

## Research Article

# Use of Nanostructured Layered Double Hydroxides as Nanofilters in the Removal of Fe<sup>2+</sup> and Ca<sup>2+</sup> Ions from Oil Wells

Emmanuel K. Ephraim,<sup>1</sup> Chinyere A. Anyama,<sup>1</sup> Ayi A. Ayi <sup>1,2</sup> and Jude C. Onwuka <sup>2</sup>

<sup>1</sup>Inorganic Materials Research Laboratory, Department of Pure and Applied Chemistry, University of Calabar, P.M.B. 1115 Calabar, Nigeria

<sup>2</sup>Department of Chemistry, Federal University Lafia, Lafia, Nasarawa, Nigeria

Correspondence should be addressed to Ayi A. Ayi; ayiayi72@gmail.com

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Four new metal-aluminum layered double hydroxides (LDHs), Mg-Al(OH)<sub>2</sub>PO<sub>4</sub> (1), Mg-Al(OH)<sub>2</sub>PO<sub>4</sub>PF<sub>6</sub> (2), Ca-Al(OH)<sub>2</sub>SO<sub>4</sub> (3), and Ca-Al(OH)<sub>2</sub>PO<sub>4</sub>PF<sub>6</sub> (4), were prepared by the coprecipitation method followed by mild hydrothermal processing at 60°C. Mg<sup>2+</sup> and Ca<sup>2+</sup> in solution with Al<sup>3+</sup> were titrated with NaOH over 3–5 h to yield Mg-Al and Ca-Al layered double hydroxides, respectively, incorporating PO<sub>4</sub><sup>3-</sup>, PO<sub>4</sub><sup>3-</sup>PF<sub>6</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> anions in the interlamellar spaces. The isolated compounds were characterized with the help of XRD, IR, and SEM/EDAX, and their ability to remove scale-forming ions from the 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<sub>4</sub><sup>3-</sup> and/or [PO<sub>4</sub>PF<sub>6</sub>]<sup>4-</sup> anions are similar consisting of uniform nanospheres with an average size of 100 nm, while the M-O-Al-OH layer of compound 3, intercalated with SO<sub>4</sub><sup>2-</sup> anions, consists of hexagonal nanoplate crystals. In the infrared spectra, the characteristic absorption band for water molecules was observed in all the compounds. The XRD pattern showed that *d*<sub>012</sub> and *d*<sub>104</sub> peaks of M-Al-PO<sub>4</sub> LDHs corresponding to interplanar spacing of 3.4804 and 2.5504 Å, respectively, shifted to higher 2θ values for the M-Al-PO<sub>4</sub>PF<sub>6</sub> system, which indicates a decrease in the interlamellar spacing as PF<sub>6</sub><sup>-</sup> was incorporated along with PO<sub>4</sub><sup>3-</sup> anion. The XRD pattern for Ca-Al-SO<sub>4</sub> LDHs was quite different, showing the presence of low-angle peaks at 2θ = 11.68 and 14.72°. The results of the column adsorption studies showed that there was a significant removal of Ca<sup>2+</sup> by all the compounds under investigation with an efficiency of 84–99%. However, compounds 1 and 2 remove Fe<sup>2+</sup> effectively with the efficiency of 98.73 and 99.77%, respectively; compounds 3 and 4 were shown to have little or no effect.

## 1. 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 sulphate 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<sub>2</sub>). 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<sub>2</sub>, it forms a weak carbonic acid (H<sub>2</sub>CO<sub>3</sub>), as shown in (1).

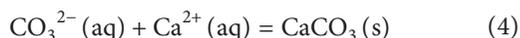
Scaling is caused by salts and can occur when the produced water contains formation water [4]:



This carbonic acid will continue to dissociate hydrogen, creating new deprotonated species of carbonic acid, as seen in the following equation:



In the water mixture, there will be a mixture of H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>. Finally, in the presence of calcium and carbonic acid, calcium carbonate will precipitate out [5, 6]:



The composition of the formation water varies greatly with the reservoirs, but the usual constituents are  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ . 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:

