Gamma-Irradiations Effects on Structural and Micro-Structural Parameters of Chromium(III) – Silicate Base Mica Clay

Khaled M. Elsabawy[a,b,*], Morsy M. Abou-Sekkina[a]

[a]Chemistry Department, Faculty of Science, Tanta University,
Tanta - 31725, Egypt

[b]Chemistry Department, Faculty of Science, Materials Science Unit,
Taif University, 888 - Alhawya, Taif City, Kingdom of Saudi Arabia

*E-mail address: khaledelsabawy@yahoo.com ; ksabawy@yahoo.com

ABSTRACT

Solution route was applied to synthesize new family of free-fluoride synthetic clay. All starting solutions were made by applying carbon tetra-chloride (CCl_4) as a solvent. The selected sample of synthetic free fluoride – Na-4-mica was having the general formula ($Na_4Mg_6M_4Si_4O_{22}\cdot nH_2O$) where M = Cr^{3+} was exposed to two different ɤ-irradiation doses 1st dose = 1.5 MR/h and 2nd dose = 3 MR/h at 25 cm distance. Structural parameters such as lattice constants, volume and phase quality were monitoring carefully by using both of XRD and SEM evaluating grain size of the mica bulk. Structural investigations proved that Cr-clay exhibits monoclinic phase accompanied with structure quality in comparison with both of Bi-and Al-clays

Keywords: Synthesis, Mica clay, Free fluoride, XRD, SEM, Structural Parameters

1. INTRODUCTION

Recently many studies were carried out to investigate the effects of nuclear irradiations such as gamma irradiations [1-3] on the physico-chemical parameters (degree of crystallinity, specific surface area, cation exchange capacity and main layers charge).

"Swelling micas". This group of synthetic clays, of which Na-4-mica is only one, were originally developed expressly for water treatment. They expand as they absorb metal ions, then collapse, sealing the metals inside. Na-4-mica is formed by combining kaolinite, a soft clay mineral used in the ceramics industry, with magnesium oxide in sodium fluoride at a temperature of 890 ºC. The resulting product has natural mica's sheet like structure and brittle composition, but the space between the layers.

Waste streams encountered in mining operations, and various chemical processing industries, contain heavy metals which are non-biodegradable, toxic priority pollutants. Due to their tendency to accumulate in living organisms, causing various diseases and disorders, the treatment methods for metal-bearing effluents are essential for environmental and human health protection. Among numerous commonly used techniques for water purification, adsorption technologies have gained the most attention because of their low cost and easy operation [4-18].

Since the nylon-6/clay nanocomposites with some excellent properties [2,4], such as enhanced mechanical properties [1,2], increased heat distortion temperature, and decreased gas/vapor permeability [3], were successfully prepared by Toyota researchers in the late 1980s [4], many researchers from both academic and industrial labs have been focused on the polymer/clay nanocomposites [5-8]. Polypropylene (PP), as one of the most widely used plastics, possesses a relatively high performance-to-price ratio. However, inferior properties of PP, such as toughness [9], thermal stability, and barrier properties [10], hinder its application as high performance materials and special materials. Clay is one of very abundant phyllosilicate resources [11].

To improve PP properties, clay layers were hoped to disperse uniformly in PP matrix, exerting its rigidity, heat resistance, and dimension stability. However, it is difficult to prepare exfoliated PP/clay nanocomposites because of the incompatibility of hydrophobic PP and hydrophilic clay.

In order to improve the compatibility of clay and PP, surfactants have been used to modify clay [12]. However, it was found that some surfactants at the PP processing temperature not only accelerated the aging and decomposition of PP [13], but also led to the restacking of the silicate sheets [14-21]. Therefore, the design of surfactants with higher thermal stability is becoming more and more crucial.

In recent years, an intensive research was conducted focusing on the selection and/or production of low-cost adsorbents with good metal-binding capacities, which could be utilized as an alternative to the most widely used adsorbent in wastewater treatment-activated carbon. Natural materials of both organic and inorganic nature (such as chitosan, zeolites, minerals, etc.) and certain waste products from industrial operations (such as fly ash, coal and oxides) are classified as low-cost adsorbents because they are economical and locally available [22-43] Na-4-mica has much the same composition as natural mica, containing aluminum, silicon, and magnesium. But natural mica also contains potassium ions, which sit in hexagonal holes in the mineral's layers, superimposed upon one another, bonding the sheets tightly together.

