Adsorption of Hazardous Petroleum Constituents by Ordinary and Modified Bentonites

Mohammad Ali Hosseinpour*, Tehran Oil Refining Company, Tehran, IRAN.
(*Corresponding Author: Tel: 0098- 9361137249; E-mail address: hosseinpour83@ gmail.com).
Hossein Ghoreishi, Tehran Oil Refining Company, Tehran, IRAN. The head of environment in T.O.R.C.
Feriya Ghanaat, Master of Science Student, Azad University, Tehran, IRAN.
Mohsen Eskandari, Iranian Oil Products Distribution Company, Tehran, IRAN.

ABSTRACT

Hazardous chemicals are the major cause of soil contamination in the environment. To prevent the leaching of pollutants in soils, different stabilization and containment techniques have been developed in recent years.

Organophilic bentonites, due to their large surface areas, negative charges on their particles, and high adsorption characteristics have many applications for remediation of contaminated sites. The above characteristics of modified bentonites have enabled them to adsorb contaminants from solutions or to stabilize them in soils.

This study focuses on interlayer changes of bentonite clays due to the adsorption of hydrocarbons (i.e, Crude Oil, MTBE, BTEX compounds and Gasoline). Free swell tests and X-ray diffraction analysis were conducted on the clays. The free swell test results showed that modified bentonites effectively intercalated crude oil into their particles and adsorb them, hence presenting 410 % volume increase when exposed to this compound.

Results of X-ray diffraction analysis for modified bentonite samples indicated a 63.15% interlayer increase after their exposure to the crude oil while that of ordinary bentonites was relatively insignificant (0.50%). Similar observations were noted for other hydrocarbonic compounds, denoting the organophilic properties of modified bentonites.

Key Words:
Modified clay, Xrd analysis, Free swell test, BTEX compounds, MTBE, Crude oil, Gasoline.

INTRODUCTION

Major soil and groundwater contamination with petroleum constituents (i.e., BTEX compounds, MTBE, etc.) occur from small leaks or large ruptures from underground storage tanks (USTs).

Most of current research in this area focuses on modified bentonite particles, formed by exchanging the naturally occurring cations (i.e., Na^+, K^+, Ca^{2+}, and Mg^{2+}) with larger organic cations. The modification is achieved by stationing organics (i.e., quaternary ammonium salts (QAS)) on bentonite platelets, thus resulting in increased basal spacing and enhanced adsorption of organic contaminants [1]. Figure 1 presents the adsorption of organic compounds in the clay's interlamellar spacing as a result of such modification [2].

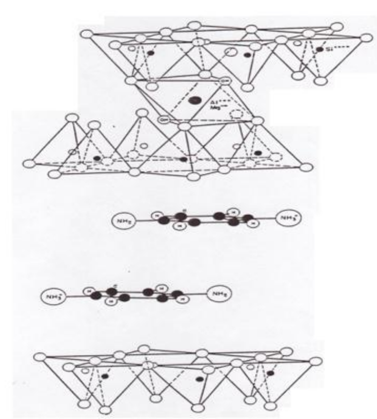


Figure.1.
Position of Organic Cations Between Layers of Bentonitic Clay[2].

Modified bentonites are the most promising adsorbing agents for removing organic hazardous wastes [3,4]. The effectiveness of modified bentonites in removing BTEX compounds was studied by Gitipour et al who showed that modified bentonites were about 74.3% more efficient than ordinary bentonites in removing BTEX compounds from aqueous solutions [5]. Because of their organophilic nature, the modified bentonites has been proposed for use as earthen liners at waste disposal facilities [6,7].

The objectives of this study were to evaluate the efficiency of modified bentonites as an adsorbent in geosynthetic liners and solidification/stabilization treatment techniques for removing hazardous organic compounds from contaminated soils and liquids. To accomplish these goals, free swell tests, and Xrd analysis were carried out at this research.

MATERIAL AND METHODS

Laboratory Modification of Bentonite

The process of the clay's modification is as follows: An amount of tailoring agent (quaternary ammonium salt (QAS) of hexadecyl-trimethyl ammonium (HDTMA)) equal to the CEC (cation exchange capacity) of the clay was weighed and dissolved in warm distilled water. Next, the mixture was added slowly to the clay suspension while being agitated in a large beaker by a magnetic stirrer. After the sample was stirred for four hours, the tailoring agent-clay suspension was centrifuged and washed four times with distilled water to remove thoroughly all the replaced cationic compounds in the clay. The sample was then quick frozen and freeze-dried for the experiments [8].

