INVESTIGATION OF NOVEL COMPOSITES AS BACKFILL MATERIALS IN RADIOACTIVE WASTE DISPOSAL FACILITIES

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Abstract

The work aims to assess a novel prepared composite of Poly Acrylic Acid/Charcoal/Montmorillonite (PAACM) as a backfill material for radioactive waste disposal facilities. Characterization of the prepared composite has been done using Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA), Energy Dispersive X-ray (EDX), and Scanning Electron Microscopy (SEM). Cs^+ and Sr^{2+} ions were determined using Inductive Coupled Plasma (ICP). Some factors which may affect in the sorption process such as contact time, pH of the aqueous phase, mass of the sorbent, competing ions and temperature of the aqueous medium has been studied. The obtained data show that the sorption process is rapid and the PAACM composite has a high sorption capacity towards Cs^+ and Sr^{2+} ions, the PAAMA has high thermal stability, and the PAACM has highly enormous swelling properties. The swelling of PAAMA is pH and temperature dependent; of the aqueous phase. K^+ and Ca^{2+} ions are good competing ions for Cs^+ and Sr^{2+} ions, respectively, during sorption process. Application of the principles of radioactive waste management requires the implementation of measures the activity level of radioactive waste that afford protection of human health and the environment, now and in the future. The prepared material contributes in the protection of the environment and groundwater from contamination with both radio-Cesium and radio-Strontium.

1. INTRODUCTION

Nowadays, there are huge amounts of the radioactive which are produced as a result of the using the nuclear activities in many fields (Research, Industrial, Agriculture, Medical or for the production of electricity) [1, 13, 16]. There are many steps for waste management system within which the radioactive waste passes through till its final disposal. The aim of the waste management system is protection of human health and the environment [10, 12]. Backfill material is one of the barriers that should be studied well to ensure the safety of the selected site [8]. Bentonite is the most common backfill material, spatially the montmorillonite (MMT) or smectite [2]. This was attributed to the formation of stern-Gouy- layer which occurs due to interaction between electrical charge of the clay matrix at the interface and any dissolved particle in pore water. This phenomena led to impeding the passage of any dissolved particle in the water as the pore space which is accessible for diffusion is reduced. [4, 9]. The new trend of research is directed to mixing MMT with Polymers to prepare Polymer/ clay nano composites [15, 18].

Leaching is possible in this case and if fissuring occurs in the MMT layer the leachate with a high concentration of radionuclides flows to the environment.

In this issue, it will be important to differentiate between two composites from their suitability to withstand their use as a backfill. The comparison will take into consideration their mechanical, physical and chemical properties.

2. MATERIAL AND METHODS

2.1. Materials

Acrylic acid with 99% purity supplied by Acrôs, Belgium. Activated Charcoalsupplied by El Nasr Company for chemicals, Egypt. Montmorillonite supplied by International Company for Mining and Investments (ICMI) was used without any further purification, Methanol supplied by Fluka-Sigma-Aldrich. De-ionized water was supplied by pure lab apparatus, ELGA, UK.

2.2. Methods

Preparation of the investigated composite samples (PAACM): Acrylic acid, as a monomer, was irradiated by Gamma ray to obtain Poly Acrylic acid followed by hot mixing with similar ratios of Montmorillonite and Activated charcoal in presence of methanol as a solvent till homogeneity to obtain PAACM. The prepared samples were dried in an oven at 80°C for 24 hours.

2.3. Characterization

The prepared samples were characterized using different tools. The infrared spectroscopy analyses were carried out using Jasco Japan 6100 FTIR with a KBr disk. Thermo Gravimetric Analyses (TGA) was performed using TGA-50 Shimadzu Thermo Gravimetric Analyzer. Scanning Electron Microscopy (SEM) was performed using JEOL, JSM-6510LA Analytical SEM, manufactured in Japan. Identification of the contents was performed using EDX (Energy Dispersive X-ray), Japan, linked to SEM.

3. RESULTS AND DISCUSSION

3.1. IR studies

The prepared composite samples were studied using Fourier Transform Infrared Spectroscopy 6100 (FTIR); (Fig. 1). It is clear that there many peaks are appeared in the blank sample due to the reaction between MMT, Acrylic acid and charcoal while most of them are disappeared in the investigated composite sample.

The FTIR spectrum reveals the absorption band at 1723 cm^{-1} which is characteristic of C=O group; this is an indication of polymerization of Acrylic acid. A broad band exists at 3439.0 cm^{-1} for alcoholic (OH) group. This agrees with what was reported in [14].