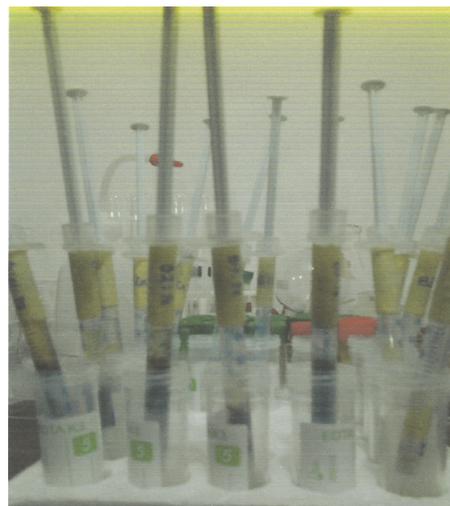


The formation of scale blockage inside oil wells constricts the flow of geothermal fluids in these wells thus significantly reducing their output [7]. Furthermore, fresh water and marine sediments are contaminated by oil spills along with urban runoffs and industrial and domestic effluents. This poses 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 wastewater 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- ( $\text{Mg}(\text{OH})_2$ -) like layers [11–15]. The lattice structure of LDHs, with the general formula  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}\cdot y\text{H}_2\text{O}$ , has a positively charged brucite-shaped layers, consisting of a divalent metal ion  $\text{M}^{2+}$  (e.g.,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ni}^{2+}$ ) octahedrally surrounded by six  $\text{OH}^-$  hydroxyl groups [16–18]. The substitution of the  $\text{M}^{2+}$  metal with a trivalent  $\text{M}^{3+}$  cation gives rise to the periodic repetition of positively charged sheets (lamellas) alternating with charge-counter balancing  $\text{A}^{n-}$  ions. These LDHs have found widespread applications in diverse areas as sensors [19, 20], adsorbents in wastewater treatment [21–23], catalytic removal of soot and  $\text{NO}_x$  in vehicle engine exhausts [10], and as drug and gene carriers [24–26].

During the course of our investigation of LDHs as a 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  $\text{PO}_4^{3-}$ ,  $\text{PO}_4^{3-}/\text{PF}_6^-$ , and  $\text{SO}_4^{2-}$  anions, and we have been successful in synthesizing four new LDHs with nanostructures, namely, Mg-Al( $\text{OH}$ ) $_2$ PO $_4$  (**1**), Mg-Al( $\text{OH}$ ) $_2$ PO $_4$ PF $_6$  (**2**), Ca-Al( $\text{OH}$ ) $_2$ SO $_4$  (**3**), and Ca-Al( $\text{OH}$ ) $_2$ PO $_4$ PF $_6$  (**4**). In this work, the synthesized LDH nanostructures are being investigated as nanofiltration materials to remove scale forming ions like  $\text{Fe}^{2+}$  and  $\text{Ca}^{2+}$ . The synthesis, characterization, and adsorption properties of these four new compounds have been reported.

## 2. Materials and Methods

**2.1. Materials.** Orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ), magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2$ ), aluminum sulphate ( $\text{Al}_2(\text{SO}_4)_3$ ), sodium hydroxide ( $\text{NaOH}$ ), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ), calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), and 1-butyl-3-methyl-imidazolium



SCHEME 1: The experimental setup for the column adsorption studies.

hexafluorophosphate ( $\text{BMIMPF}_6$ ) were used. Analytical grades of all the chemicals were obtained from commercial sources and used without further purification.

**2.2. Methods.** The standard procedure of coprecipitating a divalent with trivalent metal ions in the presence of a base was followed in the present studies [27–30]. The coprecipitation 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  $60^\circ\text{C}$ , and then it was washed with distilled water and separated by centrifugation. The resulting material was dried overnight at  $70^\circ\text{C}$  in the incubator. For compound **1**, orthophosphoric acid was used as the source of the  $\text{PO}_4^{3-}$  anion. For compounds **2** and **4**, 1-ethyl-3-methylimidazolium hexafluorophosphate and orthophosphoric acid were used to introduce  $\text{PF}_6^-$  and  $\text{PO}_4^{3-}$  anions, respectively. For compound **3**, the source of the  $\text{SO}_4^{2-}$  anion was  $\text{H}_2\text{SO}_4$ . In a typical synthesis of **1**, a 250 mL solution containing  $\text{Mg}(\text{NO}_3)_2$  (0.0375 mmol),  $\text{Al}(\text{OH})_3$  (0.0125 mmol) (with the Mg-Al ratio of 3:1), and  $\text{H}_3\text{PO}_4$  (0.5 mmol) was added dropwise from burette into a 15 mL solution of  $\text{NaOH}$  (2 M) under constant stirring at room temperature for 3 h. The mixture with a pH of 10 was heated at  $60^\circ\text{C}$  for 18 h, and the resulting slurry was collected via centrifugation (10 min,  $500\text{ min}^{-1}$ ). The product was washed thrice with deionized water before drying. A similar procedure was used for compounds **2–4**, the difference being in the metal and  $\text{SO}_4^{2-}$  ions for compounds **3** and **4**.