Examples of research and utilization of organobentonites (also called organophilic clays) can be found throughout the literature [9,10,11,12]. Organobentonites can be created by exchanging the hydrated exchangeable cations of clay (usually bentonite) with various types of quaternary ammonium cation [13] or by other techniques [14,15].

Free Swell Tests

In this research free swell tests were carried out to determine the volume change of modified and natural bentonites due to adsorption of crude oil, BTEX compounds. MTBE and water. To carry out the tests, $2cm^3$ of ordinary and modified bentonite samples were placed in different glass tubes. Then $20cm^3$ of crude oil, MTBE and water (each separately) were added slowly to each of the tubes (two soils, eight liquids, duplicate runs). A total of twelve samples were tested during the study. To evaluate the swelling of the clays, the glass tubes were kept intact in laboratory for a period of 48 hours.

X-ray Diffraction Analysis

The adsorption of organic compounds on bentonite can be studied by X-ray diffraction analysis (Xrd). This method establishes the fact of adsorption and provides information regarding the absorbed molecules into the basal spacing of the clay particles [16].

Xrd analysis were carried out by mixing the modified and ordinary bentonites with crude oil, MTBE, BTEX compounds, gasoline and water to evaluate the changes that occur in the interlamellar distance of the clays as a result of their interaction with these organics. Prior to the analysis, samples of the clays sufficient to fill an aluminum sample holder (approximately 1 gram of the clays for each sample) were mixed separately with each of the above compounds. A porcelain crucible and a spatula were used to mix the samples to help prevent the shrinking of the samples and to inhibit the formation of cracks resulting from the loss of the chemicals to the air. Next, with the aid of a glass slide, each of the samples was placed in the sample holder and smoothly leveled to introduce a dispersed horizontal orientation of clay particles in the samples. The sample holder was then immediately transferred to the x-ray diffractometer for analysis.

X-rays are electromagnetic radiation of wavelength about $1A^{\circ}$, about the same size as an atom. The Xrd technique helps measure the size and shape of the unit cells for clay. The analyses were conducted at the Xrd laboratory of the Mineral Engineering Department of University of Tehran. A Bruker AXS D8 Advanced X-ray powder diffractometer with a Cu-K=1.54 A◦ radiation source was used to analyze the clays. The analyses were performed at a 10-minute running period for each sample.

RESULTS

Free Swell Test

As presented in Table 1, crude oil's constituents have been positioned on the surfaces of modified bentonites particles, thus introducing 410% volume change in the clay. However, in case of water, increasing in volume of the particles was only 7.5% due to hydrophobicity of modified bentonites. Also

ordinary bentonites has not sufficient volume increase in case of crude oil (15 %) as compared with water (542.5 %). Regarding the BTEX compounds, as presented in the table, all of the samples showed volume increases in the range of 400% to 500%.
The results of this study support the hupothesis that organo-bentonite effectively intercalate crude oil into their particles, thus increasing the clay particles' volume; the volume increase would then reduce the permeability of the soil, hence reducing the mobility of hydrocarbons in clay liners.

Xrd Analysis

Summary of Xrd analysis conducted on ordinary and modified bentonite samples have been presented in Tables 2 and 3. The same compounds tested in free swell tests were used for these analysis as well.
Xrd analysis on ordinary and modified bentonites indicated that the basal spacing of the bentonite modified by QAS has increased 136.4 % (from 12.1 Ǻ to 28.6 Ǻ). Positioning of QAS on the surface of the clay particles would be the major reason for the basal increase. For ordinary bentonites mixed with water, the basal spacing increased from 12.1Ǻ to 21.26Ǻ (75.7% increase) while for that of modified bentonite samples the basal spacing change was from 28.6Ǻ to 29.9Ǻ (4.5 %). This shows the little tendency of modified bentonite to adsorb water.
In case of the mix of modified bentonite and crude oil (as shown in Figure 2), the basal spacing was changed from 28.6Ǻ to 46.66Ǻ; presenting a 63% interlaminar increase. Almost a similar change was observed for MTBE. For this compound, the basal spacing of the modified bentonite was increased from 28.6Ǻ to 42.32Ǻ (almost 48% changes)
(see Figure 3).
Regarding the ordinary bentonite subjected to crude oil, very low interlayer increase (from 12.1Ǻ to 12.16Ǻ) indicates insignificants tendency of this clay in adsorbing crude oil. Similar findings were noticed for BTEX compounds (as presented in Figure 4). For modified bentonites, however, much higher adsorption of BTEX compounds was noticed. On average, a 29.8% increase in adsorption of these compounds onto the modified bentonite was noticed. Figure 5 presents Xrd test results for all the hydrocarbons tested.
Differences between the adsorption of ordinary and modified bentonites exposed to water and oily compounds confirms the strong affinity of modified bentonites to various hydrocarbons tested.