For Montmorillonite the peak around 3696 cm^{-1} represents Si —OH stretching motion and residual H_2O. The two bands at 1032 cm^{-1} and 795 cm^{-1} are indication for Si-O vibration in plane and out of plane of silica. The band at 914 cm^{-1} represents Al-Al OH motion as reported by [11]. The last two bands at 524 cm^{-1} and 421 cm^{-1}are assigned for Si-O-Al and Si-O-Si vibration motion. While for Charcoal it has characteristic bands at 3422 cm^{-1} for residual water, 2975 cm^{-1} for C-k Asymmetric stretching and 1456 cm^{-1} for its bending motion. The absorption at 1541 cm^{-1} represents C=C stretching, while the band at 670 cm^{-1} C-C represents stretching motion.

For PAACM composite; this is the obtained due to the reaction between PAA, MMT and Charcoal. The characteristic band at 1723 cm^{-1} which is characteristic for C=O. the high value than PAA peak at 1702 cm^{-1} is corresponding to OH edge function groups may be due to the high cross-linking between PAA and MMT. The peak at 3400 cm^{-1} for characteristic of OH group but it is noticed that its intensity is low and this may due to the reaction between the MMT and PAA. Also, the peak of OH representing to MMT in reduced respectively.

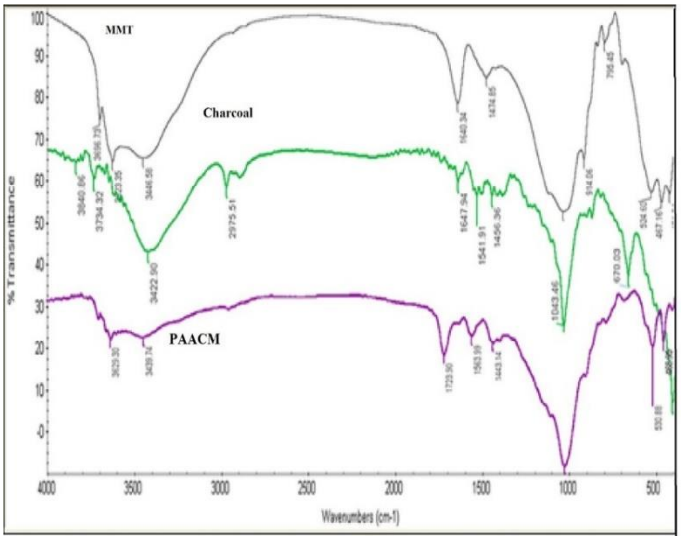
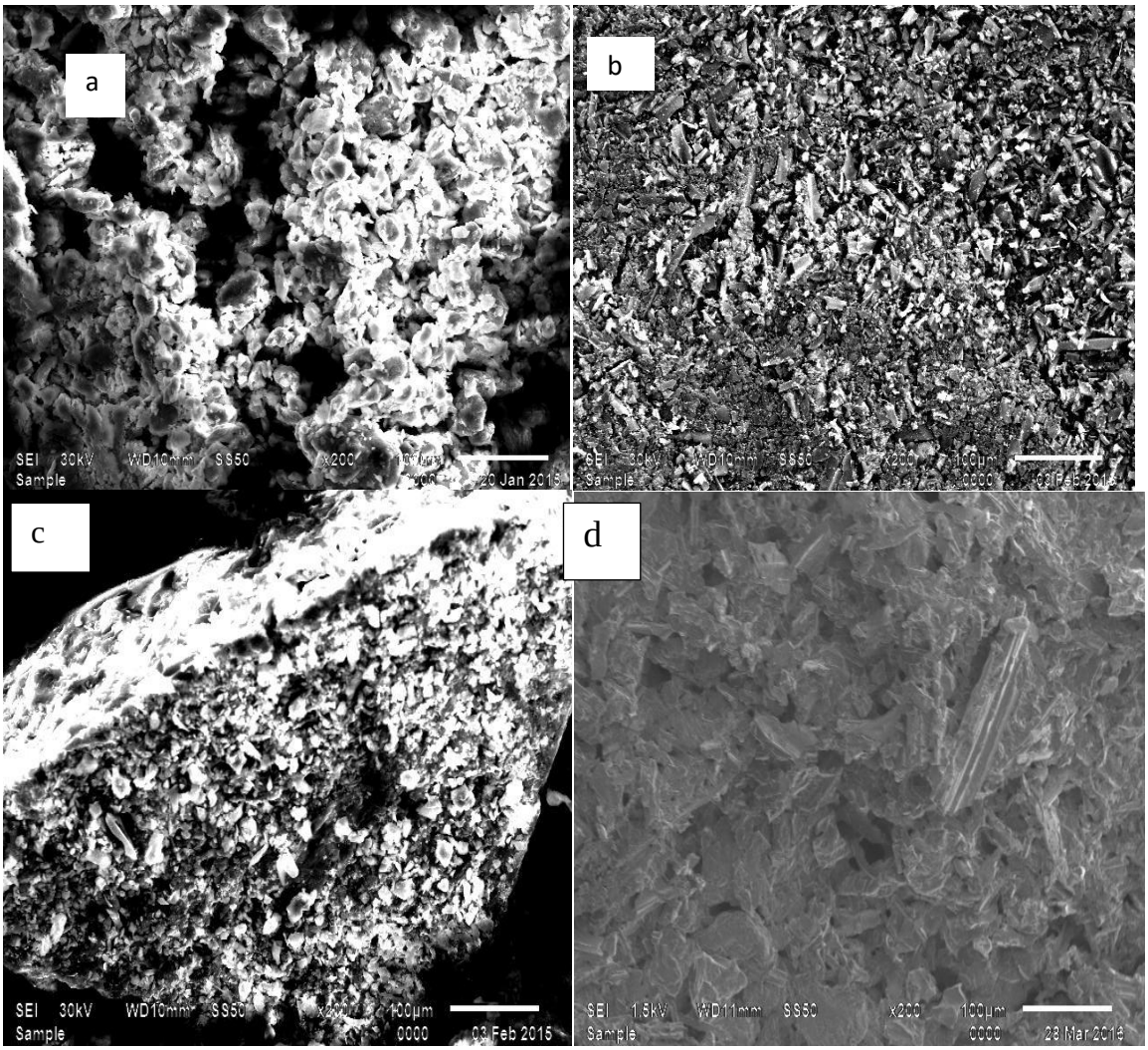


