H_2(g) \tag{5}$$

The formation of scale blockage inside oil wells constricts the flow of geothermal fluids in these wells thus significantly reducing their output [7]. Furthermore, fresh water and marine sediments are contaminated by oil spills along with urban runoffs, industrial and domestic effluents. This poses a serious concern as the presence of contaminants affects aquatic organisms. Inorganic nanomaterials with well-defined cavities and surfaces have great potential for remediating today's environmental and industrial problems [8]. Nanostructured layered double hydroxides (LDHs) are promising materials in waste water treatment due to their ability to capture organic and inorganic anions [9,10].

Layered double hydroxides (LDHs) are a class of anionic clays with the structure based on brucite ($Mg(OH)_2$)-like layers [11-15]. The lattice structure of LDHs with the general formula $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot yH_2O$, have a positively charged brucite-shaped layers, consisting of a divalent metal ion M^{2+} (e.g., Ca^{2+}, Zn^{2+}, Mg^{2+}, and Ni^{2+}) octahedrally surrounded by six OH^- hydroxyl groups [16-18]. The substitution of the M^{2+} metal with a trivalent M^{3+} cation gives rise to the periodic repetition of positively charged sheets (lamellas) alternating with charge-counter balancing A^{n-} ions. These LDHs have found wide spread applications in diverse areas as sensors [19-20], adsorbents in waste water treatment [21], catalytic removal of soot and NOx in vehicle engine exhausts [22] and as drug and gene carriers [23-25].

During the course of our investigation of LDHs as scale inhibitor, we were interested in using Mg and Ca as divalent metal ions to prepare Mg-Al and Ca-Al layered double hydroxides intercalated with PO_4^{3-}, PO_4^{3-}/PF_6^- and SO_4^{2-} anions and we have been successful in synthesizing four new LDHs with nanostructures viz: Mg-$Al(OH)_2PO_4$ 1, Mg-$Al(OH)_2PO_4PF_6$ 2, Ca-$Al(OH)_2SO_4$, 3 and Ca-$Al(OH)_2PO_4PF_6$, 4. In this work, the synthesized LDHs nanostructures is being investigated as nano-filtration materials to remove scale forming ions like Fe^{2+} and Ca^{2+}. The synthesis, characterization and adsorption properties of these four new compounds have been reported.

MATERIALS AND METHOD

Materials

Ortho phosphoric acid (H_3PO_4), magnesium nitrate $Mg(NO_3)_2$, aluminum sulphate [$Al_2(SO_4)_3$], sodium hydroxide (NaOH), sulphuric acid (H_2SO_4), aluminum hydroxide $Al(OH)_3$, calcium nitrate tetrahydrate [$Ca(NO_3)_2.4H_2O$], 1-butyl-3-methyl-imidazolium hexafluorophosphate ($BMIMPF_6$). Analytical grade of all the chemicals were obtained from commercial sources and used without further purification.

Method

The standard procedure of co-precipitating a divalent with trivalent metal ions in the presence of a base was followed in the present studies [26-29]. The co-precipitation was carried out at room temperature and the gel was continuously and magnetically stirred. The mixture was kept under magnetic stirring for 3 h. The precipitate was heated in the mother liquor for 18 h at 60°C, and then it was washed with distilled water and separated by centrifugation. The resulting material was dried overnight at 70 ºC in the incubator. In compound 1, orthophoshoric acid was used as the source of the PO_4^{3-} anion. For compounds 2 and 4, 1-Ethyl-3-methylimidazoliumhexafluorophosphate and orthophosphoric acid were used to introduce PF_6^- and PO_4^{3-} anions respectively. In compound 3, the source of the SO_4^{2-} anion was H_2SO_4. In a typical synthesis of **1**, a 250 mL solution containing $Mg(NO_3)_2$ (0.0375 mmol), $Al(OH)_3$ (0.0125 mmol) (with Mg-Al ratio of 3:1,) and H_3PO_4 (0.5 mmol) was added dropwise from burette into a 15 mL solution of NaOH (2 M) under constant stirring at room temperature for 3 h. The mixture with a pH of 10 was heated at 60 °C for 18 h and the resulting slurry was collected via centrifugation (10 min, 500 min^{-1}). The product was washed thrice with deionized water before drying. Similar procedure was used for compounds 2-4, the difference being in the metal and SO_4^{2-} ions for compounds 3 and 4.

