

# Geo-environmental behavior of marly soils, application for landfills and comparison to bentonite behaviour



Ouhadi<sup>1</sup>, Vahid R., and Ahoughalandari<sup>2</sup>, Bahar

<sup>1</sup> Professor – Department of Civil Engineering – University of Bu-Ali Sina, Hamedan, Iran

<sup>2</sup> Master of Geotechnical and Geo-environmental Engineering – Department of Civil Engineering – Bu-Ali Sina University, Hamedan, Iran

## ABSTRACT

The current study aims at experimental investigation of geo-environmental behaviour of marly soils. The retention behaviour of soil samples is evaluated using batch equilibrium tests with different concentrations of Zn and Pb contaminants. The results for marly soils are compared with those for bentonite. Furthermore, the contribution of different marly soil phases in retaining Pb is investigated using a series of selective sequential extraction experiments. The results confirm that the marly samples possess high buffering capacity, high specific surface area, and high contaminant retention capacity. Moreover, carbonate and exchangeable phases showed, respectively, the highest and lowest association for Pb retention. In comparison to bentonite, marl has a higher buffering capacity and complete retention capacity.

## RÉSUMÉ

Cette étude expérimentale concerne le comportement géo-environnemental de sols marneux. La capacité de rétention d'échantillons de sols est évaluée en faisant une série de tests d'équilibre pour différentes concentrations en zinc et plomb. Les résultats obtenus pour les sols marneux sont comparés avec ceux pour la bentonite. De plus, en réalisant un ensemble d'essais d'extraction séquentielle sélective, la contribution de différents sols marneux dans la rétention du plomb a été étudiée. Les résultats obtenus indiquent que les échantillons marneux ont une grande capacité tampon, une surface spécifique élevée et une capacité de rétention considérable. Selon ces résultats, la phase de carbonate et la phase échangeable ont respectivement le plus grande et la plus faible participation dans la rétention du plomb. En comparaison avec la bentonite, la capacité tampon et la capacité de rétention de la marne est remarquable.

## 1 INTRODUCTION

Marly soils, which exhibit unique behaviour, are observed in several locations of the world such as Italy, Spain, Britain, Canada, France, United States, the Persian Gulf states and Iran, from the north to the south-west (Oostwoud Wijdenes and Ergenzinger, 1998; Palumbo et al., 2000; Lamas et al., 2002; Ouhadi and Yong, 2003a; Lamas et al., 2005; Sadrekarimi et al., 2006; Frydman et al., 2007; Yong and Ouhadi, 2007; Ramezanzpour and Smaelnejad, 2008).

There are diverse definitions for this type of soil in the literature which explain it as a simple combination of clay and calcium carbonate (Terzaghi and Peck, 1967; Pettijohn, 1975; McCarthy, 1982; Mitchell, 1985). The characteristics of marly soils depend on the quality and quantity of these two phases (Lamas et al., 2002). Low slake durability, collapsible, dispersive and swelling behaviour, different types of erosion, sink-holes, landslides and failure in foundations, road sub-bases and slopes are some examples of common features and symptoms of ensuing existence of marly soils. They are caused by special structure of their clay minerals and a remarkable amount of salinity (Mohamed et al., 1991; Ouhadi, 1997; Oostwoud Wijdenes and Ergenzinger, 1998; Ouhadi and Yong, 2003a; Frydman et al., 2007; Ramezanzpour and Smaelnejad, 2008).

Generally, the clay portion of the marly soils consists of chain-like minerals called Palygorskite and Sepiolite which usually accompany other kinds of non-silicate minerals, like carbonates and sulphates (Yong et al., 1993b; Ouhadi et al., 1996; Yong et al., 1996). They are alumino-magnesium-silicates minerals which differ with regard to the proportion of aluminum and magnesium. The inner-layer spaces are composed of rectangular channels in which the exchangeable cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and Zeolite water exist (Ouhadi, 1997; Neaman and Singer, 2004; Aiben, 2006; Krekeler and Guggenheim, 2008; Zhang et al., 2008; Chang et al., 2009). In other words, they can provide two sites of retention; one on the external surface of the mineral and the other the Zeolite channels (Aiban, 2006). So, despite these two minerals possess low cation exchange capacity- in the range of 9 to 30 cmol/kg-soil- their specific surface area is significant- around 600 m<sup>2</sup>/g- which results from its open structure. Hence, they have high liquid limit and exhibit great retention capacity in comparison with other clay minerals (Ouhadi, 1997; Neaman and Singer, 2004; Aiben, 2006; Krekeler and Guggenheim, 2008; Zhang et al., 2008; Chang et al., 2009). Furthermore, the buffering capacity of a soil is a function of cation exchange capacity and the amount of carbonate (Yong and Phadangchewit, 1993). Calcite is a carbonate mineral which can perform as a good buffer against pH variations in a soil-water system,