FIG. 1. FTIR diagram of MMT, Charcoal and PAACM composite.

3.2. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX)

The scanning electron micrograph images with a 200X and 500X magnification for Charcoal, Montmorillonite, the prepared composites and the materials loaded with Cs^{+} & Sr^{2+} ions are shown in Fig. 2(a-m). SEM and EDX allow the visualization and elucidating the surface chemistry for the studied samples. The surface texture and porosity are clearly shown for Charcoal. It shows a regular porous surface indicating high surface area. This agreement was reported in [7].The results reveal the high porous structure of MMT and the prepared composites.

Energy Dispersive X-ray (EDX), is a quantitative analysis method to determine the chemical composition for each material. Table 1 illustrates the variation of chemical composition between blank materials formation, the prepared composite and composite samples loaded with Cs^{+} or Sr^{2+}. The changes may be attributed to replacement of MMT internal cations by Cs^{+} or Sr^{2+} ions. The chemical composition for each material was calculated by Quantitative analysis method with the following fitting coefficients; 0.6382 (Charcoal), 0.4441 (MMT), 0.6259 (PAACM), 0.6187 (PAACM/Sr), 0.5787 (PAACM/Cs). The results for PAACM are shown in Table (1).


a
b
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SEI 30kV WD10mm SS50 x200 100µm
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Sample 0000 28 Mar 2013