Characterization

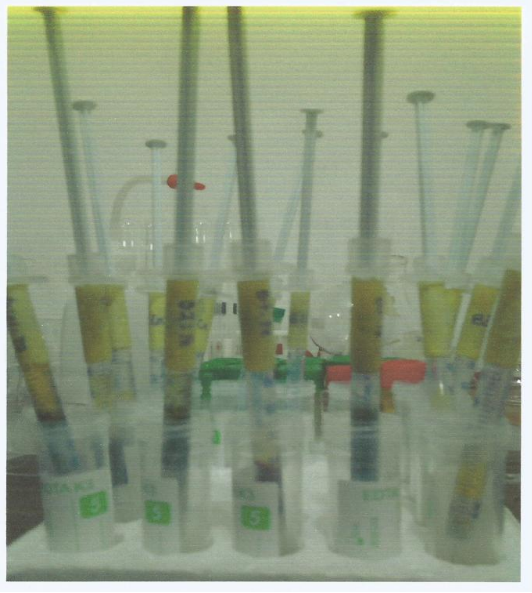
The samples were analyzed by Rigaku MiniFlex II X-ray diffractometer using monochromatic Cu Kα radiation (λ = 0.1541nm) at the speed of 3s in 2θ range between 5 - 75^0 and step size of 0.03.

The scanning electron microscopy (SEM) studies of the LDHs were made with a Field Emission Electron Microscope (FESEM JSM-6700 F), coupled with an energy dispersion analyzer (EDX). The specimens were Au coated (sputtering) to make them conductive. The SEM acceleration voltage was 10 kV

The Fourier transform infrared (FTIR) spectra for the synthesized LDHs were recorded over the wave number range of 400 - 4000 cm^{-1} using Perkin Elmer FTIR spectrometer. The powdered samples were mixed with KBr (in a 1: 200 ratio of their weight) and pressed in the form of pellets for measurement.

Adsorption Column Experiments

Aqueous solutions of Fe^{2+} and Ca^{2+} prepared from their salts $FeSO_4.7H_2O$ and $CaCl_2$, respectively were analyzed by atomic absorption spectroscopy. The Column was set up by packing 5 g of LDHs in 20 mL syringes and the metal ion solution poured through the packed samples as filter (Scheme 1). The metal ion solutions collected at the outlet of the LDH column, the eluded portion (i.e. the filtrate) were also analyzed by AAS. The removal efficiency of Fe^{2+} and Ca^{2+} by the LDHs in percentage was calculated using the formula: $Efficiency\,(\%) = \frac{C_e}{C_o}$ (C_o = initial concentration of the ions, C_e = eluded concentration of the ions after passing through the packed column).



Scheme 1. The experimental set up for the column adsorption studies

RESULTS AND DISCUSSION

All the metal-aluminum layered double hydroxides were prepared by co-precipitation method followed by mild hydrothermal treatment at 60 °C. Divalent metal ions (Mg and Ca) in solution with Al^{3+} titrated with NaOH over 3-5 h yielded Mg-Al and Ca-Al layered double hydroxides, respectively. In the present studies, SO_4^{2-}, PO_4^{3-} and PF_6^- anions were used in the interlamellar space to balance the layer positive charge. The conditions chosen for the synthesis provided an aqueous solution of Al^{3+} and M^{2+} (molar fraction $Al^{3+}/(Al^{3+} + M^{2+}) = 0.25$ and $M^{2+} /Al^{3+} = 3$ molar ratio), prepared by dissolving metal salts in distilled water to give M^{2+}-Al–LDH with 'x' around 0.25 (i.e. the composition is more likely represented by $M^{2+}_{0.75}Al_{0.25}(OH)_2A^{n-}_{x/n}\cdot yH_2O$. Where x/n = 0.083, 0.0625 and 0.123 respectively, for $A^{n-} = PO_4^{3-}$, $[PO_4PF_6]^{4-}$ and SO_4^{2-}).

