EVALUATION OF THE POTENTIAL OF USING AN OMANI ATTAPULGITE AS A SORBENT IN TREATMENT OF CONTAMINATED WATER

Ahmed Al-Futaisi, Ahmed Al-Jamrah, and Amer Al-Rawas

Department of Civil and Architecture Engineering, Sultan Qaboos University
P. O. Box: 33, Al-Khoudh 123, Oman
E-mail: futaisi@squ.edu.om

ABSTRACT

The goal of this study is to investigate and develop a cost-effective procedure for the treatment of contaminated water by sorption technology using an Omani clay mineral. Attapulgite (Palygorskite) is a clay mineral that exists in the Sultanate of Oman in huge reserves in two deposits in the southern part of Oman. In this paper, we present our first findings about this important clay in the region stressing its great potential as adsorbent to certain contaminants in water. The XRD analysis indicates that the purity of some selected samples of attapulgite clay is very high (about 70% of the clay minerals are palygorskite and 30% Kaolinite). The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images clearly support this conclusion. The clay cation exchange capacity is 19 meq/100g and the specific surface area is estimated to be 125 m2/g. Batch adsorption studies were performed to evaluate the adsorption performance of Methlyene Blue (MB) and Crystal Violet (CV) dyes on the local clay mineral. The results obtained from these laboratory-scale adsorption tests indicate the strong adsorption capability of the Omani attapulgite in reducing the level of concentration of these two dyes in water.

INTRODUCTION

In a very arid country like Oman, a very precious element of the Omani environment is the groundwater. It is the most important source for drinking and other essential domestic, agricultural, industrial, and commercial applications. However, with the rapid development that the country witnessed in the last three decades, groundwater contamination has become one of the major problems facing the country and its people. The contaminated groundwater is not only reducing the available water resources for use but also pose a threat to the human health. In Oman there are wide variety of materials that have been identified as contaminants in groundwater such as synthetic organic chemicals, hydrocarbons, inorganic cations and anions, and pathogens [2]. These contaminants originate from under storage tanks (UST), oil pipeline, septic tanks, municipal landfills, saltwater intrusion, oil injection wells and others. Many locations in different areas have been contaminated by enormous amount of contamination [2, 7, 19]. With this widespread groundwater contamination over the

country, new innovated treatment technologies should be investigated and implemented.

The application of clay minerals in various processes of environmental engineering is gaining an increasing interest worldwide [10]. For example, the clay minerals bentonite and attapulgite are used as sorbents for treatment of contaminated water [5, 15, 17, 21, 23], as a slurry trench cut-off walls [8] for environmental pollution control, and as a liner [3] in properly-designed waste landfill. The worldwide clay markets have changed significantly over the past years resulting initially in consolidation and expanded production from traditional high-grade clay sources but also creating opportunities for development of new discoveries [12]. Unfortunately, clay minerals industry (or market) in Oman is not yet very well developed. A clay mineral that exists in the Sultanate of Oman in huge reserves is attapulgite (or palygorskite). Attapulgite has been recorded at many locations in Dhofar, the southern part of Oman: in the Hasik Member of the Umm er Radhuma formation, in the Andur Member of the Dammam formation and in the Nakhlait member of the Ashawq formation. However, it has always been a problem to locate a place with a good thickness of attapulgite beds along with low overburden thicknesses. In 1995, two sites (Shuwaymiya and Tawi Attair) has bee selected by the Department of Geological Survey and Exploration for reserve estimation, taking into consideration exposure, overburden, accessibility and vegetation. The exploration confirmed that attapulgite exists in the Sultanate in huge reserves: Shuwaymiyah deposit contains 300 million to 400 million tons, and Tawi Attair deposit contains 200,00 to 1 million tons.

Presently Attapulgite is not being mined or used in Oman [6]. There is even no local fundamental research on the applications of this material. The long-term objective of our research is to evaluate the potential of using the local clay mineral attapulgite as a sorbent in treatment of hydrocarbon/heavy metals polluted groundwater. This research is the first comprehensive study in Oman trying to find application for the attapulgite. If turned to be successful, the mining and export of crude attapulgite to the local market as well as the AGCC or other neighboring countries is possible. However in this first paper on the Omani attapulgite, we attempt to fully quantify the Shuwaymiyah attapulgite and thoroughly investigate its potential adsorption to two selected basic dyes: methylene blue (MB) and crystal violet (CV). The paper is organized as follows. First, we provide an overview of the geologic settings of Shuwaymiyah deposit in Southern Oman. Second, we describe the basic physical and chemical characteristics of the Omani attapulgite. Third, we discuss the kinetics and adsorption capacity of Shuwaymiyah attapulgite to MB and CV dyes.

CLAY DEPOSITS AND GEOLOGICAL SETTING

Attapulgite has been recorded at many locations in the southern part of Oman, Dhofar: in the Hasik Member of the Umm er Radhuma formation, in the Andur Member of the Dammam formation and in the Nakhlait member of the Ashawq formation [6]. However, it has always been a problem to locate a place with a good thickness of

attapulgite beds along with low overburden thicknesses. During the execution of an exploration program for the big amounts of gypsum discovered in a Shuwaymiyah area, it was easily recognized that huge reserves of attapulgite clay occur in this coastal area. The Shuwaymiyah attapulgite deposit is located in the Shuwaymiyah and Thadbut topographic sheets that occur about 3.5 km NW of Shuwaymiyah village on the sea shore. The Shuwaymiyah area constitutes a closed coastal plain about 30 km long and 4-5 km wide. The plain is bounded to the south by the sea, and the north by by two sharp, successive scraps; Dammam Formation and Aydim Formation. To the east and west the scrap rises directly from the shore. The area is drained by numerous, south-flowing wadis the biggest of which is Wadi Shuwaymiyah. These wadis dissect the plain into numerous very low lying hills.