**2.3. Characterization.** The samples were analyzed by the Rigaku MiniFlex II X-ray diffractometer using monochromatic  $\text{Cu } \kappa\alpha$  radiation ( $\lambda = 0.1541\text{ nm}$ ) at the speed of 3 s in  $2\theta$  range between  $5$  and  $75^\circ$  and step size of  $0.03^\circ$ .

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

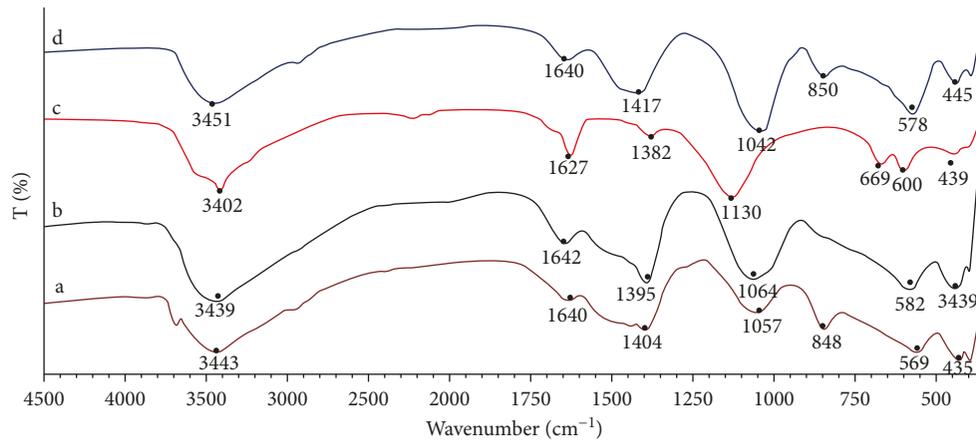


FIGURE 1: FTIR spectra of the as-synthesized layered double hydroxides: (a) Mg-Al(OH)<sub>2</sub>PO<sub>4</sub> (1), (b) Mg-Al(OH)<sub>2</sub>PO<sub>4</sub>PF<sub>6</sub> (2), (c) Ca-Al(OH)<sub>2</sub>SO<sub>4</sub> (3), and (d) Ca-Al(OH)<sub>2</sub>PO<sub>4</sub>PF<sub>6</sub> (4).

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<sup>-1</sup> using the 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.

**2.4. Adsorption Column Experiments.** Aqueous solutions of Fe<sup>2+</sup> and Ca<sup>2+</sup> prepared from their salts FeSO<sub>4</sub>·7H<sub>2</sub>O and CaCl<sub>2</sub>, 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 was poured through the packed samples as filter (Scheme 1). The metal ion solutions were collected at the outlet of the LDH column, and the eluted portion (i.e., the filtrate) was also analyzed by AAS. The degree of surface covered ( $\theta$ ) by the ions was computed using the following equation:

$$\theta = 1 - \frac{C_c}{C_0} \quad (6)$$

The effectiveness of the LDHs as adsorbent was calculated with the help of the following equation:

$$K_d = \frac{C_0}{C_a} \quad (7)$$

where  $K_d$  is the partition coefficient,  $C_0$  is the concentration of Fe<sup>2+</sup> or Ca<sup>2+</sup> ions in solution, and  $C_a$  is the concentration of the ions adsorbed in the LDHs.

The removal efficiency of Fe<sup>2+</sup> and Ca<sup>2+</sup> by the LDHs in percentage was calculated using the following equation:

$$\text{Efficiency (\%)} = \left( \frac{C_a}{C_0} \right) \times 100, \quad (8)$$

where  $C_0$  is the initial concentration of the ions and  $C_a$  is the concentration of the ions adsorbed in LDHs.