caused by contaminants, for example (Yong, 2000). Carbonate minerals can also retain heavy metals and phosphates. In the presence of carbonate, the heavy metals are retained mainly by forming their carbonate compositions (Yong, 2000; Ottoson et al., 2001; Chopin et al., 2008; Lafuente et al., 2008). According to the above mentioned points, marly soils which normally contain carbonate and Palygorskite and/or Sepiolite at the same time, are expected to effectively retain contaminants and heavy metals.

In spite of much research on the geotechnical behaviour of marly soils, only few studies can be found in which the geo-environmental aspects of their behaviour are considered. Therefore, in this paper the main target is to assess the response of marly samples toward heavy metal contaminants in order to evaluate the possibility of using them as the constituting material of landfills. It is obvious that if the efficiency of marly soils can be proven, they can be an economic choice for landfills in the areas that they exist. In addition, inasmuch as bentonite is a well-known clayey soil useful in many geo-environmental applications regarding its high specific surface area and cation exchange capacity, it seems to be an appropriate reference of comparison for marly soils behaviour, as it is in this paper. Also, the study aims at providing some insightful conclusions in using both or each separately in landfill construction.

## 2 MATERIALS AND METHODS

### 2.1 Physical and Geo-environmental Properties

The bentonite soil used in this research was provided by the "Iran Barit Company". Physical and geo-environmental properties of this soil sample have been previously reported by Ouhadi et al. (2006b).

The marly soil was provided from the city of Tabriz, located in north-western Iran. The physical properties of the samples including specific gravity, classification, Atterberg limits, slake durability and moisture content were determined in accordance with ASTM methods (ASTM, 1992). They are given in Table 1.

Table 1. Physical properties of marly samples.

Characteristic	Measured quantity
Clay, %	75
Silt, %	5
Sand, %	20
Liquid limit (LL), %	61.9
Plastic limit (PL), %	28.4
Slaking durability, %	62.7
Activity	0.66
Water content (oven dried), %	2.93
Soil classification	"clays of high plasticity,(CH)"

Geo-environmental characteristics of marly samples, including carbonate content (Hesse, 1972), cation exchange capacity (Hendershot and Duquites, 1986), specific surface area (Elthantaway & Arnold, 1973), mineral composition, using XRD analysis

(Ouhadi and Yong, 2003b), pH (ASTM, 1992), were also measured and are given in Table 2.

Table 2. Geo-environmental properties of marly samples.

Characteristics	Measured Quantity
Mineral composition	Montmorillonite, Quartz
in decreasing abundance	Palygorskite, Calcite
Carbonate content, %	45
C.E.C., cmol/kg-soil	68.2
Exchangeable Na <sup>+</sup> , cmol/kg-soil	48.5
Exchangeable Ca <sup>2+</sup> , cmol/kg-soil	14.2
Exchangeable Mg <sup>2+</sup> , cmol/kg-soil	3.4
Exchangeable K <sup>+</sup> , cmol/kg-soil	2.1
Specific surface area, m <sup>2</sup> /g	413.2
pH (1:10, soil-water ratio)	9.5

### 2.2 Sample Preparation and Experimental Methods

Prior to starting the tests, the entire representative marly sample which was in a rock state was milled and converted to a fine homogeneous mass of soil.

To evaluate the buffering capacity of the bentonite and marly samples that indicates the resistance of soil to pH changes, the method suggested in EPA (1987) was used. A suspension composed of soil plus different concentrations of nitric acid in a 1:10 soil-solution ratio was prepared. The acid concentrations ranged from 0 to 800 cmol/kg-soil. The pH of these shaken and equilibrated suspensions was then measured using a pH-meter HANNA-Hi 9321.

The response of marly samples to the interaction with contaminants was assessed using a series of batch equilibrium tests. Prepared samples, consisting of 1 g dry soil and 50 ml lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>) and zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O) solutions possessing concentrations ranging from 0 to 150 cmol/kg-soil, according to the method in EPA (1987) were shaken for 24 hours. After an appropriate time of equilibrium, they were studied with regard to the amount of retained contaminant using an atomic adsorption spectrometer GBC 932 AB PLUS and pH and EC variations.