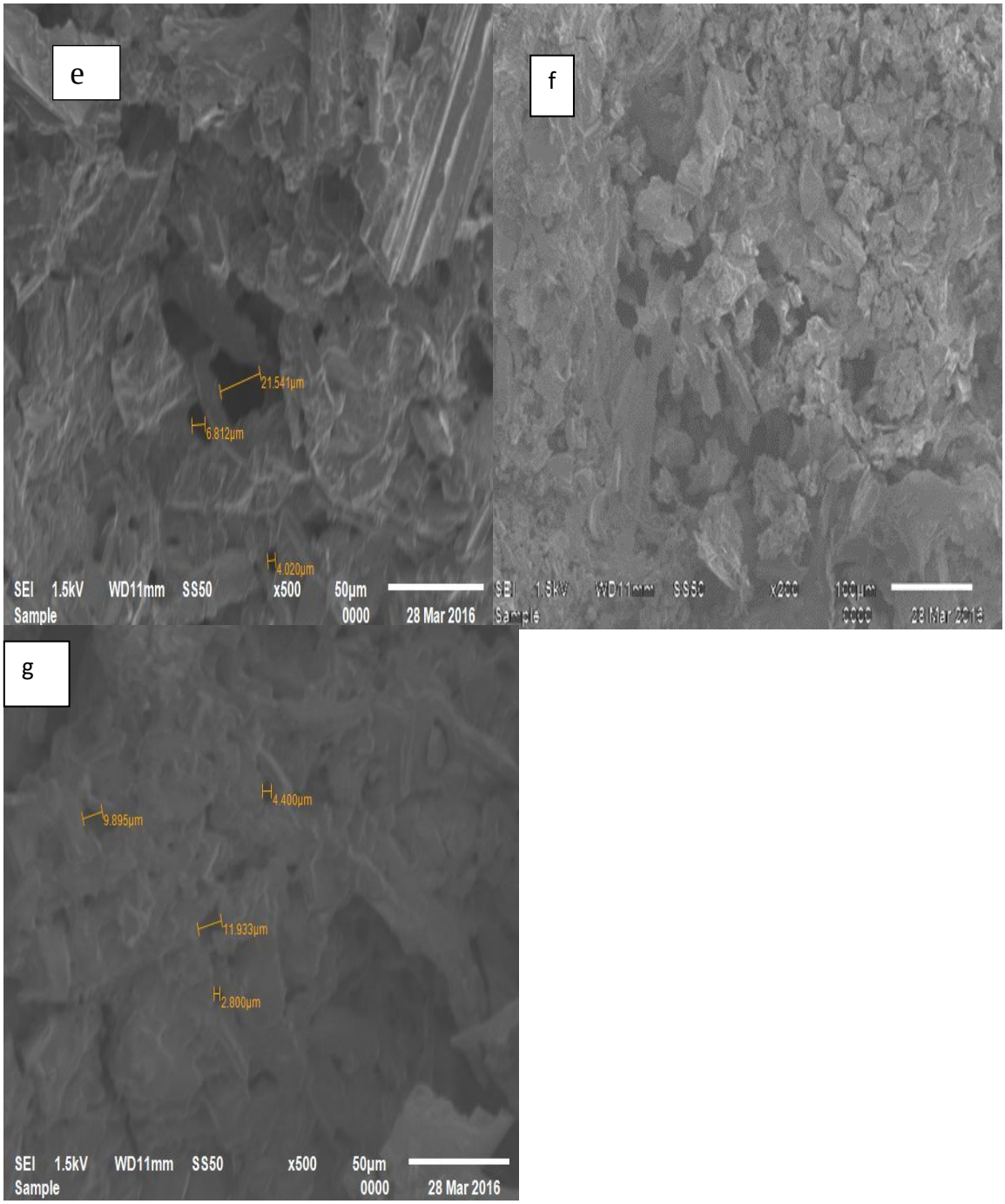

FIG. 2. SEM micrograph for (a) MMT, (b) Charcoal, (c) PAACM, (d) PAACM&Cs at 200X, and (e) PAACM&Cs at 500X, (f) PAACM & Sr at 200 and(g) PAACM & Sr at 500 X.

TABLE 1. THE CALCULATED ELEMENTS PERCENT OF THE QUANTITATIVE ANALYSIS OF MMT, CHARCOAL, PAACM COMPOSITE, PAACM /CS+ AND PAACM /SR2+ USING EDX 6510 LA WITH COUNTING RATE577 CPS, ENERGY RANGE = 0-20 KEV, REAL TIME = 52.8, LIVE TIME = 50.00, ACC. VOLT= 25 KV.

Material	O%	Na%	Mg%	Si%	Al%	K%	Ca%	Fe%	C%	Cs%	Sr%	Total %
MMT	42.41	3.22	2.04	27.31	11.73	1.25	1.19	10.86	----	-----	-----	100
Charcoal	-----	------	------	------	------	0.07	1.21	------	98.08	-----	------	100
PAACM	40.15	0.82	0.62	4.52	2.16	0.23	0.12	2.98	48.39	-----	------	100
PAACM/Cs	39.41	-----	------	1.55	0.58	0.65	0.56	0.73	55.74	0.77	------	100
PAACM/Sr	35.04	-----	------	3.24	1.47	2.58	1.06	2.11	53.86	-----	0.64	100

3.3. TGA analysis

Thermogravimetric analysis (TGA) curves of MMT, Charcoal, PAACM composite are shown in Fig. 3. Both figures show a similar behavior. For MMT a very small weight loss occurred at 160°C which corresponds to loss of moisture water [3, 5] and the second decomposition stage takes place in the temperature range 450 - 550°C which corresponds to loss of inter layer water. The rate was so high with 0.1% loss of its initial weight. For charcoal, it has one weight loss stage with a high rate. This weight loss corresponds to loss of moisture with 2% loss of its initial weight. For PAACM composite, there are three decomposition stages with a 1% total loss of its initial weight. The major loss occurs in the temperature range 200 to 400°C which corresponds to decomposition of PAA by releasing CO_2 with 0.9% weight loss at this temperature range. the rate of PAACM decomposition means that bit has high thermal stability.

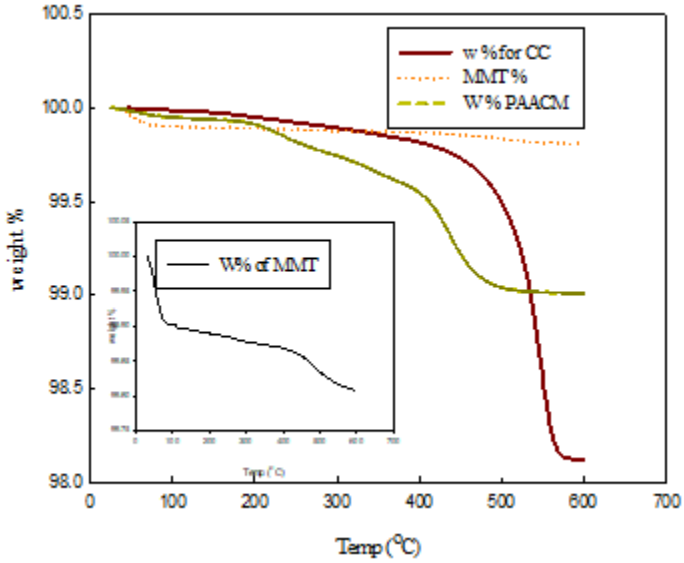

FIG. 3. Comparison between TGA diagram for MMT, blank Activated Charcoal and PAACM composite. The small TGA diagram showing the slow change in weight loss with MMT.