The geological map of Shuwaymiyah area (Fig. 1a and b) shows the distribution of the Andhur Member in Shuwaymiyah area, which more or less represents the distribution of attapulgite at the foot of the Shuwaymiyah scarpment. The Andhur Member forms a gentle slope along which a substantial amount of attapulgite can be easily scraped without having to remove much of overburden. In addition to the occurrence of attapulgite along the foot of the scrap, a good part of the Quaternary deposits on both sides of Wadi Shuwaymiyah cover low lying hills representing the lower part of Andhur Member and containing a lot of easily quarryable attapulgite deposits.

The department of Geological Survey and Exploration in the Directorate General of Petroleum and Minerals has selected in 1995 two sites (site-1 and site-2) for reserve estimation, taking into consideration exposure, overburden, accessibility and vegetation. The lithologic section shown in Fig. 1b was logged in site-2. The lithologic structure of site-1 is very similar to site-2. It is clear from the figure that the Andhur Member is composed of several clay layers (mainly attapulgite) varying in thickness with interbedded layers of chalky marly limestone. In site-1, the attapulgite horizons range in thickness from 0.4 m to 3.5 m with an average of 1.1 m. The site is estimated to contain about 321 million tons of attapulgite and an interbedded limestone of 264.6 million tons over an area of 6.7 km^2. In site-2, the limestone beds range in thickness from 0.2 m to 0.6 m, with a total thickness of 3 m. The attapulgite beds range in thickness between 0.2 m and 2 m. Their total thickness is 7.1 m. Site-2 contains about 33.6 million tons of attapulgite and an interbedded limestone of 18.7 million tons over an area of 2.4 km^2.

MINERALOGICAL, CHEMICAL AND PHYSICAL CHARACTERISTICS OF SHUWAYMIYAH ATTAPULGITE

In this section, we characterize the Omani attapulgite clay mineralogically (X-ray diffraction and electron microscopy), chemically (oxides composition), and physically (cation exchange capacity and specific surface area).
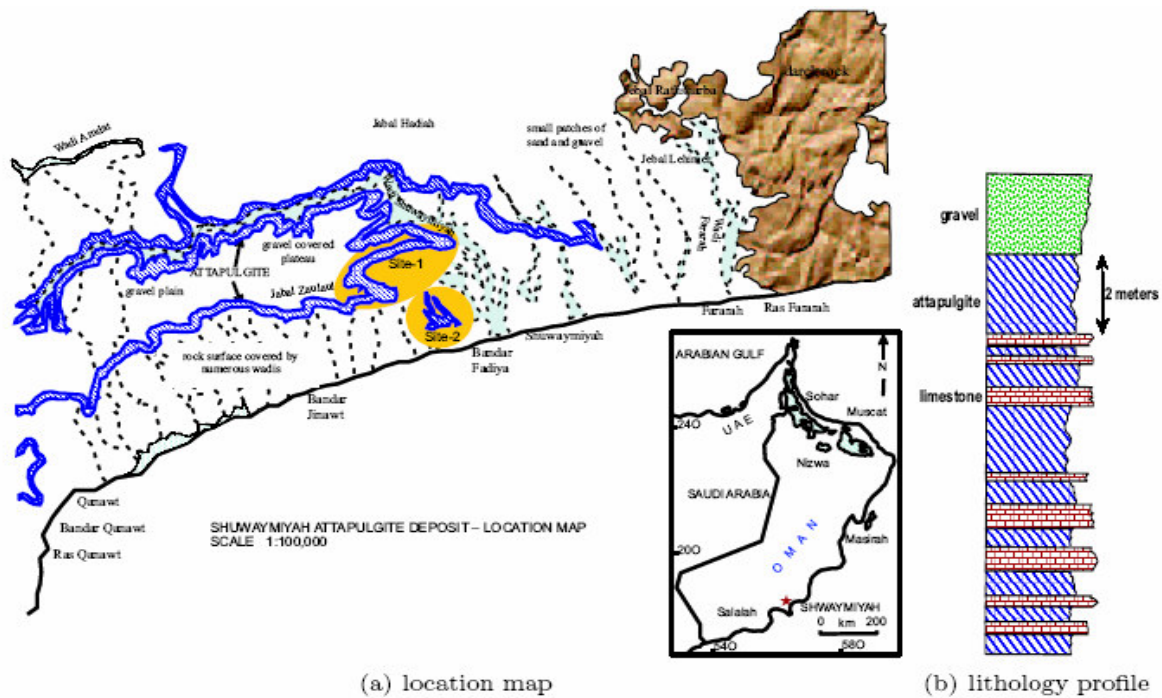
Figure 1: Al-Shuwaymiyah attapulgite deposit in Oman

1. Experimental Procedures

The crude clay has been dried and mechanically crashed and sieved to pass the 200 sieve (75m). Then, the sample was washed in ordered to remove carbonates, soluble salts and organic matters. The clay fine fraction was separated by centrifuge. These processes of clay washing and separation were implemented following the detailed procedure described in [14]. Oriented clay samples on glass slides have been prepared for phase identification by X-ray diffraction (XRD). The X-ray diffractometer used in this analysis was Philips PW1710 automated powder diffractometer, with a generator settings of 40 kV, 40 mA and nickel-filtered CuK_{α} ($\lambda = 1:54056A^{o}$) radiation over 2θ range of 2.5 - 70° at a scanning rate of 2° min^{-1}. Ethylene glycol and heat treatments were used to provide additional information essential for the identification of clay minerals. Size and morphology of particles were determined using Jeol JSM-5600LV 20 kV scanning electron microscope (SEM) and Joel JEM-1230 120 kV transmission electron microscope (TEM). Oxides content in the attapulgite samples has been measured using wet chemical analysis. The cation-exchange capacity (CEC) was determined by ammonium acetate exchange. The specific surface area (SSA) of the clay mineral was determined using the N_2-BET with Quantachrome Autosorb Automated Gas Sorption Instrument. These two properties have been also determined by the Methylene Blue (MB) adsorption method developed by Hang and Brindley [15]. Details of the experiential procedure followed for MB adsorption are described later.