Figure 1 shows the FTIR spectra of the isolated layered double hydroxides. The characteristic absorption band for the water molecules was observed in all the compounds. The band observed in the region 3402 - 3455 cm^{-1} corresponds to the OH stretching vibration, while the band at 1640 cm^{-1} is attributed to the bending mode of the lattice water. The stretching vibrational modes of PO_4^{3-} or SO_4^{2-} units were observed in the region 1067 – 1029 cm^{-1}. The bands in the region 500-400 cm^{-1} are attributable to the M –O vibrations. The various assignments are in good agreement with similar compounds in literature [28 -35].

Figure 2 shows the representative XRD patterns of the M-Al LDHs. The X-ray powder diffraction lines of Mg-$Al(OH)_2PO_4$, 1, were preliminarily indexed in the rhombohedral system space group R-3c (167) with the unit cell data : a = b = 4.7602, c = 12.9930 Å (Ref. Code= 01-075-1862). The d_{012} and d_{104} peaks of M-Al-PO_4 LDHs corresponding to interplanar spacing of 3.4804 and 2.5504 Å, respectively shifted to higher 2θ angles for Mg-$Al(OH)_2PO_4PF_6$ 2, which indicates a decrease in the interlamellar spacing as PF_6^- was incorporated along with PO_4^{3-} anion. The XRD pattern for Ca-$Al(OH)_2SO_4$, 3, was quite different, showing the presence of low angle peaks at 2θ = 11.68 and 14.72°, which are indicative of carbonate anions being incorporated into the inter-lamellar space of LDH. The presence of the carbonate is due to the fact that the synthesis was carried out in air at a pH value of 10. The result obtained is in agreement with similar compounds in the literature [27-29, 35]. Compound 3, crystallizes in monoclinic space group (Ref. Code = 00-047-0964) with the following cell parameters: a = 12.6700, b = 6.9270 and c = 12.0280 Å, Vol.= 1055.63 $Å^3$. The d_{110} peak has a d-spacing of 6.027 Å, whereas the d-spacing for the d_{013} and d_{004} peaks are 4.474 and 3.005 Å, respectively.

The surface structure and morphology of the metal-aluminum LDHs were studied with the help of Scanning Electron Microscope (SEM). The representative SEM images of the as-synthesized layered double hydroxides are presented in figure 3. The representative SEM micrographs of Mg-O-Al-OH and Ca-O-Al-OH layers intercalated with PO_4^{3-} and / or $[PO_4PF_6]^{4-}$ anions are similar consisting of uniform nanospheres of M-Al layered double hydroxides, while the Ca-O-Al-OH layer of compound 3, intercalated with SO_4^{2-} anions consists of hexagonal nano-plates.