3.4. Swelling properties

Cross-linked materials with hydrophilic functional groups have the ability to swell in aqueous solutions and aqueous organic solvent mixtures. This behavior was attributed to the formation of ion [15]. The formation of such aggregation of charged groups is partially driven by electrostatic attraction among ion-pairs consisting of charged polymers and counter ions [17]. The presence of the hydrophilic carboxylic groups of Acrylic acid allows the swelling of the composite in addition to the swelling properties of Montmorillonite. The calculation of the swelling was done using the following equation.

$$W\% = \frac{Wt - Wo}{Wo} \times 100 \;\; 1 \qquad (1)$$

Where, W_o is the initial weight of the sample, W_t is the weight of the sample after time t and W% is express the swelling percent of the sample.

The results of swelling measurements are illustrated in Fig. 4. The swelling process for PAACM composite starts so rapidly that in 1 hour it reaches a swelling ratio 23 which corresponds to 2370 swelling percent. The swelling continues reaching equilibrium in 40 days with a 8866 swelling percent. This means that PAACM composite swelling ratio equals 89.66 time its initial weight.

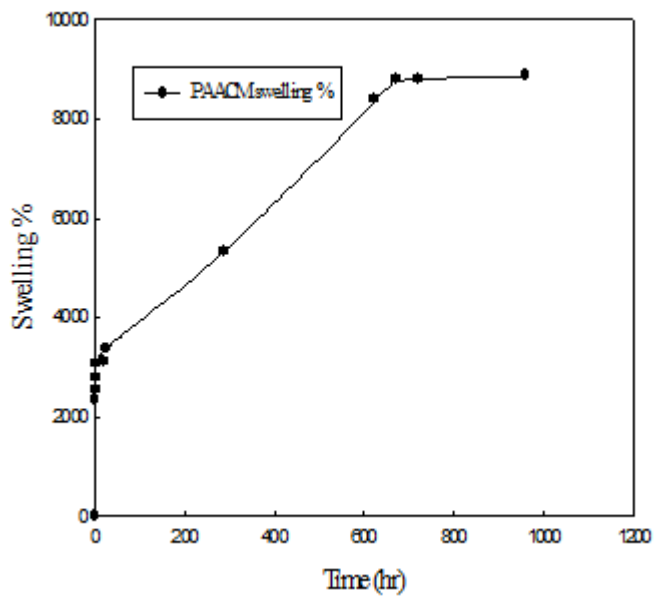

FIG. 4. Effect of time on PAACM composite swelling (W=0.1 g T=25°C, pH=5.5).

3.5. Sorption process.

Different investigations for removal of Cs^+ and Sr^{2+} ions from their solutions are carried out to know the ability PAACM-composite to be used as a backfill material in radioactive waste disposal facilities. These elements are selected because their radioisotopes are fission products, differing in half-lives time and have a high mobility in ground water.

3.6. Effect of pH in sorption process

The pH was the variable to study the Cs and Sr sorption behavior of the composites as a function of it. pH of the aqueous phase is an essential factor in the sorption process during removal of Cs^+ and Sr^{2+} onto the PAACM-composite. The experimental results are shown in Fig. 5.It is clear that sorption capacity of PAACM composite towards Cs^+ and Sr^{2+} ions increase as the pH increase till to a certain pH value, then following with decreasing in sorption capacity value. The results indicate that the optimum sorption capacity for Cs^+ and Sr^{2+} ions at pH 5.5 and 8, respectively.

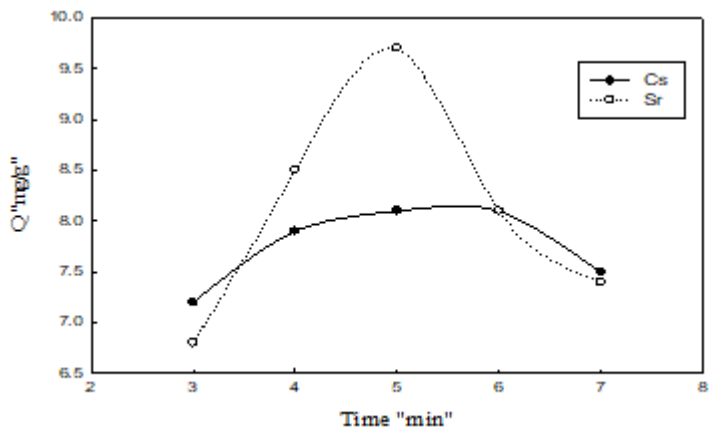

FIG. 5. Effect of pH of the medium on the removal of Cs+ and Sr^{2+} ionizing PAAMC.