2. XRD

Clay phase identification has been examined in six forms: as an oriented clay sample (un-treated), as an oriented clay sample treated with ethylene glycol, as an oriented clay sample heated to 350°C, 600°C, 700°C, and 800°C for two hours. The X-ray powder diffractogram of the Shuaimiah Attapulgite (Figure 2) shows the presence of two main sets of phases: palygorskite and kaolinite. The d-values of palygorskite are at 10.5, 6.3, 5.5, 4.5, 4.2, 3.7 and 3.2 Å, whereas the d-values of the kaolinite are at 7.1 and 3.6 Å. The figure also clearly shows that both minerals are unaffected by glycolation. When subjected to heat treatment at 350°C, the intensity of the main reection decreases for both minerals. At 600°C heat treatment, the d-value 10.5 Å for palygorskite and 7.1 Å for kaolinite completely disappeared. The constant standard minerals method [16] was used to quantify the percentages of palygorskite and kaolinite minerals in Shuwaymiyah attapulgite clay. Different percentages of clay were added to constant standard minerals of equal weights. All the prepared samples were treated by ethylene glycol. The peak area ratio was calculated from X-ray diffraction of the standard mixes with the clay. The mineral peak area ratio against the percentages of clay is linearly best fitted and the minerals percentage were calculated from the slope of the fitted line. The estimated percentage of palygorskite in Shuwaymiyah attapulgite is in the range of 67 to 72%.
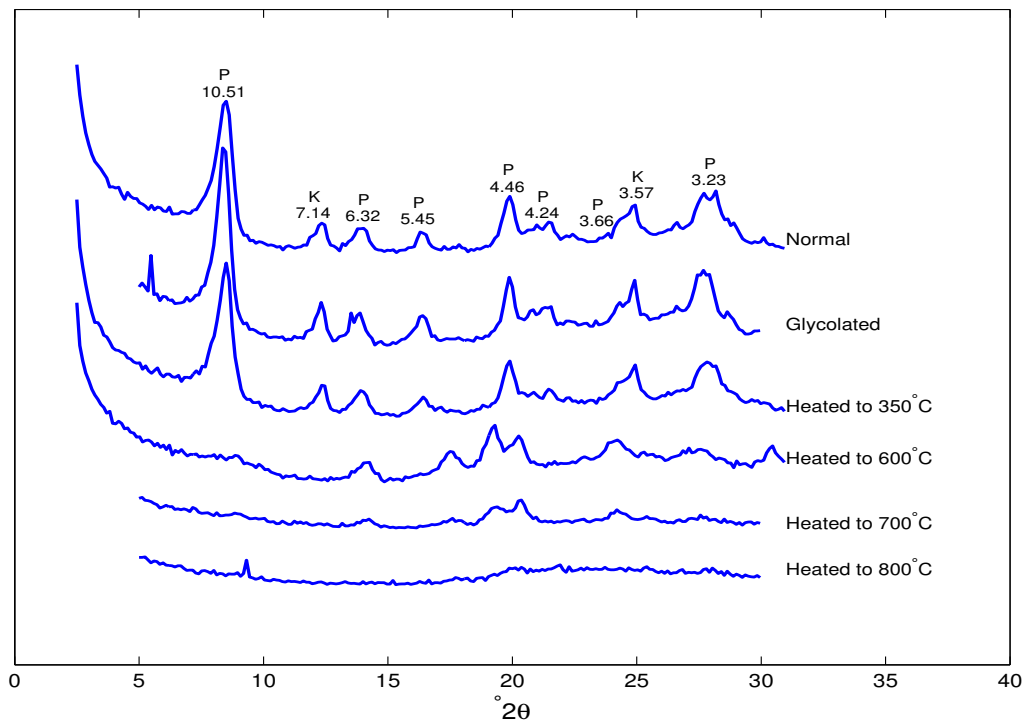

Figure 2: X-ray diffraction patterns showing the characteristic peaks of palygorskite (P) and kaolinite (K) from representative samples of Al-Shuwaymiyah attapulgite deposit in Oman

3. Electron Microscopy

Electron microscopy is an indispensable tool for observation of morphology, size and texture of the individual particles of clay minerals, particulary palygorskite [17, 18]. Selected SEM images of Al-Shuwaymiyah attapulgite are shown in Figure 3 and TEM images in Figure 4. The micrographs shown in right hand side are always obtained at higher magnification of the corresponding micrographs in the left hand side. The micrographs clearly reflect the abundance of palygorskite fibers in Al-Shuwaymiyah attapulgite. Individual palygorskite fibers are 0.2 to 0.5 μm long (Figure 4c and d). However these individual fibers often form long palygorskite bundles that are 5 to 10 μm long (Figure 4a and b). As seen from the SEM images, the palygorskite fibers may exist as individual well separated fibers (Figure 3a and b) or as elongated bundles of many fibers (Figure 3c and d) or sometimes circular aggregates of clay fibers (Figure 3e and f). Due to such variations in the existence of palygorskite fibers, the pore space in the formation consists of tiny pores between the individual fibers and larger pores between the bundles of fibers (Figure 3c and d).