This "closed" structure makes natural mica a poor ion exchange medium, [1,2]. The major goal in the present article is to investigate the effect gamma irradiation doses on structural and micro-structural properties of $Na_4Mg_6Cr_4Si_4O_{22} \cdot nH_2O$ mica clay sample.

2. EXPERIMENTAL

2. 1. Samples preparation

The selected samples of synthetic free fluoride – Na-4-mica which having the general formula $(Na_4Mg_6M_4Si_4O_{22} \cdot nH_2O)$ where $M = Cr^{3+}$ was synthesized by applying solution route and sintering procedure using the molar ratios of $Na_2O \cdot 2SiO_2 \cdot 2H_2O$, $MgCO_3$ and Cr_2O_3 each of highly pure chemical grade purity. The mixture were ground carefully then dissolved in few drops of concentrated nitric acid forming nitrate extract which diluted by water/carbon tetra-chloride 50% volume.

Mixture I was for sodium silicates solution and mixture II was for rest of component $(Mg + Cr)$ nitrates according to chemical formula desired. Mixture I was diluted by CCl_4 to be 100 ml then pH was adjusted to be 8.5 concentrated solution of ammonia was added carefully till heavy white precipitate from Metals hydroxide is obtained and the pH must be higher than 8. The precursor is filtered and washed by 2.5 % ammonium nitrate solution. Mixture II of $(Mg + Cr)$ was passing through the same treatment but in present of ethylene glycol as complexing agent to produce gelatinous precipitate of metals cations hydroxide precursor.

The Mixture I + Mixture II precursors were forwarded to muffle furnace and calcinations process was performed at 880 °C under a compressed air atmosphere for 10 hrs. then reground and pressed into pellets (thickness 0.2 cm and diameter 1.2 cm) under 10 Ton / cm^2. Sintering was carried out under air stream at 1000 °C for 10 hrs. The samples were slowly cooled down (20 °C /hr) till 500 °C and annealed there for 3 hrs. under air stream. The furnace is shut off and cooled slowly down to room temperature. Finally the materials are kept in vacuum desiccator over silica gel dryer.
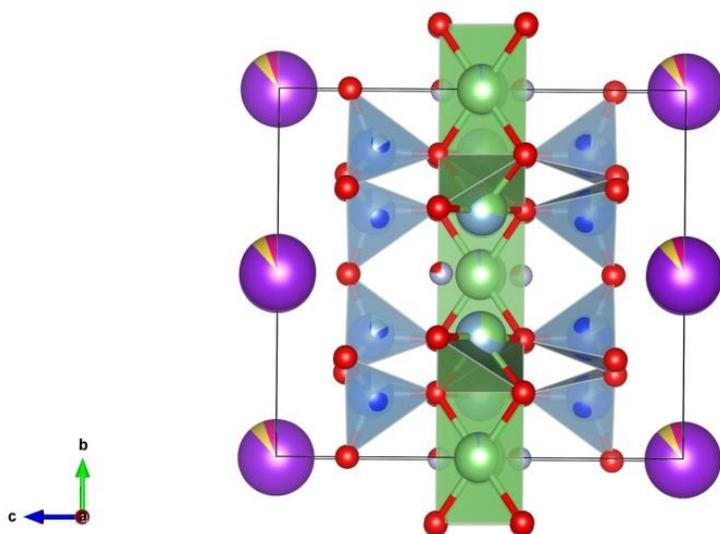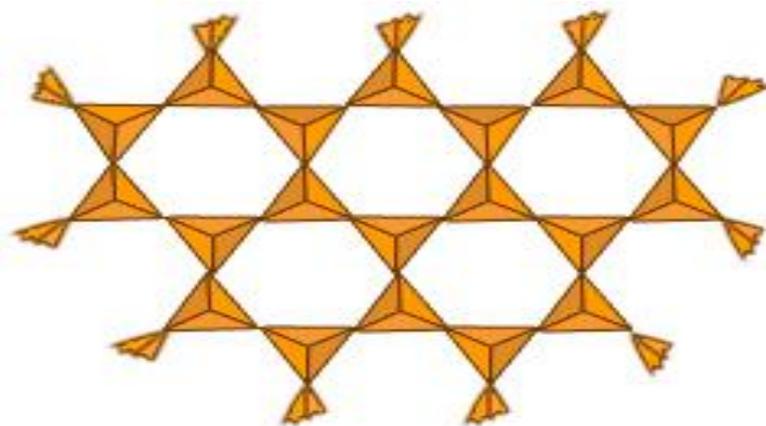
Fig. 1(a). Molecular Sieving Structure of Cr-III-Silicates - Clay.