3.7. Effect of mass of the sorbent (V/m)

Preliminary experiments show that the suitable V/m for Cs^+ and Sr^{2+} ions are 180 and 120 ml/g, respectively.

3.8. Effect of contact time

The effect of time on sorption of Cs^+ and Sr^{2+} using the prepared composites has been studied. The variation of the amount sorbed of the investigated ions onto the studied composites as a function of time is shown in Fig. 6. The figures show that the amount sorbed increase with time, till it reaches a constant value depending on the type of the adsorbate and the nature of the sorbent. Capacity of each composite was derived from the following Equation:

$Q = (C_o - C_t)$ (V/m)

where Q is the capacity of the composites, C_o is the initial concentration of Cs^+ and Sr^{2+}, C_t is the concentration at definite time, V is the volume of the adsorbate and m is the weight of the sorbent. For PAACM composite; it can be noticed from Fig. 5 and Fig. 6 that its sorption process occurs at a high rates as in the first 5 minutes the composite sorb about 78.6 % in case of Cs^+ which corresponds to a Q value of 9.4 mg/g. The sorption process continues until 60 minutes where the sorption starts to be slow that it is nearly constant. The equilibrium capacity of PAACM equals 11.5 mg/g (95.7%).

In case of $Sr2^+$ with PAACM, it has a close result of sorption of $Cs^{+,}$ nearly about 76.42 % at the first 5 minutes of the sorption process. The fast adsorption of both Cs + and Sr^{2+} onto PAACM surface can be attributed to the chemical adsorption rather than physical adsorption as reported by X. Wang et al., 2005; after 90 min with Sr^{2+} with a sorption percent 91.38%. This proves the ability of this material to retain Cs^+ ion; this monovalent cation which is easily diffuses in the soil with a higher percent than Sr^{2+} the divalent one. This is added to the composite properties beside its fast rate of reaction also retaining the

difficult cation which is easily dissolved in water and migrate. The sorption capacity of PAACM in case of Sr^{2+} is 10.9 mg/g. Fig. 6.

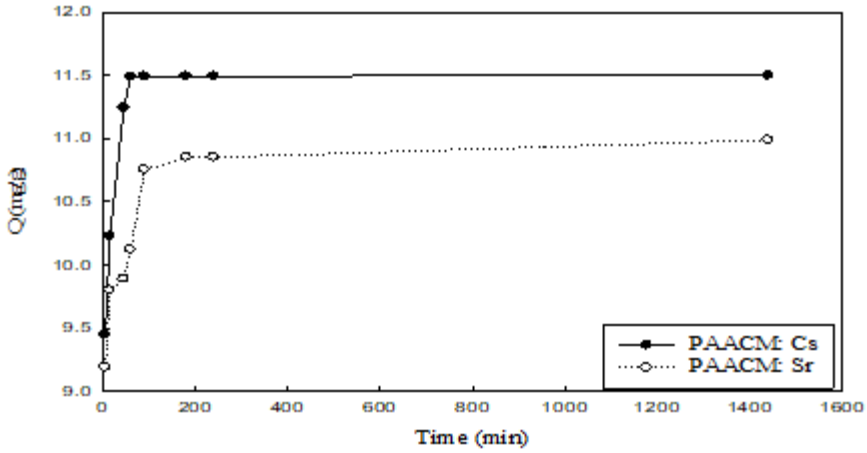

FIG. 6. Effect of contact time on removal of Cs+ and Sr^{2+} using PAACM composite (V/m = 120 ml/g, T = 25°C, pH = 5.5).

3.9. Effect of temperature

The effect of temperature in the uptake of Cs^{+} and Sr^{2+}onto PAACM-composite was investigated in the temperature range 25°C to 65°C. The experimental results are shown in Fig. 7, it is noticed that its capacity increases as the temperature increases till 55°C. Beyond 55°C there is a decrease in the sorption capacity of PAACM. As to PAACM: Sr Fig. 7 It is noticed that the maximum capacity occurs at 25°C. Beyond 25°C, the capacity decreases as the temperature increases. This only enhance the selectivity of this composite towards Cs^{+}.