4. Physio-Chemical Properties

The chemical composition of the raw and washed Shuwaymiyah attapulgite is reported in Table 1. The table shows that the main constituent of the clay is SiO_2 (53-55%). This high content of silica in attapulgite gives its structure credibility as a good adsorbent. It is also observed that the difference in chemical composition between raw and washed Shuwaymiyah attapulgite is minimal. The measured surface area and the cation exchange capacity of Al-Shuwaymiyah attapulgite are reported in Table 2. The values are also compared with those estimated from the MB adsorption experiment described later. MB adsorption is largely used as an efficient procedure for determining of cation exchange capacity and specific surface area [19]. The difference between the determined values of SSA obtained by the two methods is expected since it is known that the MB adsorption method allows to measure the total surface area of clay mineral, whereas the BET technique measures the external specific surface area only. On the other hand, the CEC obtained by MB adsorption is slightly less than the corresponding value obtained by ammonium acetate extraction reflecting the fact that MB was not able to replace all the cations on the clay surfaces. When compared to the attapulgite in the Hawthorne formation in Florida, the Shuwaymiyah attapulgite has exactly the same CEC but slightly less specific surface area.
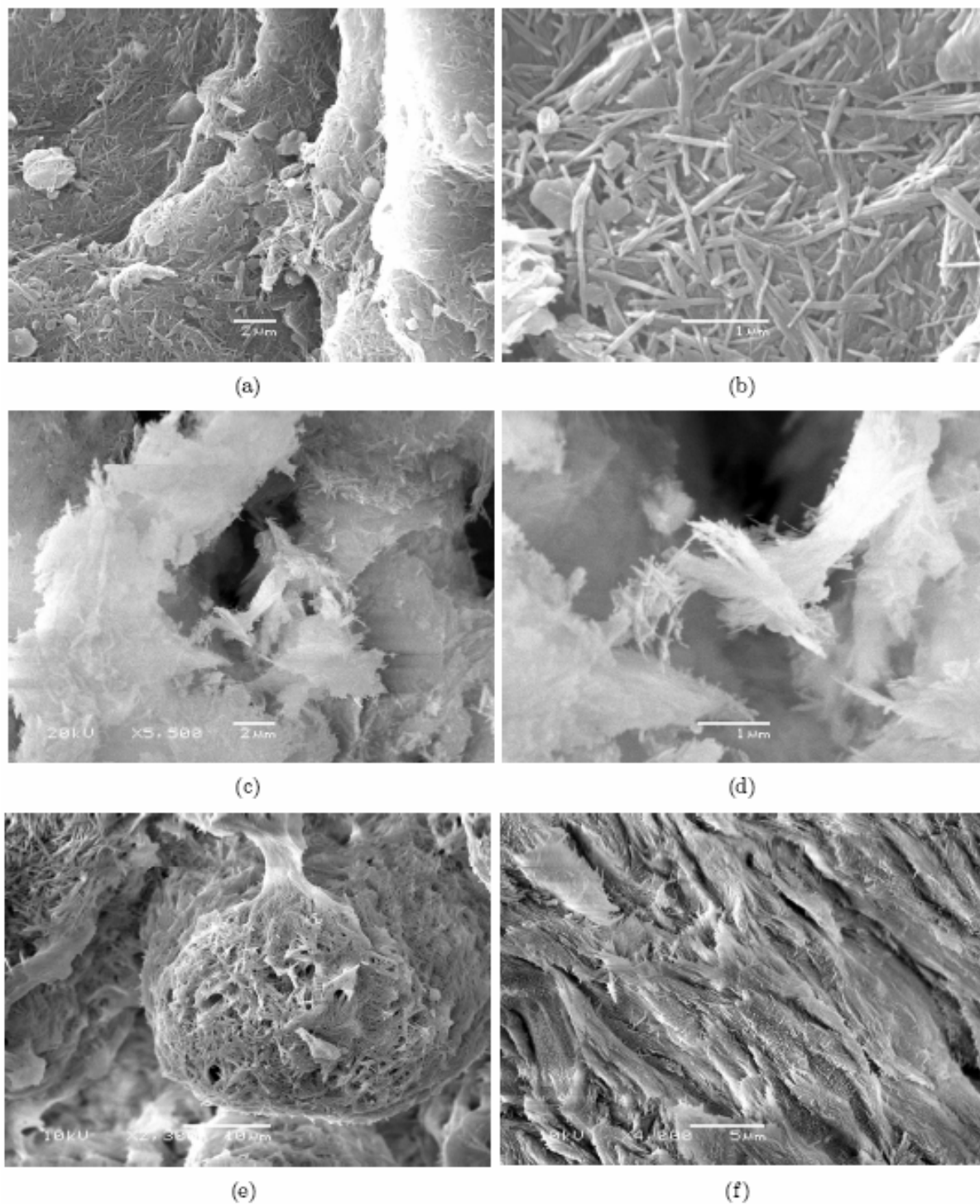
**Figure 3: SEM images of palygorskite fibers and aggregates in
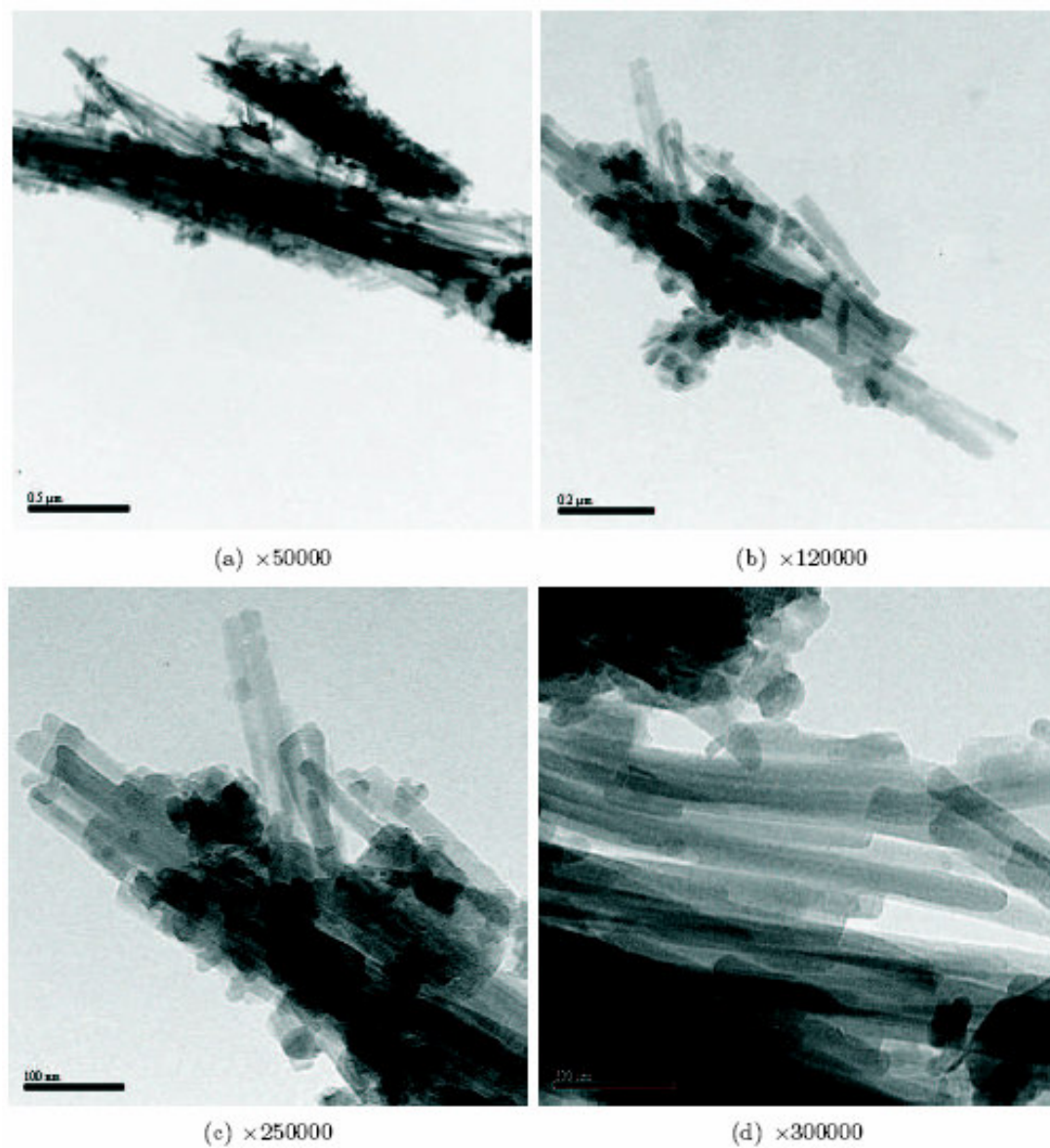Al-Shuwaymiyah attapulgite**