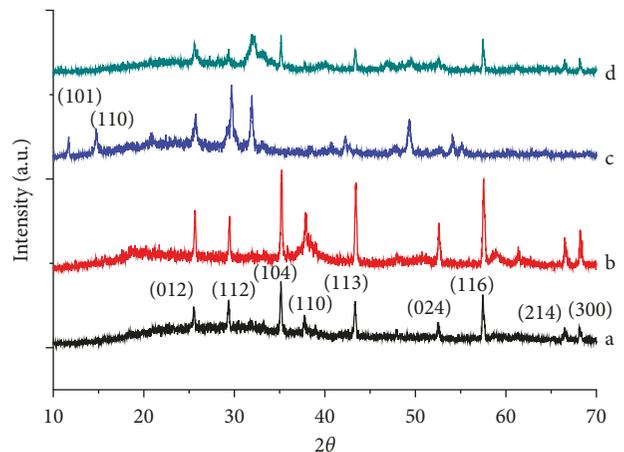


FIGURE 2: XRD pattern of as-synthesized compounds: (a) Mg-Al(OH)<sub>2</sub>PO<sub>4</sub> (1), (b) Mg-Al(OH)<sub>2</sub>PO<sub>4</sub>PF<sub>6</sub> (2), (c) Ca-Al(OH)<sub>2</sub>SO<sub>4</sub> (3), and (d) Ca-Al(OH)<sub>2</sub>PO<sub>4</sub>PF<sub>6</sub> (4).

### 3. Results and Discussion

All the metal-aluminum layered double hydroxides were prepared by the coprecipitation method followed by mild hydrothermal treatment at 60°C. Divalent metal ions (Mg and Ca) in solution with Al<sup>3+</sup> titrated with NaOH over 3–5 h yielded Mg-Al and Ca-Al layered double hydroxides, respectively. In the present studies, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, and PF<sub>6</sub><sup>-</sup> 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<sup>3+</sup> and M<sup>2+</sup> (molar fraction Al<sup>3+</sup>/(Al<sup>3+</sup> + M<sup>2+</sup>) = 0.25 and M<sup>2+</sup>/Al<sup>3+</sup> = 3 molar ratio), prepared by dissolving metal salts in distilled water to give M<sup>2+</sup>-Al-LDH with  $x = 0.25$  (i.e., the composition is more likely represented by M<sup>2+</sup><sub>0.75</sub>Al<sub>0.25</sub>(OH)<sub>2</sub>A<sup>n-</sup><sub>x/n</sub>·yH<sub>2</sub>O. Where  $x/n$  for PO<sub>4</sub><sup>3-</sup> (0.23/3) = 0.083, [PO<sub>4</sub>PF<sub>6</sub>]<sup>4-</sup> (0.23/4) = 0.0625, and SO<sub>4</sub><sup>2-</sup> (0.25/2) = 0.125).

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<sup>-1</sup> corresponds to