The sample was named as Clay I = $(Na_4Mg_6Al_4Si_4O_{22}\cdot nH_2O)$, Clay II = $(Na_4Mg_6Bi_4Si_4O_{22}\cdot nH_2O)$ and Clay III = $Na_4Mg_6Cr_4Si_4O_{22}\cdot nH_2O$. As described in Figure 1 tetrahedral units of silicate are the backbone structure of mica clay indicating that each unit cell surrounded by 4-Na-atoms that can be replaced if it is applied as cations exchanger or molecular sieving material.
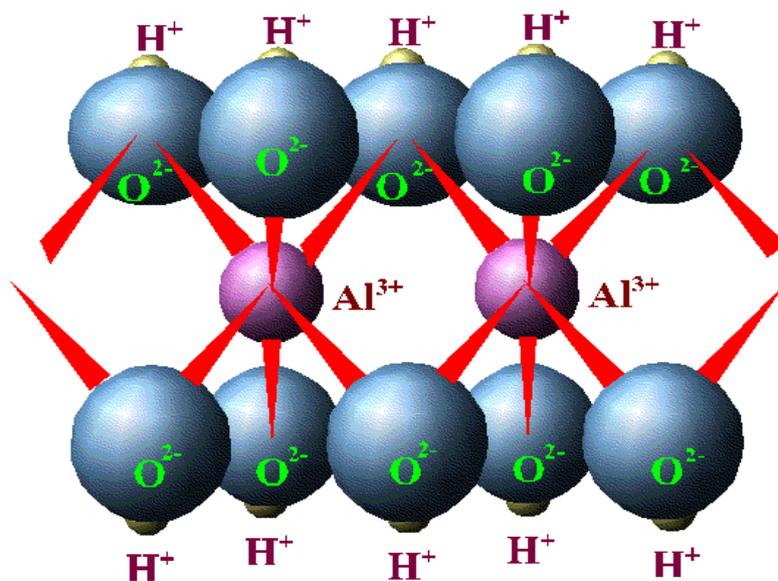

Fig. 1(b). Structure of Al-Silicates - Clay I.

2. 2. Samples irradiation

The sample was cut as three dimensional rectangle and exposed to perpendecular gamma-irradiations source by two different doses 1st dose = 1.5 MR/h at 25 cm distance and 2nd dose = 3 MR/h at 25 cm distance, by using Cs^{137} as gama-ray irradiations source .

2. 3. B. Phase Identification

The X-ray diffraction (XRD) measurements were carried out at room temperature on the fine ground samples using Cu-K$_\alpha$ radiation source, Ni-filter and a computerized STOE diffractometer / Germany with two theta step scan technique. Scannig Electron Microscopy (SEM) measurements were carried out at different sectors in the prepared samples by using a computerized SEM camera with elemental analyzer unit (PHILIPS-XL 30 ESEM /USA).