(a) ×50000

(b) ×120000

(c) ×250000

(d) ×300000

**Figure 4: TEM images of palygorskite fibers and aggregates
in Shuwaymiyah attapulgite**

**Table 1: Chemical composition (in wt. %) of the raw and washed Shuwaymiyah
Attapulgite**

	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	K$_2$O	Na$_2$O	TiO$_2$	Cl	LoI
Raw Clay	53.28	14.2	4.93	0.2	3.62	0.3	0.94	0.84	1.06	1.02	19.09
Washed Clay	55.76	14.13	4.78	0.1	3.64	0.23	0.96	0.32	1.12	0.23	17.69

Table 2: Specific surface area and cation exchange capacity of the Shuwaymiyah Attapulgite

	SSA (m^2/g)		CEC (meq/100g)	
	BET	MB	Ammonium Acetate	MB
Al-Shawaymiah attapulgite (Oman)	90	125	19	16
Hawthorne attapulgite (Florida, USA)	136.35		19.5	

METHYLENE BLUE AND CRYSTAL VIOLET SORPTION TO SHUWAYMIYAH ATTAPULGITE

In this section, the adsorption of natural Shuwaymiyah attapulgite clay powder to the organic cations methylene blue (MB) and crystal violet (CV) is studied. First, the adsorption experimental procedure is described. Then, the kinetic experiment is discussed. Finally the derivation of adsorption isotherms is presented.

1. Experimental Setup

Sorption experiments were performed using the standard batch technique. Initially, kinetic experiments were performed to study the effect of contact time on the adsorption processes. In the kinetic experiment, fixed mass of attapulgite (30 mg) and fixed concentration of dye (100 mg/l) were added in 40-ml borosilicate glass bottles with Teflon-lined caps. The mixture total volume was set to 20 ml. Several identical bottles were placed on a specially designed end-over-end shaker with fixed speed motor. At specified times; bottles were removed from the shaker and centrifuged at 3000 rpm for 30 minutes. Then, the dye concentration in the supernatant was measured using UV-visible spectrophotometer (PerkinElmer) at wavelength of 665 nm for MB and 580 nm for CV. For the adsorption isotherms, one set of several 40 ml glass bottles containing constant attapulgite clay mass (30 mg) and variable initial concentrations of dye (5 to 100 mg/l) was prepared. A second set of glass bottles containing the dye with constant initial concentration (100 mg/l) but variable attapulgite clay mass (10 to 90 mg) was simultaneously prepared. The volume of the mixture was also set to 20 ml. Both sets, along with blank bottles (bottles contain MB without attapulgite clay), were placed on the shaker for overnight (18 hrs) at room temperature (25°C) in order to reach equilibrium. Then, the bottles were centrifuged at 3000 rpm for 30 minutes. The equilibrium concentration of MB was measured using the UV-visible spectrophotometer at the previously mentioned wavelengths. In all cases, dye solutions were prepared using distilled water. All experiments were performed in duplicates. The amount of dye adsorbed on the surface of attapulgite, q_e (mg/g), was obtained as follows:

$$q_e = \frac{(C_i - C_e)V}{M}$$

(1)

where C_i and C_e (mg/l) are the initial and final or equilibrium contractions of MB, respectively, V (ml) is the solution volume and M is the attapulgite clay mass (mg).

2. Adsorption Kinetics

In order to study the rate-determining step for the adsorption of MB and CV onto the surface of attapulgite, two kinetic models [20, 21] were employed: pseudo-first-order and pseudo-second-order models. The simple Lagergren pseudo-first-order model assumes that the rate of change of solute uptake with time is directly proportional to the difference in the amount of solute adsorbed at time of equilibrium q_e [mg/g], and the amount of solute adsorbed at any time, $q(t)$ [mg/g]:

$$\frac{dq(t)}{dt} = k_1 [q_e - q(t)]$$

(2)

where k_1 [1/min] is the rate constant of pseudo-first-order model. When integrating over time and linearizing the model, the following equation is obtained:

$$\ln[q_e - q(t)] = \ln[q_e] - k_1 t$$

(3)

The pseudo-second-order equation based on adsorption equilibrium capacity is expressed in the form

$$\frac{dq(t)}{dt} = k_2 [q_e - q(t)]^2$$

(4)

where k_2 [g/mg.min] is the rate constant of pseudo-second-order model. With a similar manner performed for the previous model, the linearized form of the variation of clay uptake with time is

$$\frac{t}{q(t)} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

(5)

Figure 5 summarizes the results obtained from the kinetic experiments of MB and CV. Figure 5a plots the attapulgite clay uptake of MB and CV at various contact times. One can immediately observe the fast decrease in residual dye concentration at a short time scale (just few minutes) implying the strong electrostatic interaction between the negatively charged surface and the basic dye cations. The CV adsorption requires longer time to reach equilibrium than MB. The estimated equilibrium time for MB adsorption is 60 minutes, whereas the estimated equilibrium time for CV is about 200 minutes.