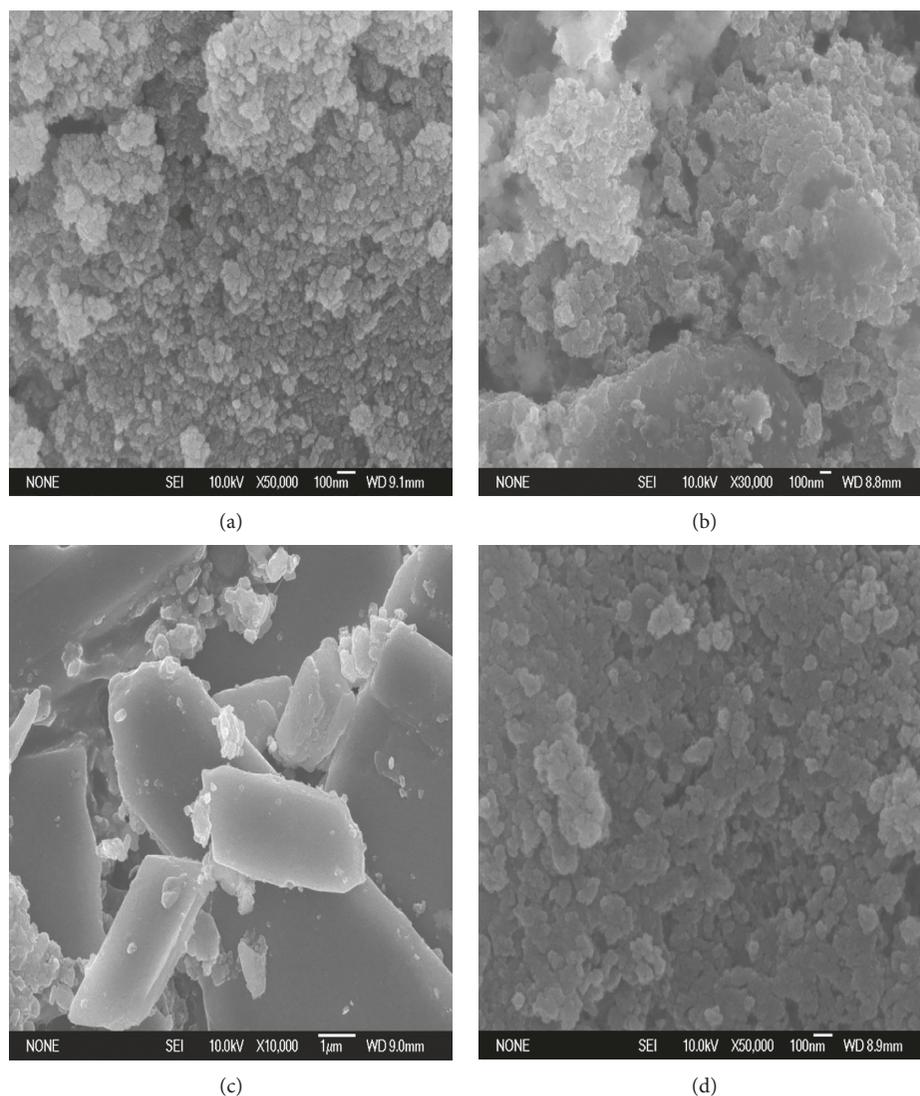


FIGURE 3: SEM images of as-synthesized compounds: (a)  $\text{Mg-Al(OH)}_2\text{PO}_4$  (1), (b)  $\text{Mg-Al(OH)}_2\text{PO}_4\text{PF}_6$  (2), (c)  $\text{Ca-Al(OH)}_2\text{SO}_4$  (3), and (d)  $\text{Ca-Al(OH)}_2\text{PO}_4\text{PF}_6$  (4).

the OH stretching vibration, while the band at  $1640\text{ cm}^{-1}$  is attributed to the bending mode of the lattice water. The stretching vibrational modes of  $\text{PO}_4^{3-}$  or  $\text{SO}_4^{2-}$  units were observed in the region  $1057\text{--}1130\text{ cm}^{-1}$ . The bands in the region  $600\text{--}430\text{ cm}^{-1}$  are attributable to the M–O vibrations. The various assignments are in good agreement with similar compounds in the literature [29–36].

Figure 2 shows the representative XRD patterns of the M-Al-LDHs. The X-ray powder diffraction lines of  $\text{Mg-Al(OH)}_2\text{PO}_4$  (1) were preliminarily indexed in the rhombohedral system space group R-3c (167) with the unit cell data:  $a = b = 4.7602$  and  $c = 12.9930\text{ \AA}$  (Ref. Code = 01-075-1862). The  $d_{012}$  and  $d_{104}$  peaks of M-Al- $\text{PO}_4$ -LDHs corresponding to interplanar spacing of  $3.4804$  and  $2.5504\text{ \AA}$ , respectively, shifted to higher  $2\theta$  angles for  $\text{Mg-Al(OH)}_2\text{PO}_4\text{PF}_6$  (2), which indicates a decrease in the interlamellar spacing as  $\text{PF}_6^-$  was incorporated along with  $\text{PO}_4^{3-}$  anion. The XRD pattern for  $\text{Ca-Al(OH)}_2\text{SO}_4$  (3) was quite different, showing the presence of low-angle peaks at  $2\theta = 11.68$  and  $14.72^\circ$ ,

which are indicative of carbonate anions being incorporated into the interlamellar 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 [28–30, 36]. Compound 3 crystallizes in monoclinic space group (Ref. Code = 00-047-0964) with the following cell parameters:  $a = 12.6700$ ,  $b = 6.9270$ , and  $c = 12.0280\text{ \AA}$  and volume =  $1055.63\text{ \AA}^3$ . The  $d_{110}$  peak has a  $d$ -spacing of  $6.027\text{ \AA}$ , whereas the  $d$ -spacing for the  $d_{013}$  and  $d_{004}$  peaks are  $4.474$  and  $3.005\text{ \AA}$ , 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  $\text{PO}_4^{3-}$  and/or  $[\text{PO}_4\text{PF}_6]^{4-}$  anions are similar consisting of uniform nanospheres of M-Al layered double hydroxides,

TABLE 1: Results of the adsorption study of  $\text{Fe}^{2+}$ .