3. RESULTS AND DISCUSSION

3. 1. Phase Identification

Fig. 2 and 3(a-c): display the high resolution X-ray powder diffraction pattern recorded for synthetic free fluoride – Na-4-mica samples which are having the general formula ($Na_4Mg_6M_4Si_4O_{22}.nH_2O$) where $M = Cr^{3+}$. The analysis of the corresponding 2θ values and the interplanar spacings $d(\text{Å})$ were carried out using computerized program and indicated that, the X-ray crystalline structure mainly belongs to a monoclinic phase $Na_4Mg_6M_4Si_4O_{22} \cdot nH_2O$ in major besides few peaks of unreacted starting oxides as secondary phase in minor. The lattice parameters of the unit cell were refined using the least-squares sub-routine of a standard computer program these refined lattice parameters were found typically to those reported in [19-23] literatures. These unit cell parameters are in good agreement with those of the reported ones for $Na_4Mg_6M_4Si_4O_{22} \cdot nH_2O$ structure [6].
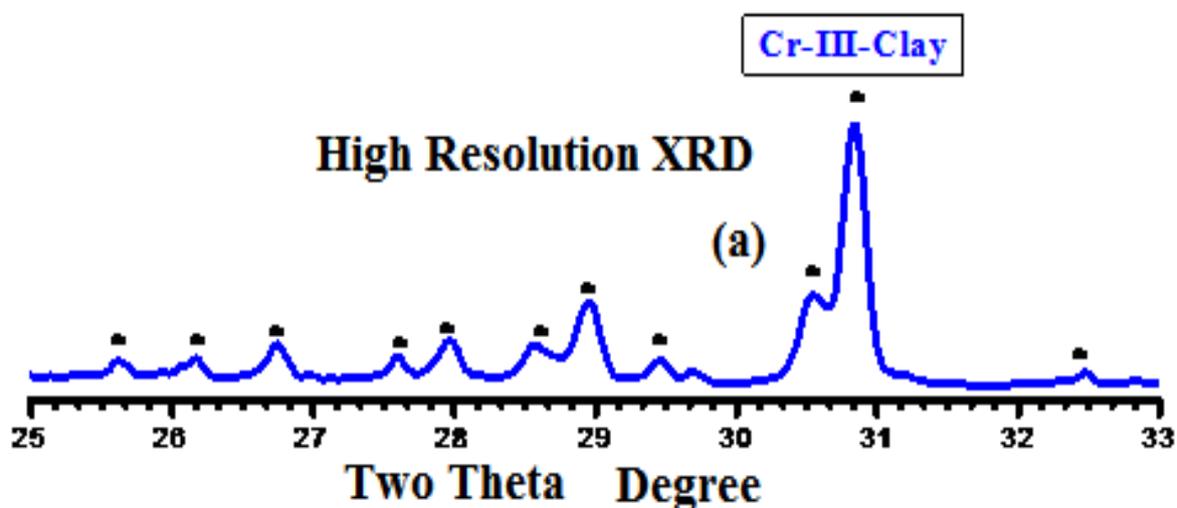

Fig. 2. Room temperature HR-XRD recorded for Cr-III-clay.

It is obviously that, gamma irradiation doses have a negligible effect on the main crystalline structure of $Na_4Mg_6Cr_4Si_4O_{22} \cdot nH_2O$ as shown in Fig. (2b,c). From Figs. 3(a,b) one can indicate that monoclinic phase of mica-clay $Na_4Mg_6Cr_4Si_4O_{22} \cdot nH_2O$ is the dominating phase by ratio exceeds than 90 % ($d_{100} = 1.12\text{-}1.13$ nm) confirming that gamma-irradiation doses does not effect on the monoclinic biotite phase.