The validity of the two kinetic models was checked using linear plots of ln $[q_e - q(t)]$ versus t (Figure 5b) for the pseudo-first-order and $t/q(t)$ versus t (Figure 5c) for the pseudo-second-order model. Even though pseudo-first-order model has provided good fit ($R^2 = 0.90$) at early time stages, the experimental data has shown considerable deviation at later times. However, in the other hand, pseudo-second-order model has shown almost perfect fit ($R^2 = 0.9999$) in the whole range of considered time. The rate constant of pseudo-first-order model is $k_1 = 0.035$ [1/min], whereas the corresponding rate constant for the pseudo-second-order model is $k_2 = 0.031$ [g/mg.min]. This perfect fit of the pseudo-second-order kinetic model suggests that the model can be efficiently used to predict the kinetic of adsorption of MB or CV by attapulgite. Since this model is based on the adsorption capacity, it will help to predict the adsorption behavior over the whole range of concentration and supporting chemisorption (chemical reaction) as rate controlling mechanism. Chemisorption usually indicates that the adsorption process is irreversible. Views of similar kind have been put forward by other workers [20-22] who had studied basic dyes adsorption.

3. Adsorption Isotherms

When the system is in the state of equilibrium distribution of dye between the adsorbent and the dye solution, it is important to establish the absorption isotherms and the capacity of the adsorbent to the dyestuff. Figure 6a shows the experiential curves of equilibrium clay uptake (q_e) and equilibrium concentration (C_e) for adsorption of MB and CV. Both dyes show strong affinity for attapulgite clay. In both cases, the clay uptake increased sharply with increasing the solution concentration from 0 to about 5 mg/l to reach an adsorption capacity of 40 mg/g. Only beyond this equilibrium solution concentration, the adsorption behavior of the MB and CV starts to deviate. In the case of MB, this sharp increase in adsorption is followed by a gradual increase in the adsorption capacity in the regions from 5 to 20 mg/l beyond which the adsorption is leveled to a maximum value equal to 51 mg/g. In the case of CV the gradual increase in the adsorption continues with increasing the concentration of the solution. The largest adsorbed amount of CV was 70 mg/g.

Table 3: Isotherm constants for the adsorption of MB and CV onto attapulgite clay

			MB	CV	
Langmuir:					
	q_{max}	=	50.76	57.8	mg/g
	b	=	1.7	1.2	l/mg
	R^2	=	0.999	0.854	
Freundlich:					
	K_f	=	40.15	34	$(mg/g)(l/mg)^{1/n}$
	1/n	=	0.06	0.17	
	R^2	=	0.722	0.975	

