Interaction of Original and Heat-Treated Sepiolites with Quaternary Amines

E.Sabah
Mineral Processing Program, Afyon Kocatepe University, Afyon, Turkey

MS.Çelik
Department of Mining Engineering, Istanbul Technical University, Istanbul, Turkey

ABSTRACT: In this study, the adsorption of quaternary amines onto original and heat-treated sepiolite was investigated as a Junction of several variables. Adsorption of dodecyltrimethylamrnonium bromide ($Ci2H_25N(CH3)3$ Br) and hexadecyltrimethylammonium bromide {$Ci6H2sN(CH_3)_3$ Br) onto sepiolite at a constant temperature of 25°C exhibits typical isotherms with plateaus. The adsorption densities, as represented by mole per m^2 of the adsorbate, reveal that although heat activation results in a several-fold increase in the specific surface area, practically, it produces no appreciable difference in the adsorption values.

1 INTRODUCTION

Abatement of mining and mineral processing wastes without harming the environment is an important technical problem in the development of the mining industry. The use of flotation reagents such as cationic-amine-rype reagents in the flotation of silicates, oxides and salt-type minerals results in the contamination of process water. These aliphatic and aromatic compounds are also used in the production of pigments, rubber and pesticides, leading to substantial organic wastes. The adsorption process is usually applied to those wastes that cannot be removed by biological techniques. Activated carbon is the most common adsorbent used in such processes. Sepiolite, which was used in this investigation, is cheaper and is considered an alternative to activated carbon. It is not only used in the abatement of organic compounds, but İs used for inorganic metal cations as well.

Sepiolite exhibits a variety of attractive properties, such as high specific surface area, high porosity and surface activity, and the ability to form high and stable viscosities at low solids concentrations. Sepiolite is therefore used in a range of areas where sorptive, catalytic and rheological properties are exploited. The sorption ability of sepiolite is mainly ascribed to its high surface area. Thus, it is commonly used in oil refining, wastewater treatment, İn the removal of odor, drug and pesticide carriers, paper, detergent, etc.

Similar to other chain-type silicate minerals, İt contains a continuous two-dimensional tetrahedral sheet but without continuous octahedral sheets. This unique fibrous structure with interior channels of 3.6x10.6 A in size permits adsorption of organic and inorganic ions (Gonzalez-Pradas et al. 1990, Singer and Huang 1989). Sepiolite has a total specific surface area of 800-900 m^2/g, of which meroretically 400 m /g is external and 500 m^2/g is internal (Alvarez 1984, Sema and Van Scoyoc 1978). The penetration of organic molecules into the channels depends upon the polarity, ability to make hydrogen bonds, and the match of the size and shape of the molecule (Çetişli 1989, Hoyoetal. 1993).

It was therefore the objective of this study to investigate the ability of the uptake of typical quaternary amine surfactants, dodecyltrimethylamrnonium bromide (DTAB) and hexadecyltrimethylammonium bromide (HTAB), onto original and heat-treated sepiolites and elucidate the adsorption mechanism.

2 EXPERIMENTAL

2.1 *Materials*

The sepiolite sample used in this study was obtained from the Mayas Mining Company in Sivrihisar, Turkey. The cation ratios of sepiolite calculated using oxygen as the basis of 33 {Jones and Galan 1984) yielded the data presented in Table I.

This brown sepiolite, ground to minus 65 um, produced an average particle size (dsu) of 1.99 |jm as determined by Zetasizer. The XRD together with the chemical analysis results given elsewhere indicate that calcite and dolomite are the major impurities

accompanying sepiolite (Sabah et al. 1997). The specific surface areas of the original and heat-treated sepiolite at 300°C as determined by BET technique are 68 m^2/g and 253.3 m^2/g respectively.

Table 1. Cation ratios of sepiolite.

	Cation Ratios
Tetrahedral Layer	
Si	11.84
Ti	0.01
Al	0.41
Octahedral Layer	
Mg	8.23
Fe[*3]	0.12
Cations Between Sheets	
Ca	0.19
Na	0.05
K	0.10

Dodecyltrimethylammonium bromide (DTAB), $C_{12}H_{25}N(CH_3)_3Br$ and hexadecyl trimethylammonium bromide (HTAB), $C_{16}H_{33}N(CH_3)_3Br$ were used as the cationic surfactants. Both were specified to be of high purity. Distilled and deionized water with a conductivity value of 2×10^{-6} mhos/cm was used in all experiments. The experiments were conducted at 25°C. pH was adjusted using either HCl or NaOH solutions.

2.2 Methods

Adsorption tests were conducted in 20- or 40-ml glass vials. 500 mg of sepiolite sample was mixed in 10 cc or multiples of this with a solid-to-liquid ratio of 0.05. The vials were shaken for 2 h on a shaker and centrifuged for 15 min. The supernatant was analyzed for the cationic surfactant by a two-phase titration technique originally applied to anionic surfactants using dimidium bromide and disulfine blue as indicators. This technique is based on the formation of a complex between an anionic surfactant (sodium dodecylsulfate) and cationic reagent (DAH). This complex is soluble in chloroform and changes from blue to pink in the presence of indicators (Powers 1970, Reid et al. 1967).

The adsorption density was calculated by the following formula (1).

$$\Gamma = \frac{(C_i - C_r) \cdot V}{m.S.1000} \qquad (I)$$

where C_i and C_r = the initial and residual concentrations (moles/l); m = the amount of solid (grams); V = the volume of the solution (ml); S = the specific surface area of sepiolite (m /g); and F =

the adsorption density (M/m^2).