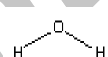
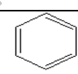
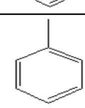
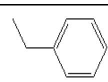
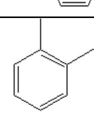
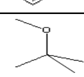
CONCLUSION

Ordinary and modified bentonites characteristics including high adsorption capacity and large surface areas have made them suitable for use as stabilizing and adsorbing agents in treatment and containment of hazardous wastes (i.e. liner systems). Ordinary bentonites have high hydrophilic characteristics while modified bentonites present promoted organophilic properties.
Adsorption of water molecules by ordinary bentonites causes increase in clay basal spacing, while modified bentonites adsorb hydrocarbon contaminants instead. Geosynthetic clay liners are widely used in hazardous waste landfills as barrier systems to contain hazardous contaminants. As there are different types of contaminants in hazardous waste leachates, application of both ordinary and modified bentonites is recommended to increase the liner efficiency as barrier systems at hazardous waste sites. Also, to adsorb water and organic-based liquids in leachates, it is proposed to use both ordinary and modified bentonites in different combinations in landfills.
Further researches should focus on application of different mixtures of modified and ordinary bentonites as well as the use of various tailoring agents (quaternary ammonium salts) with the clays to enhance the clays adsorption properties for each class of contaminants and help fabricate the most effective liners for organics removal from leachates at contaminated sites.

Table 1.
Changes in Volume of Ordinary and Modified Bentonites Exposed to Water, BTEX Compounds, Crude Oil and MTBE

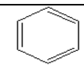
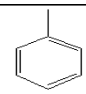
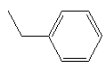
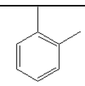
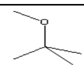
Solution Type	Dry clay volume (cm^3)	Clay Type					
		Ordinary Bentonite			Modified Bentonite		
		Volume(cm^3)		Average percent change	Volume(cm^3)		Average percent change
Water	2.0	12.9	12.8	542.5	2.1	2.2	7.5
Crude Oil	2.0	2.3	2.3	15.0	10.6	9.8	410.0
MTBE	2.0	2.3	2.3	15.0	12.0	11.9	497.5
Gasoline	2.0	2.2	2.2	8.8	11.3	11.8	477.5
Benzene	2.0	2.1	2.2	7.5	10.2	9.9	402.5
Toluene	2.0	2.2	2.2	10.0	10.9	11.2	452.5
Ethyl-benzene	2.0	2.2	2.3	12.5	11.0	11.8	470.0
O-xylene	2.0	2.1	2.2	7.5	10.9	11.3	455.0

Table.2.
Xrd Results for Ordinary Bentonite Samples Exposed to BTEX Compounds, MTBE, Crude Oil, Gasoline, and Water.

Organic Chemical	**Molecular Formula**	**Structure**	**Basal Spacing of Ordinary Bentonite, A°**			
			Original	**After Exposure**	**Amount of change**	**Percent of change**
water	H_2O		12.1	21.26	9.16	75.7
Benzene	C_6H_6		12.1	12.28	0.18	1.49
Toluene	C_7H_8		12.1	13.11	1.01	8.35
Ethyl-benzene	C_8H_{10}		12.1	14.8	2.7	22.31
O-xylene	C_8H_{10}		12.1	12.23	0.13	1.07
MTBE	$C_5H_{12}O$		12.1	14.3	2.2	18.18
Crude Oil	NA	NA	12.1	12.16	0.06	0.50
Gasoline	NA	NA	12.1	12.72	0.62	5.12

NA: Not Applicable

Table.3.
Xrd Results for Modified Bentonite Samples Exposed to BTEX Compounds, MTBE, Crude Oil, Gasoline, and Water.