(a) effect of contact time

(b) pseudo-first-order model
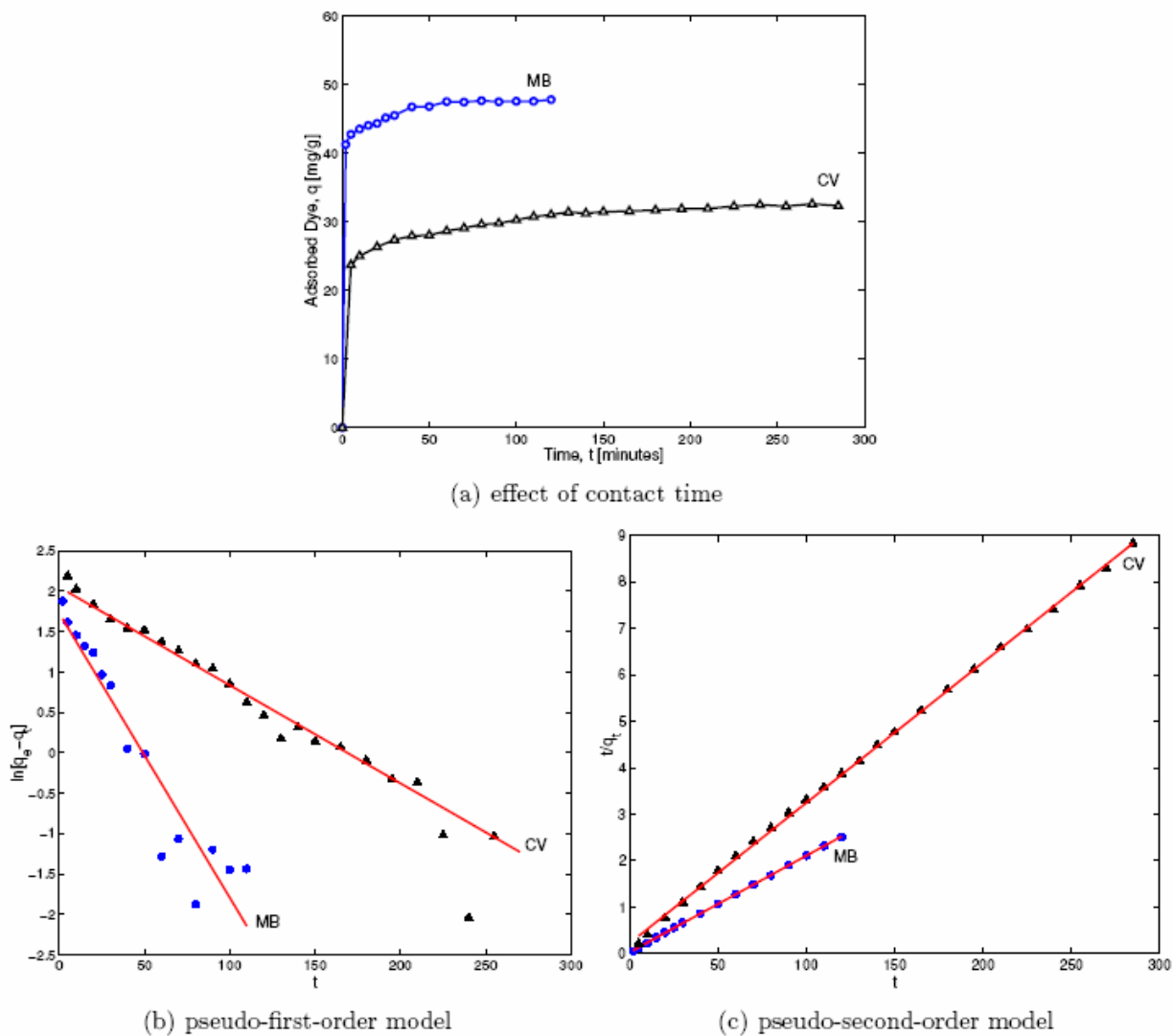

(c) pseudo-second-order model

Figure 5: Kinetic experiments of MB and CV adsorption onto attapulgite and goodness of fit of pseudo-firrst-order and pseudo-second-order models to the experimental data

The adsorption isotherms that are usually used for describing dye adsorption are the Langmuir and the Freundlich. The linear transformation of the Langmuir isotherm is

$$\frac{C_e}{q_e} = \frac{1}{q_{max}}C_e + \frac{1}{b\,q_{max}}$$

(6)

where q_{max} and b are Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. Using a least square linear fit of C_e/q_e versus C_e, the two unknown parameters can be determined from the slope of the line $(1/q_{max})$ and the intercept $(1/[b\,q_{max}])$. In the other hand, the Freundlich isotherm is linearly transformed to

$$\ln(q_e) = \frac{1}{n}\ln(C_e) + \ln(K_f)$$ (7)

where K_f and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption, respectively. A linear fit of $\ln(q_e)$ versus C_e would give $\ln(K_f)$ (intercept) and $1/n$ (slope). The value of n is usually greater than 1 and must reach some limit when the surface is fully covered.

(a) experiential adsorption isotherms

(b) fitting isotherm models

(c) goodness of fit of Langmuir isotherm
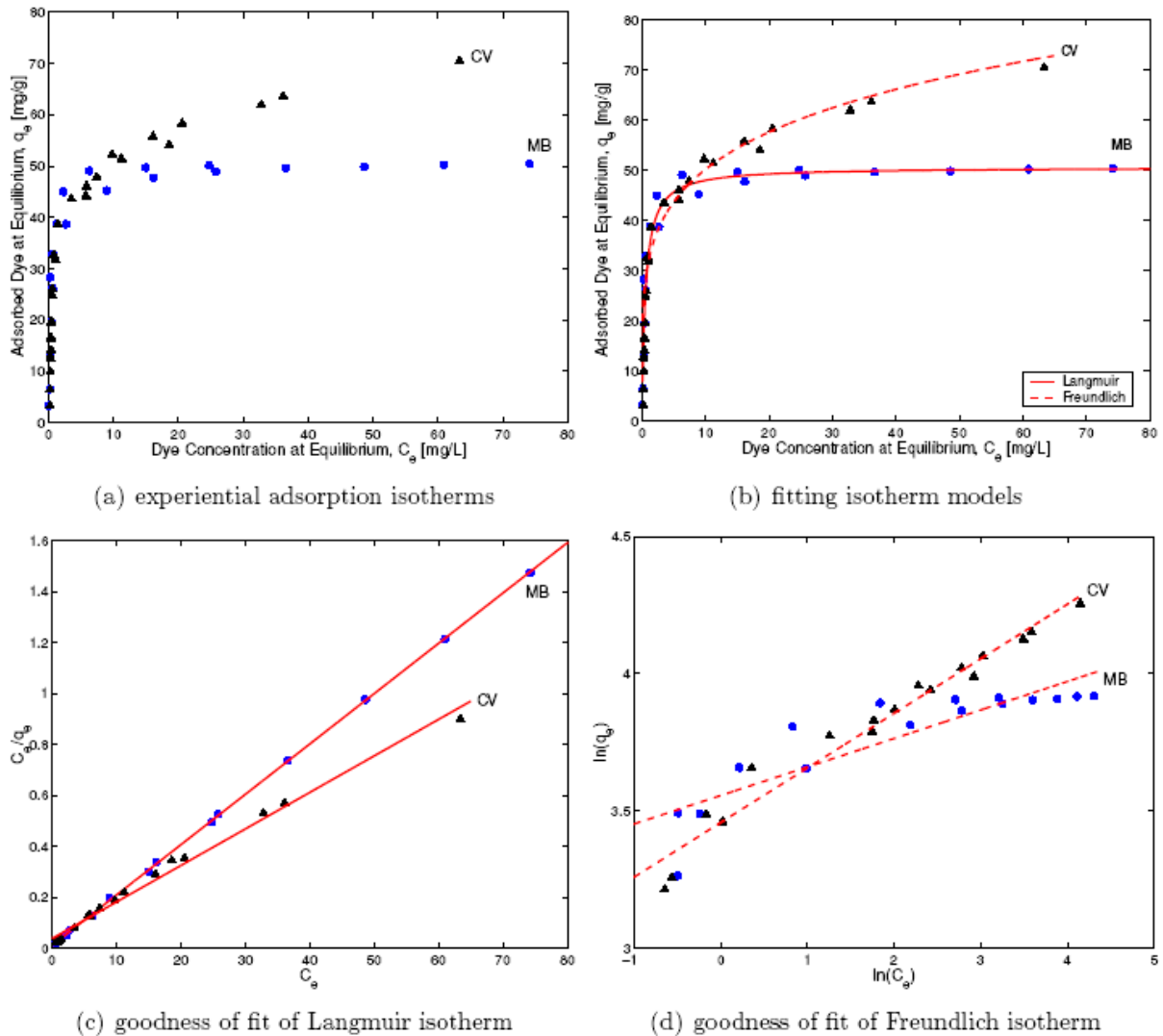
(d) goodness of fit of Freundlich isotherm

Figure 6: The variation of adsorbed amount of dye with the equilibrium concentration of dye solution and their goodness of fit to the theoretical Langmuir and Freundlich isotherms

The goodness of fit of the Langmuir model to the MB and CV experimental data is shown using the liner plot in Figure 6c. Whereas the goodness of fit of the Freundlich model is shown in Figure 6d. The parameters of the fitted models with their regression coefficient are tabulated in Table 3. Visual inspections and values of regression

coefficient yield the conclusion that MB adsorption is best fit by Langmuir isotherm, whereas CV adsorption is best fit by Freundlich isotherm as summarized in Figure 6b.