These results are in full agreement with those reported by Allard and Calas [31] who are confirmed that radiations effects have negligible on both of structural and chemical properties of clay mineral. The lattice constants *a,b.c* of domain monoclinic phase were calculated after 1st and 2nd irradiation dose indicating that no sharp changes occurred in these values.
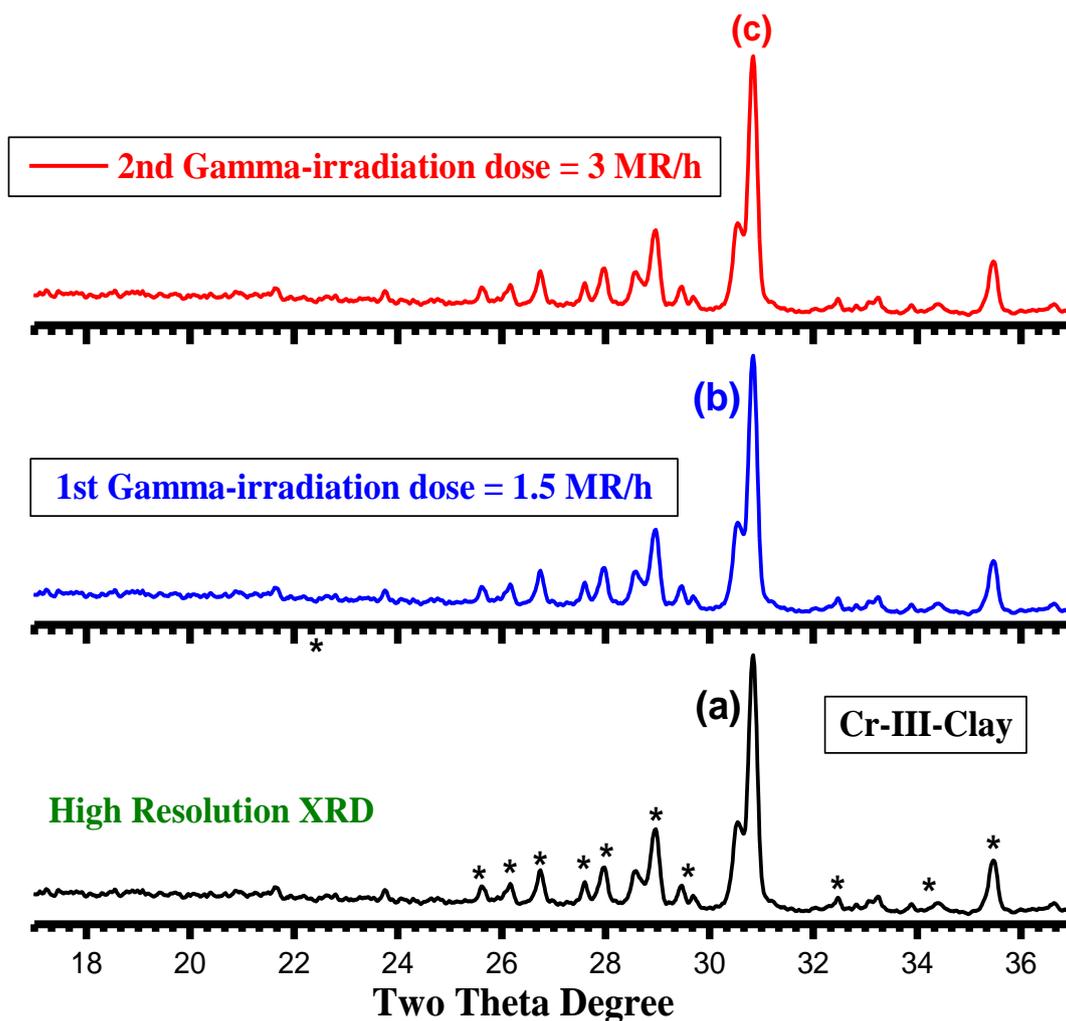

Fig. 3(a-c). HR-X-ray diffraction patterns recorded for;
(a) Cr-III-clay (Non-irradiated Sample)
(b) After 1st gamma-irradiation dose = 1.5 MR/h.
(c) After 2nd gamma-irradiation dose = 3 MR/h.

Table 1 explain EDX-elemental analysis data recorded for $Na_4Mg_6Cr_4Si_4O_{22}\cdot nH_2O$ that prepared via solution route. It is clear that the atomic percentage recorded is approximately typical with the molar ratios of the prepared sample emphasizing the quality of preparation through solution technique.

On the basis of molar ratio the allowed error in experimental procedures throughout solution rout is lesser than those reported in literatures for those synthesized by solid state routes [24,25].

Table 1. EDX-Elemental analysis data recorded for Cr-clay-III.

Cr-Clay-III

Element	Wt %	At %	K-Ratio	Z	A	F
O K	37.81	57.25	0.1069	1.7334	0.1481	1.0804
NaK	18.21	35.13	0.0479	1.1733	0.7353	1.0131
MgK	12.22	16.48	0.2731	1.0746	0.9607	1.0813
Cr L	16.66	16.65	0.0513	0.5181	1.0718	1.1498
Si L	18.98	16.23	0.2364	0.2175	1.0501	1.1212

3. 2. SE-microscopy measurements

Fig. 4(a-c) shows the SEM-micrographs recorded $Na_4Mg_6M_4Si_4O_{22} \cdot nH_2O$ that prepared via solution route where $M = Cr^{3+}$ before and after gamma irradiation doses. The estimated average of grain size for non – irradiated was calculated and found in between 2.37-3.43 µm while grain size decreases as irradiation dose increases from 1.5 to 3 MR/h recording 1.8 and 1.95 µm respectively. These results with accordance with data reported in [23] since gamma-irradiation energy increase grain splitting to lower grain size.