Organic Chemical	**Molecular Formula**	**Structure**	**Basal Spacing of Modified Bentonite, A°**			
			Original	**After Exposure**	**Amount of change**	**Percent of change**
water	H_2O		28.6	29.9	1.3	4.55
Benzene	C_6H_6		28.6	36.57	7.97	27.86
Toluene	C_7H_8		28.6	35.29	6.69	23.39
Ethyl-benzene	C_8H_{10}		28.6	38.5	9.9	34.62
O-xylene	C_8H_{10}		28.6	38.12	9.52	33.29
MTBE	$C_5H_{12}O$		28.6	42.32	13.72	47.97
Crude Oil	NA	NA	28.6	46.66	18.06	63.15
Gasoline	NA	NA	28.6	41.24	12.64	44.20

NA: Not Applicable

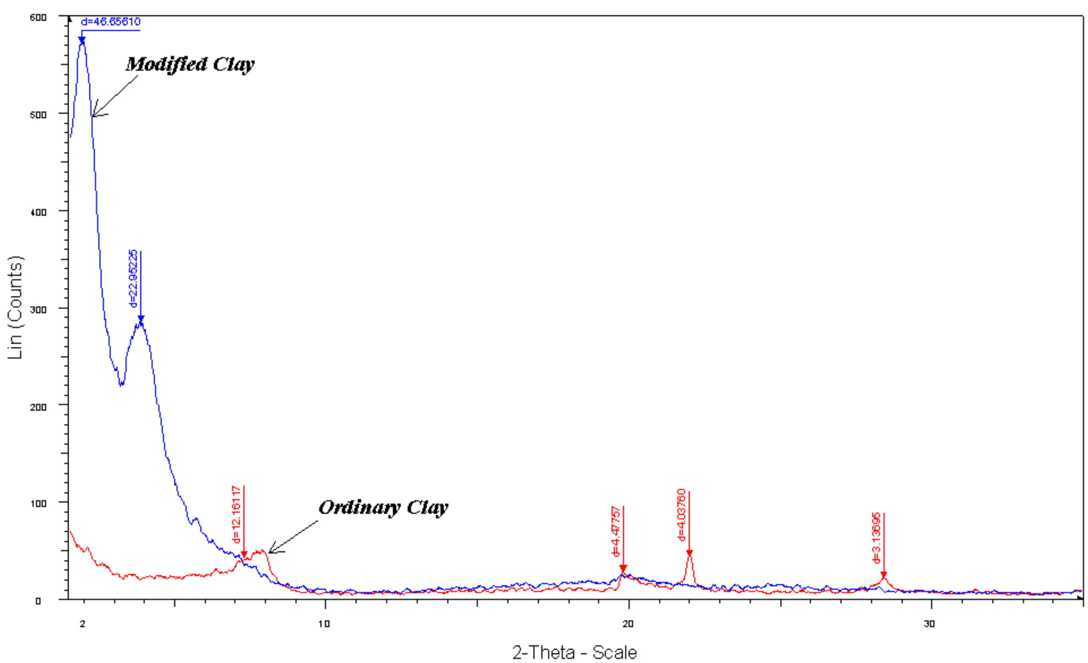


Figure.2.
X-ray Diffraction Analysis of Modified and Ordinary Clay Particles Subjected to Crude Oil