Moreover, the contribution of different soil phases in retaining Pb was investigated, using a series of selective sequential extraction experiments in accordance with the process mentioned by Yong et al. (1993a), Yong et al. (2001), Chagu'e-Goff (2005) and Han (2007). In this case, the soil-contaminant solution ratio was also 1:50.

## 3 RESULTS AND DISCUSSION

Figure 1 shows the variation of buffering capacity,  $\beta$ , versus pH for the marly sample and bentonite. It is defined as follows, in which C<sub>B</sub> is concentration of the added acid in cmol/kg-soil:

$$\beta = - \frac{dC_B}{d(pH)} \quad [1]$$

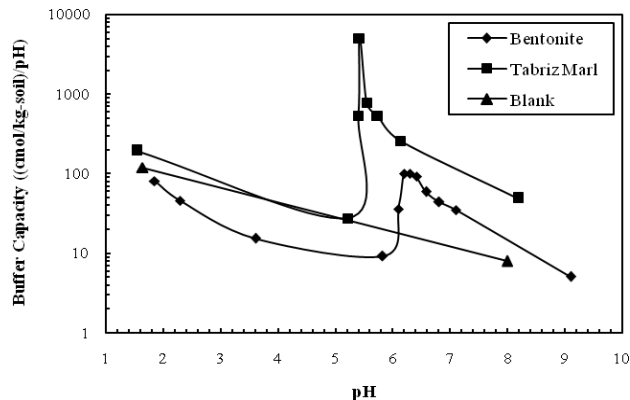


Figure 1. Buffering capacity of marly and bentonite samples in comparison with blank acid solution.

As can be seen in this figure, at all pH ranges greater than 1, the buffering capacity of the marly soil is significantly larger than that of bentonite which implies the greater withstanding of the marl sample to pH variation. The maximum amount of buffering capacity of the marl is 5000 cmol/kg-soil)/pH, in other words, 55 times more than the maximum amount for bentonite, which is 91 cmol/kg-soil)/pH. In fact, in spite of the lower cation exchange capacity of marl in comparison to that for bentonite, the marl sample shows a greater buffering capacity than the buffering capacity of bentonite. This larger buffering capacity can be interpreted as a consequence of the 45% carbonate content of the marly soil, which is only 8% in bentonite. According to previous research, carbonate can neutralize  $H^+$  ions of an added acid solution; therefore the pH of a soil-electrolyte system will not vary significantly (Yong et al., 1990; Yong & Phadungchewit, 1993; Yong, 2000). It is notable that contamination is one of the sources of pH changes (Yong, 2000).

Variation of soil suspension pH versus contaminant concentration can provide information about how a given soil can resist contamination. Thus, changes in pH and EC of contaminated samples with different concentrations of Pb and Zn heavy metals are studied and the results are given in Figures 2 and 3.

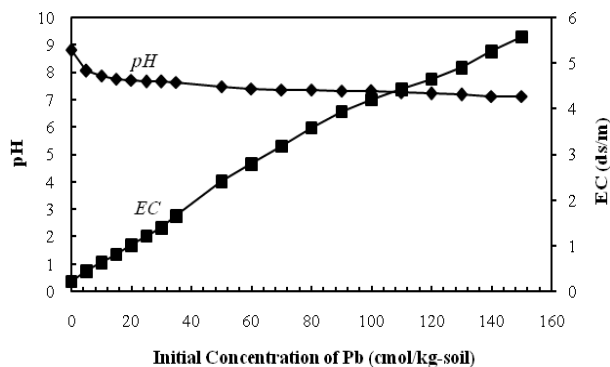


Figure 2. pH and EC of Pb-contaminated marly suspensions.

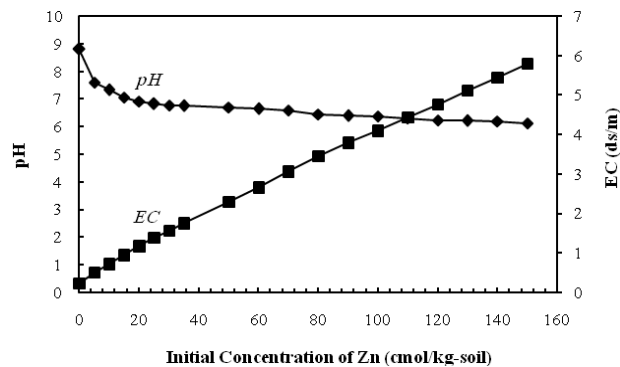


Figure 3. pH and EC of Zn-contaminated marly suspensions.