This behavior may be attributed to what is known about silicate minerals where mutual is amorphous replacement occurs frequently between similarly charged and nearly the same size ions (Mg^{2+}, Ca^{2+}, Fe^{2+}). These replacements have been confirmed using SEM & EDX analysis as shown by Fig. 2 and Table 1. Also, from Goldschmidt coordination number of anions radius by ratio of RX: RA. This coordination number determines the positions of the atoms in the compound. According to this ratio the element may be at the corner of cube or close-packing or corner of octahedron etc. The formation of these lattices makes a gap inside the structure itself and the distance in the same plane equals 5.20 Å and the inter planer space 9.00 Å. According to the last facts about silicates it may affect the behaviour of Sr^{2+} ions equilibrium adsorption which can be attributed not only to increasing surface area of the composite as it reached to nanoscale and micro scale as shown in Fig. 2, but also to the small atomic and ionic radii of Sr^{2+} ions which equals 2.19Å and 2.00 Å , which is smaller than Cs^{+} atomic and ionic radii which equals 2.98Å and 2.60Å. This behaviour occurred only with Sr^{2+} , but in case of AMC: Cs it follow the normal behaviour as the following; Capacity of AMC increased rapidly with the temperature till 35°C, after this value there are a noticeable loss on sorption properties compared to AMC: Sr. this may be due to enlargement of pores size or activation of the adsorbent surface or creation of some new active sites on the PAACM surface [6] the swelling properties increase by increasing temperature.

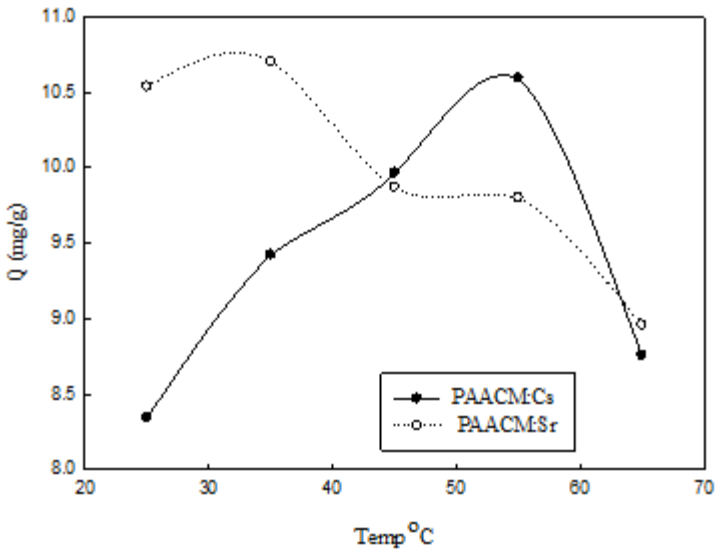

FIG. 7. Effect of temperature on removal of Cs^+ & Sr^{2+} using PAACM composite ((V/m = 269.96, pH = 5.5, t = 90 min).

4. DESORPTION

The relative desorption of the studied element from the loaded prepared composite is presented in Fig. 8. the desorption percent of Cs^+ ions is plotted as a function of contact time. From the characterized samples the maximum concentration sorbed in the medium is within the range of 0.6950 ppm till 2.9788 ppm. This indicates that the prepared composites bond strongly with applied elements by a chemical bond (ionic with the prepared composite. For PAACM composite, it is clear that the total desorption percent equals 1.67% of Cs^+ ions which had been sorbed and calculated early. In case of ACM, the total desorption percent equals 3.59 % of Cs^+ ions into the solution.

These values could enforce the results obtained from kinetic calculations that those composite bend with the elements through a strong chemical bond (Ionic bond within the composite) and precipitation of elements on the surface of polymer-clay composite and formation of more than a layer bonding together with a metallic bond. They can arise via polymeric metal complexes (dimers, trimers, etc.) that form on mineral surfaces and via the sorption of aqueous polymers.

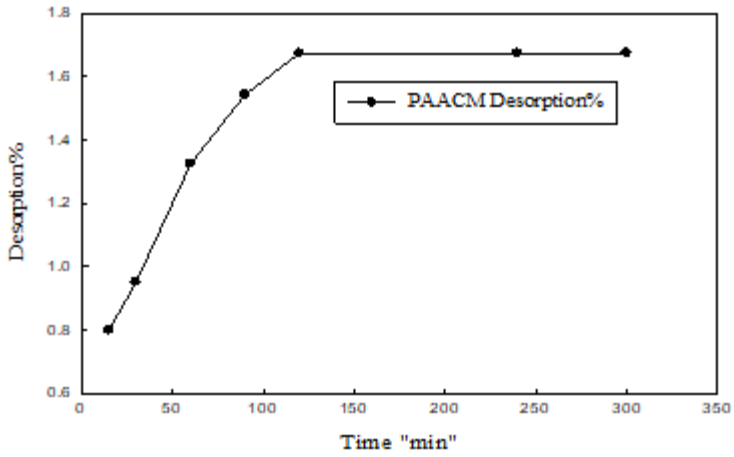

FIG. 8. Effect of contact time on Desorption of Cs^+ using PAACM composite.

5. CONCLUSION

The polymer clay nanocomposites prepared by two methods resulted in a mixture and a composite different in their physical and mechanical properties.

SEM micrograph revealed that the surface structure of AMC is of higher porosity than PAACM.

Both composites have high thermal stabilities; this was verified by TGA curves. As the total loss of their initial weights didn't exceed 1%.