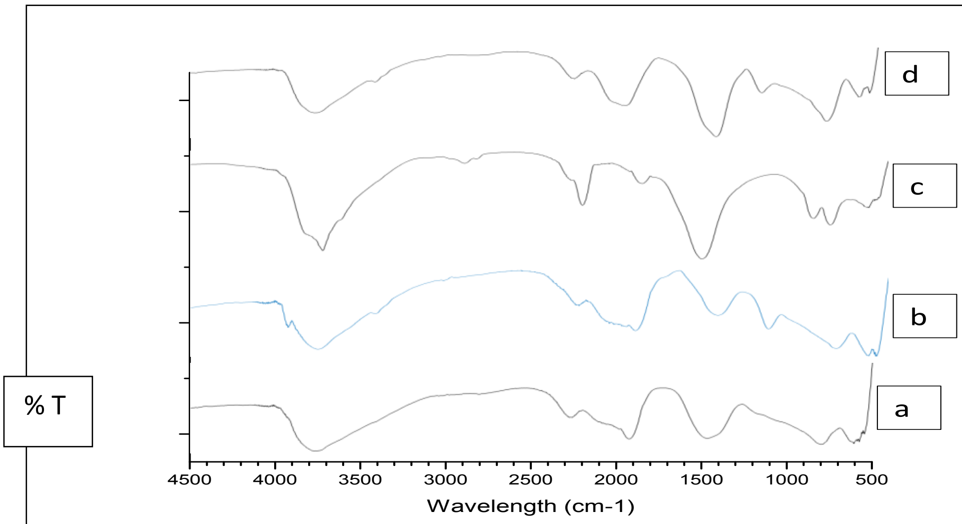


Figure 1 . *FTIR spectra of the as-synthesized layered double hydroxides (a) Mg-Al(OH)$_2$PO$_4$ 1, (b) Mg-Al(OH)$_2$PO$_4$PF$_6$ 2, (c) Ca-Al(OH)$_2$SO$_4$, 3 and (d) Ca-Al(OH)$_2$PO$_4$PF$_6$,* ***4****.*

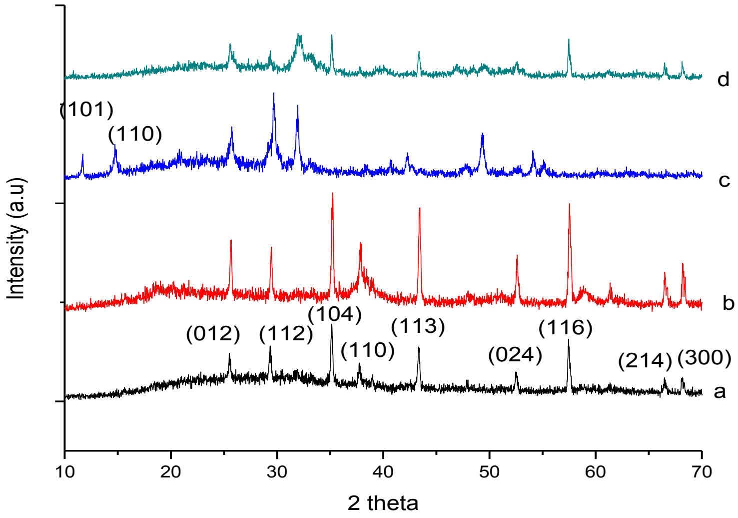


Figure 2. *XRD pattern of as-synthesized compounds (a) Mg-Al(OH)$_2$PO$_4$* ***1****, (b) Mg-Al(OH)$_2$PO$_4$PF$_6$ 2, (c) Ca-Al(OH)$_2$SO$_4$,* ***3*** *and (d) Ca-Al(OH)$_2$PO$_4$PF$_6$,* ***4***

The adsorption efficiency of the LDHs in the removal of Fe^{2+} and Ca^{2+} scale-forming ions from aqueous solutions is presented in Table 1 and 2, respectively. The analyses of the results are shown in figure 4. The results presented in Table 1 showed that there was a significant removal of Fe^{2+} by compounds 1 and 2 with efficiency of 98.73 and 99.77 %, respectively, while compounds 3 and 4 have little or no effect in removing Fe^{2+}. The reduction in the adsorption efficiency of compound 3 for Fe^{2+} is due to the presence of SO$_4^{2-}$ in the inter-lamellar space. Literature reports have shown that the presence of SO$_4^{2-}$ in the inter-lamellar space reduces the adsorption efficiency. When both SO_4^{2-} and CO_3^{2-} coexist, they had a significant effect upon the adsorption efficiency [30]. It has also been demonstrated that the interlayer CO_3^{2-} ions in LDHs are difficult to be exchanged by other anions [31-36]. Furthermore, the reduction in the removal efficiency of Fe^{2+} by compounds 3 and 4 can be attributed to the larger size of the Ca^{2+} (100 pm) over Mg^{2+} (72 pm), in addition to the plate-like morphology of 3 with 1 μm average size. The results for Ca^{2+} removal presented in Table 2 and figure 4 showed that all the synthesized LDHs under investigation were effective in the clean-up with 84-99 % removal efficiency. The effectiveness of compound 3 in removing Ca^{2+} is attributed to its affinity for both SO_4^{2-} and CO_3^{2-} anions, which are both intercalated in the inter-lamellar space.