LDHs	Actual amount, $C_0$ (ppm)	Eluted amount, $C_e$ (ppm)	Absorbed amount, $C_a$ (ppm)	Degree of surface coverage, $\theta$	Distribution partition coefficient, $K_d$	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 the adsorption study of  $\text{Ca}^{2+}$ .

LDHs	Actual amount, $C_0$ (ppm)	Eluted amount, $C_e$ (ppm)	Absorbed amount, $C_a$ (ppm)	Degree of surface coverage, $\theta$	Distribution partition coefficient, $K_d$	Absorption efficiency (%)
1	7.7780	0.7165	7.0614	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

while the Ca-O-Al-OH layer of compound **3**, intercalated with  $\text{SO}_4^{2-}$  anions, consists of hexagonal nanoplates.

The adsorption efficiency of the LDHs in the removal of  $\text{Fe}^{2+}$  and  $\text{Ca}^{2+}$  scale-forming ions from aqueous solutions is presented in Tables 1 and 2, respectively. The analyses of the results are shown in Figure 4. The results present in Table 1 show that there was a significant removal of  $\text{Fe}^{2+}$  by compounds **1** and **2** with an efficiency of 98.73 and 99.77%, respectively, while compounds **3** and **4** have little or no effect in removing  $\text{Fe}^{2+}$ . The reduction in the adsorption efficiency of compound **3** for  $\text{Fe}^{2+}$  is due to the presence of  $\text{SO}_4^{2-}$  in the interlamellar space. The literature reports have shown that the presence of  $\text{SO}_4^{2-}$  in the interlamellar space reduces the adsorption efficiency. When both  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  coexist, they had a significant effect upon the adsorption efficiency [31]. It has also been demonstrated that the interlayer  $\text{CO}_3^{2-}$  ions in LDHs are difficult to be exchanged by other anions [32–37]. Furthermore, the reduction in the removal efficiency of  $\text{Fe}^{2+}$  by compounds **3** and **4** can be attributed to the larger size of  $\text{Ca}^{2+}$  (100 pm) over  $\text{Mg}^{2+}$  (72 pm), in addition to the plate-like morphology of **3** with 1  $\mu\text{m}$  average size. The results for  $\text{Ca}^{2+}$  removal present in Table 2 and Figure 4 show that all the synthesized LDHs under investigation were effective in the cleanup with 84–99% removal efficiency. The effectiveness of compound **3** in removing  $\text{Ca}^{2+}$  is attributed to its affinity for both  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  anions, which are both intercalated in the interlamellar space.

#### 4. Conclusion

In conclusion, four metal-aluminum layered double hydroxides were prepared by coprecipitating 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 an average size of 100 nm, whereas compound **3** consists of hexagonal plates with an average size of 1  $\mu\text{m}$ . 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 nanostructured LDHs as nanofilters to remove ions responsible for scale formation in oil wells. However, compounds **1** and

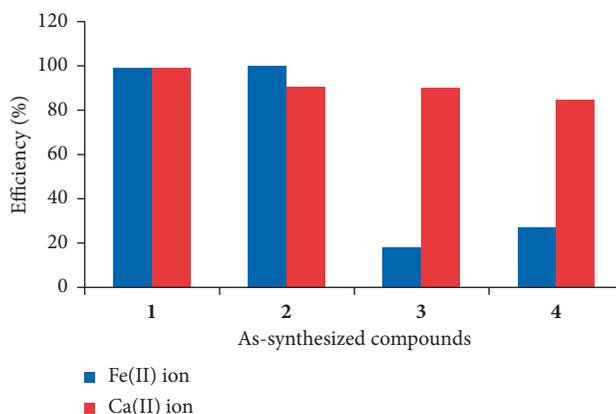


FIGURE 4: Results for the removal of  $\text{Fe}^{2+}$  and  $\text{Ca}^{2+}$  ions by compounds **1–4**.

**2** can remove  $\text{Fe}^{2+}$  with greater efficiency, and all the synthesized LDHs nanostructures have been demonstrated to effectively remove  $\text{Ca}^{2+}$  from the oil wells. However, in moving from laboratory conditions to the complicated conditions of high salinity, low permeability, and heterogeneous rock properties in oilfield core materials [38], the transport and retention properties of the nanostructured LDHs should be investigated.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest in publishing this article.

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