PAACM has high swelling properties. It continues till reaching equilibrium after 960 hours with swelling value over 8000%. Of its initial weight and a swelling ratio equals 89.66.

AMC has high swelling properties and attains its mechanical properties with a swelling value 495 % within 240 hours.

The sorption capacity preliminary results indicate that the novel composites can be promising but more investigations are needed.

REFERENCES

[1] ABDEL RAHMAN, R. O., IBRAHIM, H. A., HUNG, YUNG-TSE., Liquid Radioactive Wastes Treatment, A Review, Water **3** (2011) 551-565.

[2] ALEXANDER, W. R., MCKINLEY. I. G., The chemical basis of near-field containment in the Swiss high-level radioactive waste disposal concept, Journal of Geological Society **157** 1 (1999) 47-69.

[3] ALMUHAMED. S, BONNE. M. KHENOUSSI. N, BRENDLE. J, SCHACHER, L. LEBEAU. B, ADOLPHE. D. C., Electrospinning composite nanofibers of polyacrylonitrile/synthetic Na-montmorillonite. J. Ind. Eng. Chem. (2015) 146-152.

[4] ANDERSSON, K. G., BREWITZ, E., MAGNÚSSON, S. M., MARKKANEN, M., PHYSANT, F., POPIC, J. M., & ULFBECK, D. G., An overview of current non-nuclear radioactive waste management in the Nordic countries and considerations on possible needs for enhanced inter-Nordic cooperation: Final report from a NKS-B activity commissioned by the Nordic Council of Ministers. NKS Secretariat. (NKS; No. 351), (2015).

[5] BANU, H. T, KARTHIKEYAN, P. MEENAKSHI, S., Lanthanum (III) encapsulated chitosan-montmorillonite composite for the adsorptive removal of phosphate ions from aqueous solution. J. Bio. Macro. **112** (2018) 284-293.

[6] BANERJEE. D., KIM. D., SCHWEIGER. M. J., KRUGER. A.A., Thallapally. P. K., Removal of TcO4 ions from solution: materials and future outlook. Chem. Soc. Rev., **45** (2016) 2724.

[7] BELGACEM. A., BELMEDANI. M., REBIAI. R., HADOUN. H., Characterization, Analysis and Comparison of Activated Carbons Issued from the Cryogenic and Ambient Grinding of Used Tyres, Journal of Chemical Engineering Transaction **32** (2013) 1705- 1710.

[8] CUI. Y. J., On the hydro-mechanical behaviour of MX80 bentonite-based materials. J. Rock Mechanics and Geotechnical Engineering **9** (2017) 565-574.

[9] DANIEL R. FRO¨HLICH., Sorption of Neptunium on Clays and Clay Minerals _ A Review. J. Clays and Clay Minerals **63** 4 (2015) 262–276.

[10] EL-SAYED A. HEGAZY, H. KAMAL, M. ABDEL GELEEL, A. ABDEL MAKSOUD., Removal of Cesium-134 and Cobalt-60 with Radiation- Grafted Copolymers from Their Liquid Wastes. Wiely interscience **95** (2005) 936–945.

[11] FARMER. V.C., Layer silicates, Infrared Spectra of Minerals. Mineralogical Society, (1974) 331-363.

[12] FERNANDES M. MARQUES. A.C. SCHEINOST., AND B., BAEYENS., Sorption of trivalent lanthanides and actinides onto Montmorillonite, Macroscopic, thermodynamic and structural evidence for ternary hydroxo and carbonate surface complexes on multiple sorption sites, J. Water Research **99** (2016) 74-82.

[13] M. ABDEL GELEEL; N. S. MAHMOUD., Improvement of Radioactive Waste Solidification Process Using Modified Bentonite Materials. Nature and Science **9** 7 (2012) 26-33.

[14] SPOSITO G., ANDERSON D.M., Infrared study of exchangeable cation hydration in montmorillonite, Soil Sci. Amer. Proc. **39** (1975) 1095-1099.

[15] TAN. B, THOMAS, N.L., A review of the water barrier properties of polymer/clay and polymer/graphenenanocomposites. J.Mem. Sci. **514** (2016) 595–612.

[16] URTASUN, A. A., LUQUIN, A and GARRIDO, J. J., Nuclear fission technology in Spain: History and social concerns, Public Understanding of Science **26** 3 (2017) 207-324.

[17] WANG, Y. BERGENSTRÅHLE-WOHLERT, M. TU, Y. ÅGREN, H. BERGLUND, L. A. WOHLERT, J., 2017. Swelling and dimensional stability of xyloglucan/montmorillonitenanocomposites in moist conditions from molecular dynamics simulations. Computational Materials Science. **128** (2017) 191–197.

[18] ZARE. Y., Effects of imperfect interfacial adhesion between polymer and nanoparticles on the tensile modulus of clay/polymer nanocomposites. App. Clay (2016) 65-70.