Figures 2 and 3 confirm an increase of EC and diminution of pH with increasing contaminant concentration. The natural pH of the samples, which is 8.8, decreases to 6.12 in the presence of Zn and 7.11 in the presence of Pb. In fact, marly samples exhibit durability toward pH changes due to contaminants.

This is in good agreement with results previously obtained.

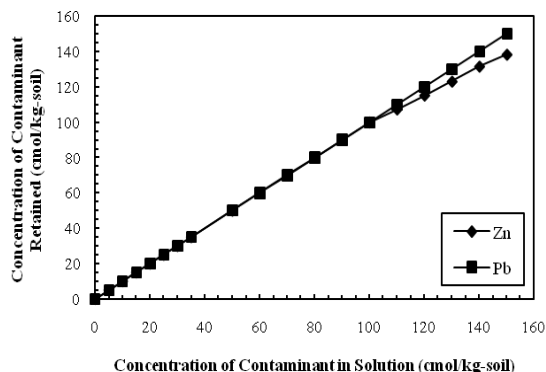


Figure 4. Retention of Pb and Zn contaminants by marly samples.

In another part of the investigation of marly soil interaction with contaminants, the concentration of heavy metal ions retained by marly samples was determined using the atomic absorption spectrometry method. According to the results of this step, shown in Figure 4, both contaminants are completely adsorbed by the soil to the concentration of 100 cmol/kg-soil. Higher concentrations of Zn cannot be retained totally, however samples still retain the entire imposed Pb. Comparison of pH changes and retained contaminants lead to the idea that marly samples can withstand the pH changes and maintain the range within the range favourable for precipitation of Pb and Zn (Ouhadi et al., 2006b). Consequently, they show high contaminant retention capacity.

Results of a similar study performed on bentonite samples of 1:10 soil-contaminant solution show that the ultimate concentration of complete retention for Pb is between 50 and 100 mol/kg-soil. In addition, bentonite samples leave a portion of even 10 mol/kg-

soil Zn contaminant in the suspended solution phase (Ouhadi et al., 2006a).

In order to determine the contribution level of absorption and precipitation mechanisms in marly samples' contaminant retention, it is necessary to run experiments like selective sequential extraction, S.S.E., which supplies data on how much each soil component retains the heavy metal contamination. The results of this study on Pb-contaminated marly samples are shown in Figure 5. The concentration of extracted Pb in the solution for each soil component shows that at all primary concentrations of contaminant, carbonate precipitation and exchange mechanisms retain Pb the most and the least, respectively. Consecutively after carbonate precipitation, hydroxide/oxide, residual and organic phases become the primary Pb sinks.

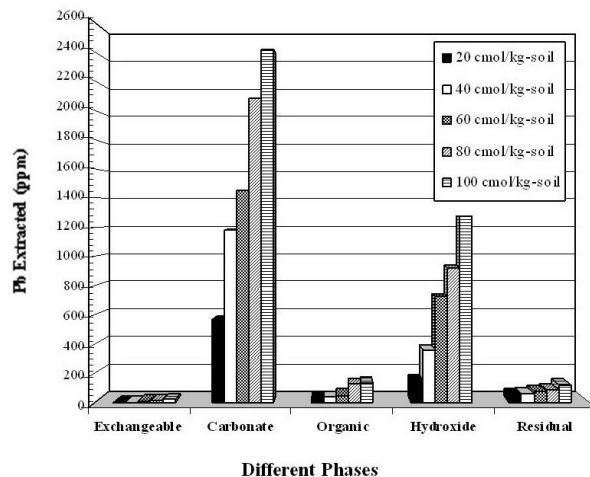


Figure 5. Extracted Pb from marly samples in the SSE test

Considering the carbonate content of the marly samples is 45%, it was somewhat expected to exhibit the highest contribution for Pb retention. In addition, at high pH levels, the precipitation mechanisms dominate.

Furthermore, the residual phase does not exhibit mobility in the environment (Chagué-Goff, 2005; Chopin et al., 2008), therefore almost 7% of Pb is retained by the soil without potential for transmission. Moreover, the exchangeable phase which has the most mobility (Chagué-Goff, 2005) contributes only 0.5% in contaminant retention. This is also the case for the carbonate phase, although it retains the most Pb in marly samples.