The EDX examinations for random spots in the same sample confirmed and are consistent with our XRD analysis for polycrystalline $Na_4Mg_6M_4Si_4O_{22} \cdot nH_2O$ that prepared via solution route,such that the differences in the molar ratios EDX estimated for the same sample is emphasized and an evidence for the existence of monoclinic - phase with good approximation to molar ratios see (Table 1).

From Fig. 4(a-c), it is so difficult to observe inhomogeneitiy within the micrograph due to that the powders used are very fine and the particle size estimated is too small.

This indicates that, the actual grain size in the material bulk is smaller than that detected on the surface morphology. Furthermore, particle size wa estimated from both of XRD and SEM analyses and its average found to be in between 25-124 nm confiming that solution route synthesis increases the fraction ratio of nano-particles formation.

In our opinion this structure quality enhanced by polar solven applied (carbon tetra chloride) that privent cooagulation of smaller grains with each other acting as grain size splitter enhancing nano-particle formation as occurred in our results.
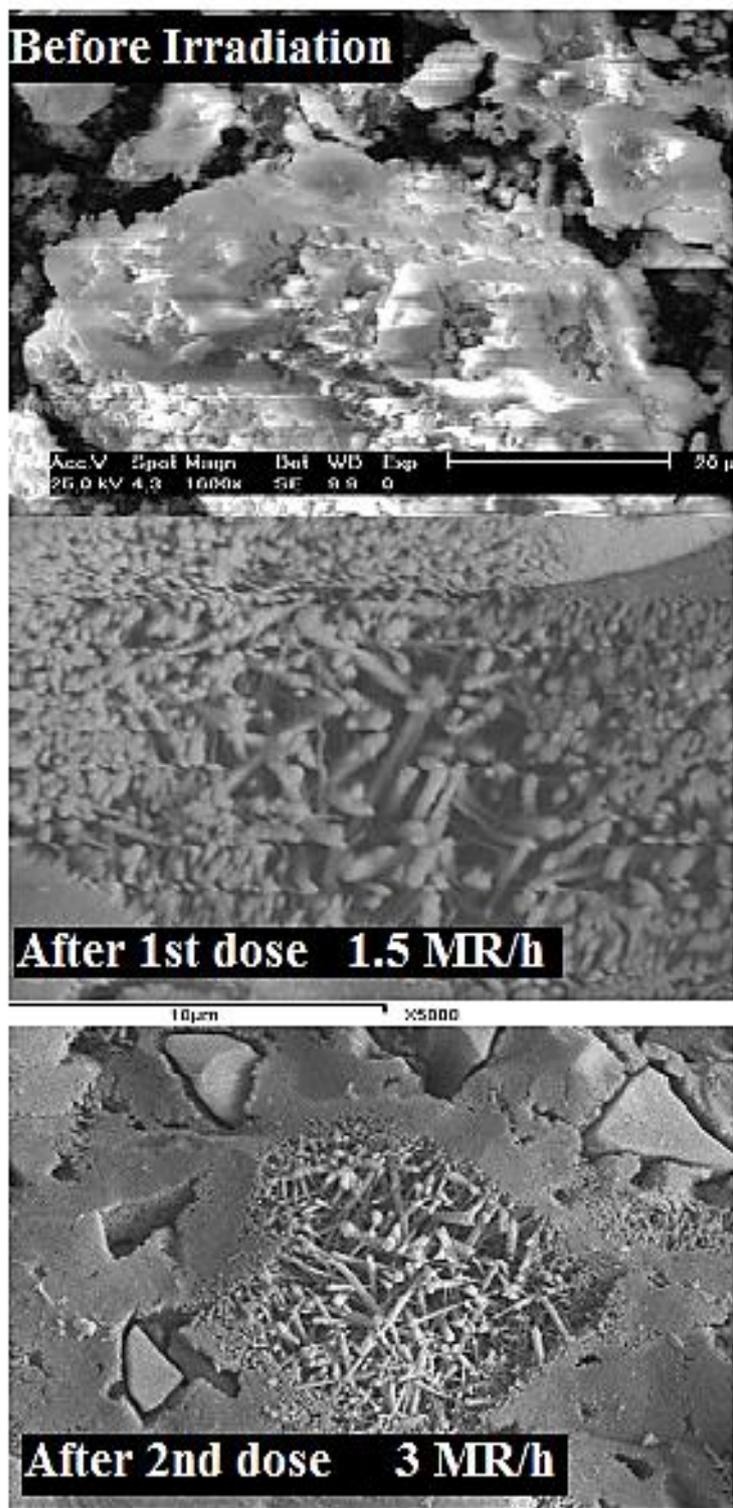
Fig. 4(a-c). Scanning electrons micrographs recorded for
(a) Non-irradiated Cr(III)-mica clay.
(b) After 1st irradiation dose 1.5 MR/h.
(c) After 2nd irradiation dose 3 MR/h.