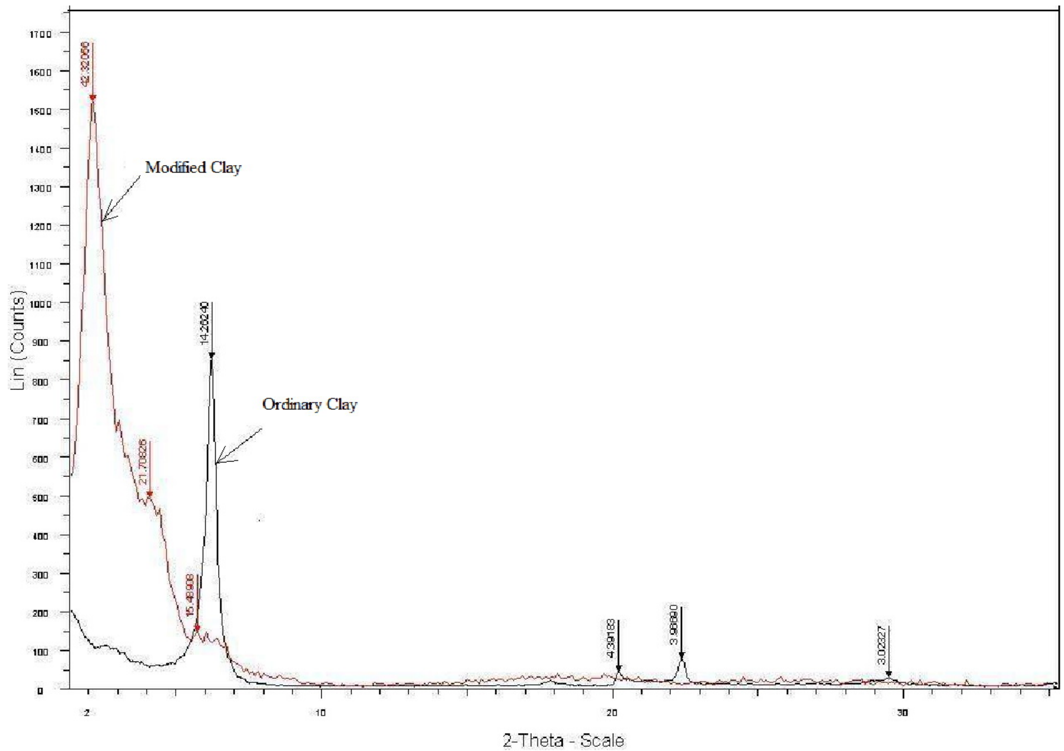


Figure .3.
X-ray Diffraction Analysis of Modified and Ordinary Clay Particles Subjected to MTBE.

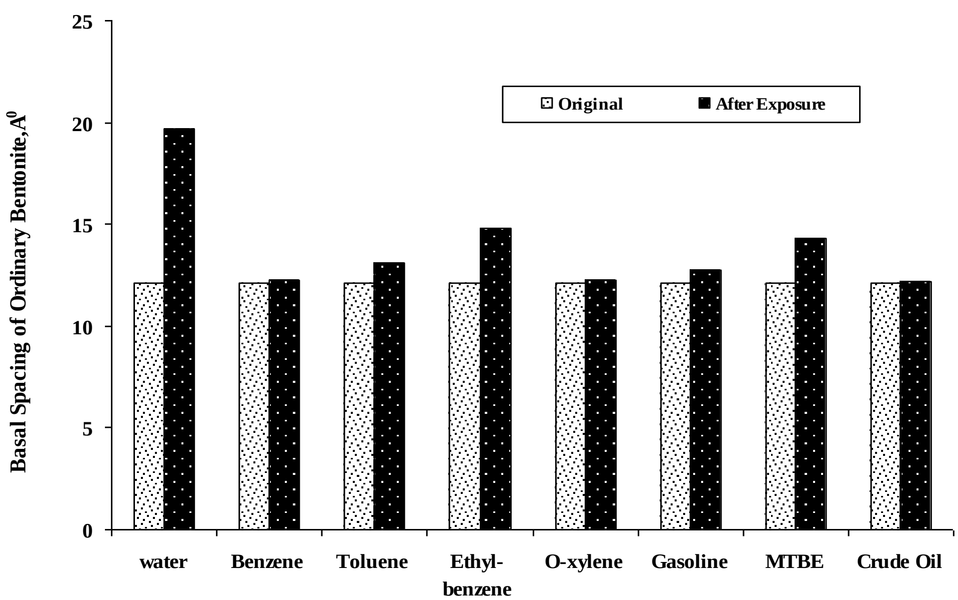


Figure.4.
Changes in Basal Spacing of Ordinary Bentonites Exposed to Various Hydrocarbons.