CONCLUSION

A very important clay mineral in the Sultanate of Oman has been characterized. The mineralogical investigation on Al-Shuwaymiyah attapulgite clearly indicates its high purity. Quantification analysis of XRD revealed that the percentage of palygorskite in the clay is at least 70%. SEM and TEM images clearly indicate the existence of palygorskite as a dominant mineral in Al-Shuwaymiyah clay. Al-Shuwaymiyah attapulgite was used as an adsorbent for the removal of Methylene Blue (MB) and Crystal Violet (CV) basic dyes from water. The adsorption equilibrium revealed that Al-Shuwaymiyah attapulgite can uptake up to 51 mg of MB and 70 mg of CV per one gram mass of clay. MB adsorption is best fit by Langmuir isotherm, whereas CV adsorption is best fit by Freundlich isotherm. A pseudo-second-order kinetic model can be efficiently used to predict the kinetic of adsorption of MB and CV by the attapulgite. This naturally occurring material could substitute in the Gulf region the use of activated carbon as adsorbent due to its availability and its low cost.

REFERENCES

[1] W. Bajjali. Groundwater contamination by hydrocarbon in Nizwa, Zukait, Jaalan Bani Bu Hasan, and Barka areas. Technical report, Ministry of Water Resources, Oman, 1996.

[2] A. El-Zawahry, A. M. Shahalam, R. Taha, and T. Al-Busaidi. An assessment of solid waste and landfills in Muscat area, Oman. Science and Technology, SQU, 6(1-11), 2001.

[3] M. Scheu. Assessment study on municipal solid waste management in Muscat. Technical report, Wetter, Germany: KaltwasserpEngineering, 1993.

[4] M. H. Haydn. Some applications of selected clay minerals. In Soccoro NM USA 24th Annual Meeting of the Clay Minerals Society, Oct 18-22 1987, editor, Applied Clay Science, pages 379-395, 1991.

[5] S. H. Chang, M. E. Ryan, and R. K. Gupta. Competitive adsorption of water-soluble polymers on attapulgite clay. Journal of Applied Polymer Science, 43(7):1293-1299, 1991.

[6] Q. Zunan, Z. Yi, and F. Yuqiao. Removal of oil from concentrated wastewater by attapulgite and coagulant. Water Quality Research Journal of Canada, 30(1):89-99, 1995.

[7] L. Z. Pillon. Effect of attapulgite clay on the composition of jet fuels. Petroleum Science and Technology, 19(7-8):875-884, 2001.

[8] L. Wang, Z. Huang, X. Sun, X. Liu, and J. Jin. Treating dyeing wastewater with modified absorbent of attapulgite. Journal of Nanjing University of Science and Technology, 22(3):240-243, 1998.

[9] S. Pamukcu and H. Hijazi. Improvement of fuel oil contaminated soils by additives. In Soil Improvement Proceedings of the 1992 ASCE Specialty Conference on Grouting and New Orleans LA USA Geosynthetics, Feb 25-28 1992, editors, Geotechnical Special Publication, pages 1285-1297, 1992.

[10] W. E. Gurbe. Slurry trench cut-o_ walls for environmental pollution control. In Construction Symposium on Slurry Walls: Design and Atlantic City NJ USA Sponsor: ASTM Quality Control, Jun 27-28 1991, editors, ASTM Special Technical Publication, pages 67-77, 1992.

[11] G. P. Broderick and D. E. Daniel. Stabilizing compacted clay against chemical attack. Journal of Geotechnical Engineering, 116(10):1549-1567, 1990.

[12] J. K. Keeling. Industrial clays: Meeting the challenge of increased technical demands and shifting markets. Australasian Institute of Mining and Metallurgy Publication, (97):239-246, 1997.

[13] Minerals Division. Shuwaymiya and Tawi-Atair Attapulgite. Technical report, Ministry of Commerce and Economy, 2002.

[14] A. A. Al-Rawas, H. Sutherland, A. W. Hago, A. A Yousif, M. Al-Shihi, and B. Al-Shihi. A comparative quantitative study of an omani soil using X-ray diffraction technique. Journal of Geotechnical and Geological Engineering, 19:69{84, 2001.

[15] P. T. Hang and G. W. Brindley. Methylene blue adsorption by clay minerals. Determination of surface areas and cation exchange capacities (clay-organic X VIII). Clays and Clay Minerals, 18:203{212, 1970.

[16] R.V Rohe C.G. Olson. Estimate of clay-mineral content: Additions of proportions of soil clay to constant standard. Clay and Clay Minerals, 27(5):322-326.

[17] H. Paquet, J. Duplay, M. Valleron, and G. Millot. Octahedral compositions of individual particles in smectite-palygorskite and smectite-sepiolite assemblages. In Proc. 8th Int. Clay Conf., Denver, pages 73{77. The Clay Minerals Society, Bloomington, Ind., 1987.

[18] A. Chahi, J. Duplay, and J. Lucas. Analysis of palgorskite and associated clays from the Jbel Rhassoul (Morocco): Chemical characteristics and origin of formation. Clays and Clay Minerals, 41(4):401-411, 1993.

[19] R. Rytow, Serban C., S. Nir, and L. Margulies. Use of methylene blue and crystal violet for determination of exchangeable cations in montmorillonite. Clay and Clay Minerals, 39(5):551-555, 1991.

[20] F. Wu, R. Tseng, and R. Juang. Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan. Water Research, 35(3):613-618, 2001.

[21] Y. S. Ho and G. McKay. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Research, 34:735-742, 2000.

[22] V. P. Vinod and T. S. Anirudhan. Adsorption behavior of basic dyes on the humic acid immobilized pillared clay. Water, Air, and Soil Pollution, 150(193-217), 2003.