#### 4 CONCLUDING REMARKS

In this study, the adsorption efficiency of marly soils with respect to heavy metals was assessed. This kind of soil, possessing a significant amount of carbonate and minerals such as montmorillonite and palygorskite, can be considered as advantageous material to be used in landfills. It even displays a much better performance in comparison with the more commonly used bentonite.

#### REFERENCES

- American Society for Testing and Materials, ASTM. 1992. Annual Book of ASTM Standards, Philadelphia, Vol. 4, 08.
- Aiban, S. 2006. Compressibility and swelling characteristics of Al-Khobar palygorskite, Eastern Saudi Arabia. *J. Engineering Geology*, 87: 205-219.
- Chagué-Goff, C. 2005. Assessing the removal efficiency of Zn, Cu, Fe and Pb in a treatment wetland using selective sequential extraction: A case study. *J. Water, Air and Soil Pollution*, 160: 161-179.
- Chang, P.H., Li, Z., Yu, T.L., Munkhbayer, S., Kuo, T.H., Hung, Y.C., Jean, J.S., and Lin, K.H. 2009. Sorptive removal of tetracycline from water by palygorskite. *J. Hazardous Materials*, 165: 148-155.
- Chopin, E.I.B., Marin, B., Mkoungafoko, R., Rigaux, A., Hopgood, M. J., Delannoy, E., Cancès, B., and Laurian, M. 2008. Factors affecting distribution and mobility of trace elements (Cu, Pb, Zn) in a perennial grapevine (*Vitis vinifera* L.) in the Champagne region of France. *J. Environmental Pollution*, 156: 1092-1098.
- Elthantaway, I.N., and Arnold, P.W. 1973. Reappraisal of Ethylene glycol monoethyl ether (EGME) method for surface area estimation of clays. *Soil Sci.* 24: 232-238.
- EPA, 1987. Batch type adsorption procedures for estimating soil attenuation of chemicals. Office of Solid Waste and Emergency Response, USEPA, Washington, D.C., EPA/530-SW-87-006.
- Frydman, S., Talesnick, M., Geffen, S., and Shvarzman, A. 2007. Landslides and residual strength in marl profiles in Israel. *J. Engineering Geology*, 89: 36-46.
- Han, F.X., and Singer, A. 2007. Biogeochemistry of trace elements in arid environments. Springer.
- Handershot, W.H., and Duquette, M. 1986. A simple barium chloride method for determining cation exchange capacity and exchangeable cations. *Soil Sci. Am. J.*, 50: 605-608.
- Hesse, P.R. 1972. A textbook of soil chemical analysis. William Clowes and Sons, London.
- Krekeler, M.P.S., and Guggenheim, S. 2008. Defects in microstructure in palygorskite-sepiolite minerals: A transmission electron microscopy (TEM) study. *J. Applied Clay Science*, 39: 98-105.
- Lafuente, A.L., González, C., Quintana, J.R., Vázquez, A., and Romero, A. 2008. Mobility of heavy metals in poorly developed carbonate soils in the Mediterranean region. *J. Geoderma*, 145: 238-244.
- Lamas, F., Irigaray, C., and Chacón, J. 2002. Geotechnical characterization of carbonate marls for the construction of impermeable dam cores. *J. Engineering Geology*, 66: 283-294.
- Oostwoud Wijdenes, D.J., and Ergenzinger, P. 1998. Erosion and sediment transport on steep marly