***Table 1.** Results of Adsorption study of Fe^{2+}*

LDHs	**Actual amount (Co) (ppm)**	**Eluded Amount (Ce) (ppm)**	**Absorbed Amount (Ca) (ppm)**	**Degree of surface coverage (θ)**	**Distribution partition Coefficient (Kd)**	**Absorption Efficiency (%)**
1	9.8526	0.1247	9.7279	0.99	1.01	98.73
2	9.8526	0.0222	9.8304	1.00	1.00	99.77
3	9.8526	8.0994	1.7532	0.18	5.62	17.79
4	9.8526	7.1938	2.6588	0.27	3.71	26.99

***Table 2.** Results of Adsorption study of Ca^{2+}*

LDHs	**Actual Amount (Co) (ppm)**	**Eluded Amount (Ce) (ppm)**	**Absorbed Amount (Ca) (ppm)**	**Degree of surface coverage (θ)**	**Distribution Partition Coefficient (Kd)**	**Absorption efficiency (%)**
1	7.7780	0.7165	7.7064	0.99	1.01	99.08
2	7.7780	0.7563	7.0217	0.90	1.11	90.28
3	7.7780	0.7937	6.9843	0.90	1.11	89.80
4	7.7780	1.2238	6.5542	0.84	1.19	84.27