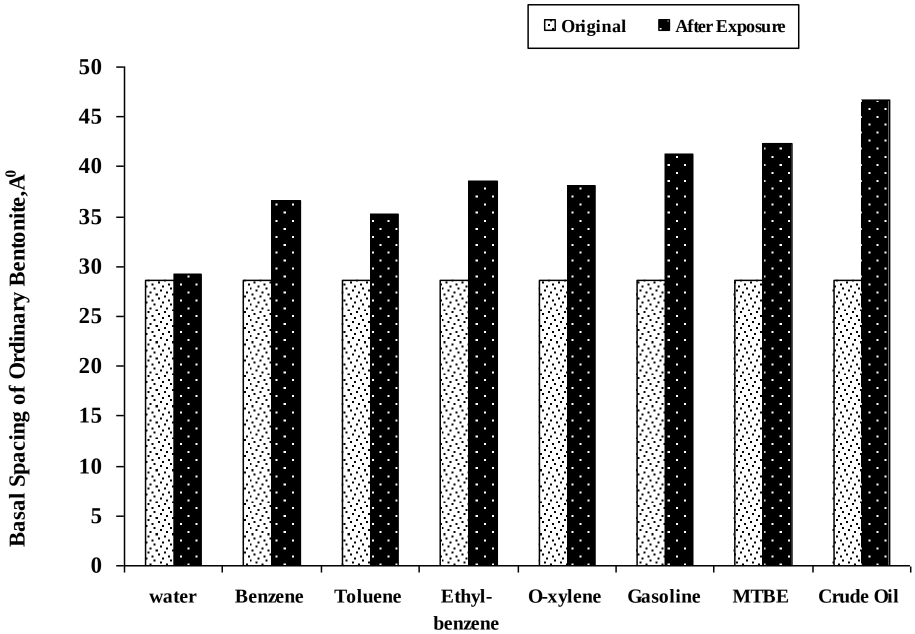


Figure.5.
Changes in Basal Spacing of Modified Bentonites Exposed to Various Hydrocarbons.

REFERENCES

1. Paria, S. and Yuet, P. K., 2006, "Solidification/Stabilization of Organic and Inorganic Contaminants using Portland Cement": A Literature Review, Environmental reviews, Vol 14, P 214-255.
2. LaGrega,Michael, D., Phillip L.Buckingham., Jeffery C.Evans., 2001."Hazardous waste management", 2nd edition
3. Lo, I.M.C., 1996. Solidification/stabilization of phenolic waste using organic-clay complex, Journal of Environmental Engineering 122: 850–855.
4. Zhu, L., Chen, B., and Shen, X., 2000. Sorption of phenol, p-nitrophenol, and aniline to dual-cation organobentonites from water. Environmental Science & Technology 34: 468–475.
5. Gitipour, S., Bowers, M.T., and Bodocsi, A., 1997. The use of modified bentonite for removal of aromatic organics from contaminated soil. Journal of Colloid Interf Science 196: 191–198.
6. Grube, W. E., Roulier, M. H., and Herrmann, J. G., 1987. "Implications of current soil liner permeability research results." U.S. EPA, Hazardous Waste Engineering Research Laboratory, Cincinnati, OH. 45268.
7. Smith, J.A., Li, J. and Galan, A., 2000, "Characterization, containment, remediation, and performance in environmental geothechnics", in: Y. Acar and D.Daniels (Eds) American Society of Civil Engineers, Vol.1, Vol.1 (New York:), pp. 806-814.
8. Janes, W.J. and Boyd, S.A., 1991, "Clay mineral type and organic sorption by Hexadecyl-trimethyl ammonium exchanged clays." Soil Science Society of America Journal, 55, 43-48.
9. Lake, C.B. and Rowe, R.K., 2005. "A comparative assessment of volatile organic compound (VOC) sorption to various types of potential GCL bentonites." Geotextiles and Geomembranes 23 (2005) 323-347.

10. Headley, J.V., Boldt-Leppin, B.E.J., Haug, M.D. and Peng, J., 2001. "Determination of diffusion and adsorption coefficients for volatile organics in an organophilic clay-sand-bentonite liners." Canadian Geotechnical Journal 38, 809-817.
11. Boldt-Leppin, B.E.J., Haug, M.D. and Headley, J.V., 1996, "Use of organophilic clay in sand-bentonite as a barrier to diesel fuel." Canadian Geotechnical Journal 33, 705-719.
12. Jaynes, W.F. and Vance, G.F., 1996. "BTEX sorption by organo-clays: cosorptive enhancement and equivalence of interlayer complexes." Soil Science Society of America
13. Xu, S., Sheng, G. and Boyd, S.A., 1997, "Use of organoclays in pollution abatement." Advances in Agronomy 59, 25-62.
14. Lo, I.M.C., 1992, "Development and evaluation of clay-liner materials for hazardous waste sites." Ph.D. Dissertation, The University of Texas at Austin.
15. Srinivasan, K.R. and Fogler, H.S., 1990. "Use of inorgano-organo-clays in the removal of priority pollutants for industrial wastewaters": structural aspects 38, 277-286.
16. Gitipour, S., Baghvand, A. and Givehchi, S., 2006, "Adsorption and permeability of contaminated clay soils to hydrocarbons." Pakistan Journal of Biological Sciences, 9(3), 336-340.