4. CONCLUSIONS

The conclusive remarks inside this article can be summarized in the following points;

1- Solution technique applying organic solvent (Polar Solvent) as media matrix exhibits structure quality as preparation technique.

2- Synthetic free-fluoride $Na_4Mg_6M_4Si_4O_{22} \cdot nH_2O$ crystallize in monoclinic phase.

3- SE-micrographs confirmed that particles size was found in nano-scale (25-135 nm)

4- Gamma-irradiations have a slight effect on both of structural and microstructural parameters.

5- HP- synthetic micas can applied as cations selectivity for water remediatio.

References

[1] M. Plotze, G. Kahr, R. Hermann, *Applied Clay Science* 23 (2003) 195-202

[2] F.T. Madsen, *Clay Mineral J.,* 33 (1998) 109-129.

[3] D.T. Reed, D.D. Scott, M.F. Weiner, Academic press – Orlando (1987) 325-338

[4] S. Komarneni and R. Ravella, *Current Applied Physics* 8 (2008) 104-106.

[5] K.O. Adebowale, I.E. Unuabonah and B.I. Olu-Owolabi, *Journal of Hazardous Materials* B134(1-3) (2006) 130-139.

[6] Y. Al-degs, M.A.M. Khraisheh and M.F. Tutunji, *Water Research* 35(15) (2009) 3724-3728.

[7] M.A. Al-Ghouti, M.A.M. Khraisheh and M. Tutuji, *Chemical Engineering Journal* 104(1-3) (2004) 83-91.

[8] S.J. Allen and B. Koumanova, *Journal of the University of Chemical Technology and Metallurgy* 40(3) (2005) 175-192.

[9] S. Aytas, S. Akyil, M.A.A. Aslani and U. Aytekin, *Journal of Radioanalytical and Nuclear Chemistry* 240(3) (1999) 973-976.

[10] S. Babel, T.A. Kurniawan, *Journal of Hazardous Materials* B97(1-3) (2003) 219-243.

[11] E.P. Barrett, L.G. Youner and P. Halenda, *Journal of the American Chemical Society* 73(1) (1951) 373-380.

[12] K.G. Bhattacharyya and S.S. Gupta, *Journal of Colloid and Interface Science* 310(2) (2007) 411-424.

[13] C. Camilo, G. Carmen and M. Paula, *Journal of Chemical Technology & Biotechnology* 80(4) (2005) 477-481.

[14] J.M. Charnock, K.E.R. England, M.L. Farquhar and D.J. Vaughan, *Physica. B, Condensed Matter* 208-209 (1995) 457-458.

[15] T.N.D. Dantas, A.A.D. Neto, M.C.P. Moura, *Water Research* 35(9) (2001) 2219-2224.

[16] M.K. Doula and A. Ioannou, *Microporous and Mesoporous Materials* 58(2) (2003)115-130.

[17] F. Ekmekyapar, A. Aslan, Y.K. Bayhan and A. Cakici, Biosorption of copper(II) by nonliving lichen biomass of *Cladonia rangiformis* Hoffm, *Journal of Hazardous Materials* 137(1) (2006) 293-298.