- hillslopes, Draix, Haute-Provence, France: an experimental field study. *J. Catena*, 33: 179-200.
- Lamas, F., Irigaray, C., Oteo, C., and Chacón, J. 2005. Selection of the most appropriate method to determine the carbonate content for engineering purposes with particular regard to marls. *J. Engineering Geology*, 81; 32-41.
- McCarthy, D.F., 1982. Essentials of soil mechanics and foundations, 2nd edition. Reston Publishing Company, Reston, Virginia, 632 p.
- Mitchel, R.S. 1985. Dictionary of rocks. Van Nostrand Reinhold. New York, 228 p.
- Mohamed, A.M.O., Yong, R.N., and Mohammed, L.F. 1991. Soil improvement using chemical treatment. 1st Geotechnical Engineering Conference, Cairo University, Egypt, 1-10.
- Neaman, A. and Singer, A. 2004. The effects of palygorskite on chemical and physic-chemical properties of soils: a review. *J. Geoderma*, 123: 297-303.
- Ottosen, L.M., Hansen, H. K., Ribeiro, A. B., and Villumsen, A. 2001. Removal of Cu, Pb and Zn in an applied electric field in calcareous and non-calcareous soils. *J. Hazardous Materials*, B85: 291-299.
- Ouhadi, V.R., Yong, R.N., and Mohamed, A.M.O. 1996. Formation of ettringite as a swelling mineral on stabilized marl soil. Proceeding of the 1st Conference on Civil Engineering by Iranian Students in Canada, Montreal, 131-138.
- Ouhadi, V.R. 1997. The role of marl components and ettringite on the stability of stabilized marl. PhD thesis, Department of Civil Engineering and Applied Mechanics, McGill University, Montreal, Canada.
- Ouhadi, V.R., and Yong, R.N. 2003a. The role of clay fractions of marly soils on their post stabilization failure. *J. Engineering Geology*, 70: 365-375.
- Ouhadi, V.R., and Yong, R.N. 2003b. Impact of clay microstructure and mass absorption coefficient on the quantitative mineral identification by XRD analysis. *J. Applied Clay Science*, 23: 141-148.
- Ouhadi, V.R., Yong, R.N., and Sedighi, M. 2006a. Desorption response and degradation of buffering capability of bentonite, subjected to heavy metal contaminants. *Engineering Geology* 85: 102-110.
- Ouhadi, V.R., Yong, R.N., and Sedighi, M. 2006b. Influence of heavy metal contaminants at variable pH regimes on rheological behaviour of bentonite. *Applied Clay Science* 32: 217-231.
- Palumbo, B., Angelone, M., Bellanca, A., Dazzi, C., Hauser, S., Neri, R., and Wilson, J. 2000. Influence of inheritance and pedogenesis on heavy metal distribution in soils of Sicily, Italy. *J. Geoderma*, 95: 247-266.
- Pettijohn, F.J. 1975. Sedimentary rocks. Harper and Row, New York, 628 p.
- Ramezanpour, H., and Smaelnejad, L. 2008. Study of relationships between different type of erosion and soil properties of marls in Southern Guilan Province, Iran. The 15th International Congress of ISCO, Budapest, Hungary.
- Sadrekarimi, J., Zekri, A., and Majidpour, H. 2006. Geotechnical features of Tabriz marl. The 10th IAEG International Congress, Nottingham, United Kingdom.
- Terzaghi, K., and Peck, R.B. 1967. Soil Mechanics in Engineering Practice. John Wiley and Sons, Inc., New York.
- Yong, R.N., Warkentin, B.P., Phadangchewit, Y., and Galvez, R. 1990. Buffer capacity and lead retention in some clay materials. *J. Water, Air and Soil Pollution*, 53: 53-67.
- Yong, R.N., and Phadangchewit, Y., 1993. pH influence on selectivity and retention of heavy metals in some clay soils. *Can. Geotech. J.*, 30: 821-833.
- Yong, R.N., Galvez-Cloutier, R., and Phadangchewit, Y. 1993a. Selective sequential extraction analysis of heavy metal retention in soils. *Can. Geotech. J.*, 30: 834-847.
- Yong, R.N., Mohammed, L.F., and Mohamed, A.M.O. 1993b. Retention and transport of oil residue in soil. ASTM symposium on analysis of soils contaminated with petroleum constituents.
- Yong, R.N., Ouhadi, V.R., and Mohamed, A.M.O. 1996. Physico-chemical evaluation of failure of stabilized Marl soil. 49th Canadian Geotechnical Conference Frontiers in Geotechnology, Vol. 2, 769-776.
- Yong, R.N. 2000. Geoenvironmental Engineering, Contaminated Soils, Pollutant Fate and Mitigation. CRC Press.
- Yong, R.N., Yaacob, W.Z.W., Bentley, S.P., Harris, C., and Tan, B.K. 2001. Partitioning of heavy metals on soil samples from column tests. *J. Engineering Geology*, 60: 307-322.
- Yong, R.N., and Ouhadi, V.R. 2007. Experimental study on instability of bases on natural and lime/cement-stabilized clayey soils. *J. Applied Clay Science*, 35: 238-249.
- Zhang, J., Wang, J., Wu, Y., Wang, Y., and Wang, Y., 2008. Preparation and properties of organic Palygorskite SBR/organic Palygorskite compound and asphalt modified with the compound. *J. Construction and Building Materials*, 22: 1820-1830.