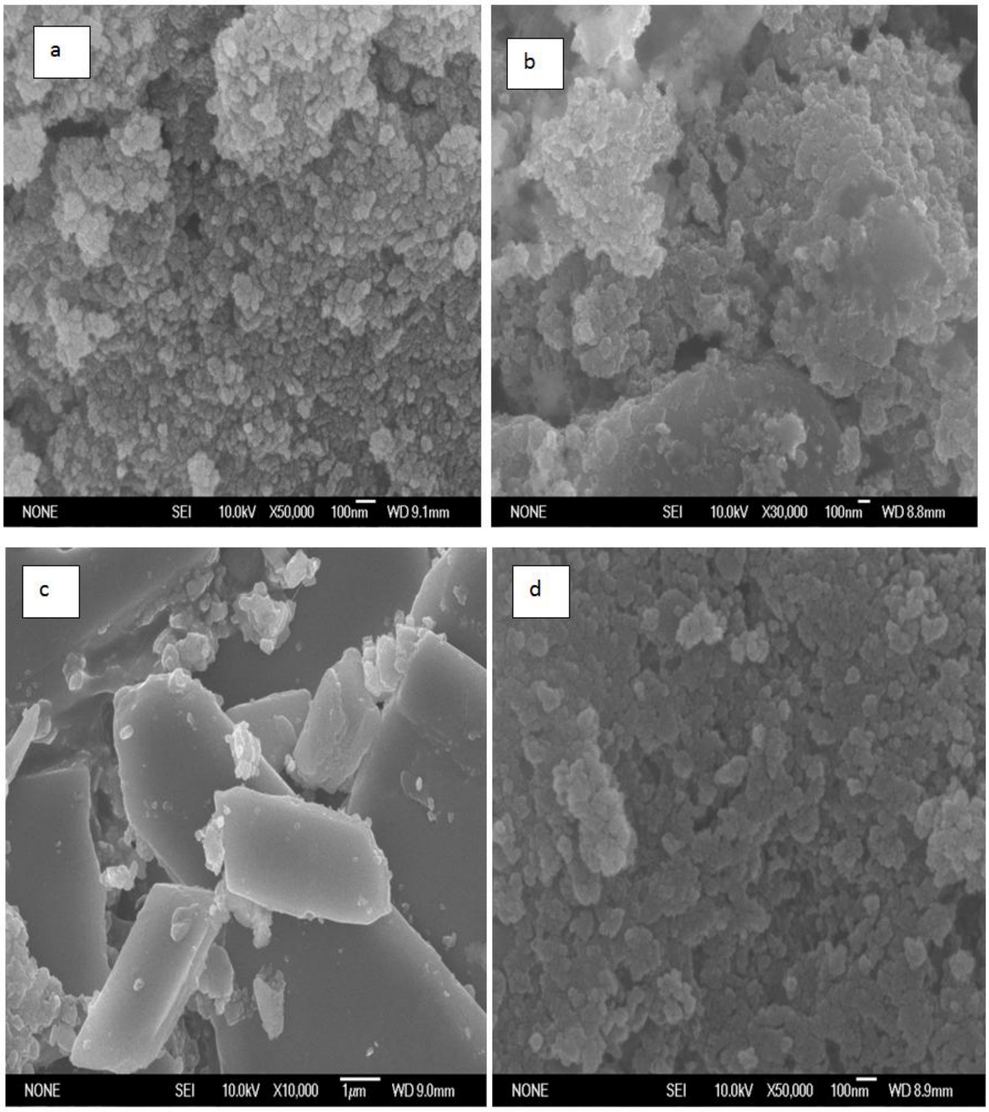


Figure 3. SEM images of as-synthesized compounds *(a) Mg-Al$(OH)_2PO_4$* ***1****, (b) Mg-Al$(OH)_2PO_4PF_6$* ***2****, (c) Ca-Al$(OH)_2SO_4$,* ***3*** *and (d) Ca-Al$(OH)_2PO_4PF_6$,* ***4****.*

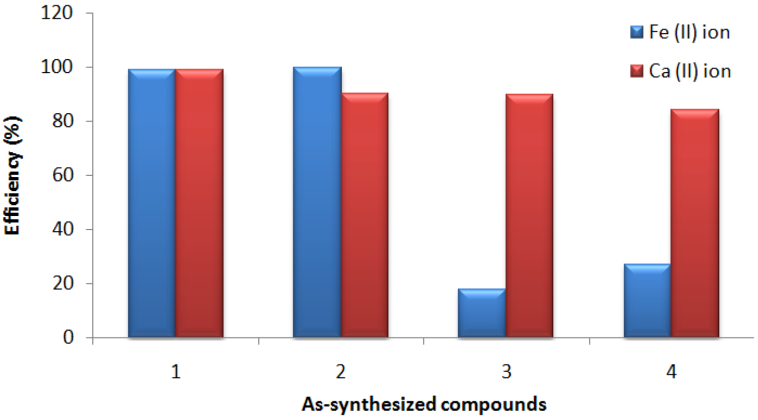


Figure 4. *Results for the removal of Fe^{2+} and Ca^{2+} ions by compounds 1-4*

CONCLUSION

In conclusion, four metal-aluminum layered double hydroxides were prepared by co-precipitating Mg or Ca and Al metal salts with a base under controlled conditions. The SEM revealed that compounds 1, 2 and 4 consist of nanoparticles with average size of 100 nm, whereas compound 3 consists of hexagonal plates with average size of 1 μm. The XRD studies showed the crystalline nature of the nano-LDHs. The results of the column adsorption studies have shown that there is significant potential for using nano structured LDHs as nanofilters to remove ions responsible for scale formation in oil wells. Whereas compounds 1 and 2 can remove Fe^{2+} with greater efficiency, all the synthesized LDHs nanostructures have been demonstrated to effectively removed Ca^{2+} from the oil wells.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest in publishing this article.

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