[18] E. Erdem, N. Karapinar and R. Donat, *Journal of Colloid and Interface Science* 280(2) (2004) 309-314.

[19] O. Hamdaouia and E. Naffrechoux, *Journal of Hazardous Materials* 147(1-2) (2007) 381-394.

[20] Y.S. Ho, J.F. Porter and G. McKay, *Water, Air, and Soil Pollution* 141(1-4) (2002) 1-33.

[21] IPCS (International Programme on Chemical Safety) 1998. Copper. Environmental Health -Criteria 200. Geneva, Switzerland: World Health Organization (1998).

[22] A. Kayaa and A.H. Oren, *Journal of Hazardous Materials* B125(1-3) (2005) 183-189.

[23] M.A.M. Khraisheh, Y.S. Al-degs and W.A.M. Mcminn, *Chemical Engineering Journal* 99(2) (2004) 177-184.

[24] S. Kubilay, R. Gürkan, A. Savran and T. Şahan, *Adsorption* 13(1) (2007) 41-51.

[25] S. Lazarević, I. Janković-Častvan, D. Jovanović, S. Milonjić, Dj. Janaćković and R. Petrović, *Applied Clay Science* 37(1-2) (2007) 47-57.

[26] S.-H. Lin and R.-S. Juang, *Journal of Hazardous Materials* B92(3) (2002) 315-326.

[27] N. Meunier, J. Laroulandie, J.F. Blais and R.D. Tyagi, *Bioresource Technology* 90(3) (2003) 255-263.

[28] T. Mishra and S.K. Tiwari, Studies on sorption properties of zeolite derived from Indian fly ash, *Journal of Hazardous Materials B* 137(1) (2006) 299-303.

[29] A.E. Osmanlioglu, *Applied Radiation and Isotopes* 65(1) (2007) 17-20.

[30] M. Panayotova and B. Velikov, Kinetics of heavy metal ions removal by use of natural zeolite, *Journal of Environmental Science and Health A* 37(2) (2002) 139-147.

[31] T. Allard and G.Calas, *Applied Clay Science* 43 (2009) 143-149.

[32] Y. Kojima, A. Usuki, M. Kawasumi et al., "Mechanical properties of nylon 6-clay hybrid," *Journal of Materials Research,* 8(5) (1993) 1185-1189.

[33] A. Oya, Y. Kurokawa, and H. Yasuda, *Journal of Materials Science,* 35(5) (2000) 1045-1050.

[34] J. W. Gilman, "Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites," *Applied Clay Science,* 15(1-2) (1999) 31-49.

[35] A. Okada and M. Kawasumi, "Synthesis and characterization of a nylon 6-clay hybrid," *Polymeric Preprints*, 28(2) (1987) 447-448.

[36] S. S. Sinha Ray and M. Okamoto, *Prog. Polym. Sci.* 28(11) (2003) 1539-1641.

[37] Y. J. Huang, K. F. Yang, and J. Y. Dong, *Macromolecular Rapid Communications*, 27(15) (2006) 1278-1283.

[38] A. He, H. Hu, Y. Huang, J. Y. Dong, and C. C. Han, *Macromolecular Rapid Communications,* 25(24) (2004) 2008-2013.

[39] L.-M. Wang, A.-H. He, K. Du, Y.-Q. Huang, J.-Y. Dong, and Z.-C. Han, "Structure characterization and physical properties of exfoliated polypropylene/montmorillonite nanocomposites synthegized via in situ polymerization," *Journal of Chemical Engineering of Chinese Universities*, 24(1) (2010) 132-137.

[40] F. Rault, C. Campagne, M. Rochery, S. Giraud, and E. Devaux, *Journal of Polymer Science, Part B: Polymer Physics,* 48(11) (2010) 1185-1195.

[41] H. Qiao, Y. Cai, F. Chen, *Fibers and Polymers,* 10(6) (2010) 750755.

[42] M. Kato, A. Usuki, and A. Okada, "Synthesis of polypropylene oligomer-clay intercalation compounds," *Journal of Applied Polymer Science,* 66(9) (1997) 1781-1785.

[43] A. H. He, L. M. Wang, W. Yao, B. C. Huang, D. J. Wang, and C. C. Han, *Polymer Degradation and Stability*, 95(4) (2010) 651-655.