In order to increase the surface area and induce physico-chemical changes in the structure of the sepiolite, heat activation was performed. In the heat activation, 20 g of sepiolite was placed in a muffle furnace for a period of 10 hours.

3 RESULTS AND DISCUSSION

3.1 Adsorption of Surfactants on Original Sepiolite

Figure 1 shows the adsorption isotherms of DTAB (C12) and HTAB (C$_{16}$) at 25 ± 2°C onto sepiolite. Plateau adsorption values for the quaternary amines in the initial concentration range of 10^{-1} - 10^{-1} M/l are $r_{mE;i} = 6.18 \times 10^{-8}$ M/m^2 for DTAB and $r_{ma} = 6.68 \times 10^{-6}$ M/m^2 for HTAB. The residual concentration values for these surfactants at the onset of the plateau in the adsorption isotherms for DTAB and HTAB respectively were found to be $C_D = 3.9 \times 10^{-2}$ M/l, and $C_D = 1.22 \times 10^{-3}$ M/l. By plugging these values in Equation 2 the cross-sectional areas for each reagent can be calculated, as 27 $Å^2$ and 25 $Å^2$ for DTAB and HTAB, respectively. If the cross-sectional area of the polar part of DTAB and HTAB is 25 $Å^2$, as reported by Harkins and Florence (1938), the degree of coverage for DTAB and HTAB on the original sepiolite is 0=1. This reveals that DTAB and HTAB adsorbs onto original sepiolite in the form of a monolayer. This has been verified by the following equation:

$$Y.A = \frac{10^{20}}{\Gamma_{max} \cdot A} \qquad Å^2/\text{molecule} \qquad (2)$$

where T_r denotes adsorption in the plateau region (M/m^2); and A represents the Avagadro number (6.02×10^{23}).

The adsorption isotherms of the original sepiolite/quaternary amines system given in Figure 1 are characterized by three distinct regions with different slopes. While the adsorption of amines shows a gradual increase in the first region, the increase in the second region is rather sharp. Despite significant differences in the rising part of the adsorption isotherms for two surfactants of different chain length onto sepiolite adsorbent with 68 m"/g of specific surface area, the adsorption densities overlap at the onset of the plateau (Region III). The solution concentration in Region III reaches saturation, which indicates that both quaternary amines concomitantly attain a region of micellar interactions and in turn point out the differences in the adsorption mechanisms of DTAB and HTAB molecules in each region.
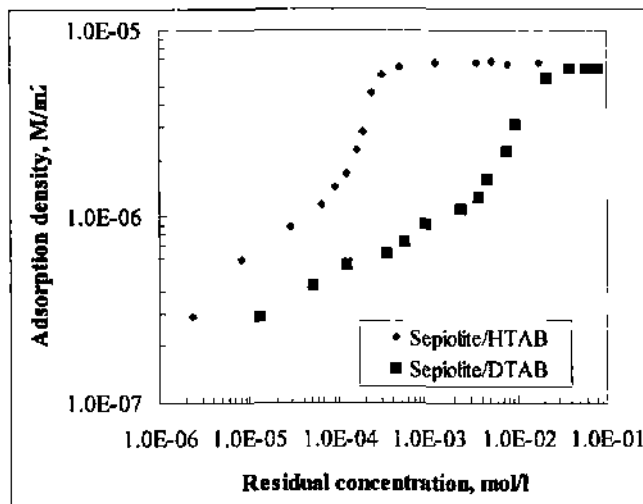
Figure I. Adsorption isotherms of septolite/DTAB and sepiolite/HTAB systems at natural pH of 8.5 (solution temperature 25°C, S/L=0.05, Cond. Time: 2h).

The data in Figure 1 also show that the cationic surfactant with 16 CHj groups exhibits, much higher adsorption densities than that with 12,CH_2 groups. This is particularly pronounced in the region of hemimicelle formation, where the slope of the isotherms is steeper. Although this finding is in agreement with the surface activity of the respective surfactants, it does disagree with the assumption that the molecules penetrate into the channels of sepiolite

The contribution of CH2 groups to the free energy of adsorption in Region H was assessed by modifying the assumptions used by Fuerstenau and his co-workers for an alumina/alkylsulfonate system as follows (Somasundaran and Fuerstenau 1966, Wakamatsu and Fuerstenau 1968):

$$C_s = C_D \cdot e\left(\frac{-Ze\psi_\delta + n\phi}{kT}\right) \qquad (3)$$

where C_s and C_D = surface and equilibrium concentrations; Z = valency of the adsorbate species; e = fundamental unit of charge; ψ_δ = Stern layer potential; n = number of straight chain alkyl groups in the surfactant; ϕ = free energy per mole of CH2 groups for hemhnicellization; and k = Boltzman constant.

Under the conditions of constant adsorption density, the above equation can be rewritten for dodecyl and hexadecyl amines as

$$\frac{C_{D-16}}{C_{D-12}} = e^{Ze\frac{(\psi_{\delta-16} - \psi_{\delta-12})}{kT}} + \frac{(16-12)\phi}{kT} \qquad (4)$$

Since at pH 8.5 the ionic strength is maintained roughly constant, under these conditions one can write

$$\psi_{\delta-16} \cong \psi_{\delta-12}$$

Equation 4 is then reduced to

$$\ln\frac{C_{D-16}}{C_{D-12}} = \frac{4\phi}{kT} \qquad (5)$$

Substituting the values for bulk concentrations corresponding to an adsorption density of 10^{-6} M/m^2 in Equation 5:

$$\ln\frac{6\times10^{-5}}{2.28\times10^{-3}} = \frac{4\phi}{kT}$$

$$\phi = -540 \text{ Cal} / \text{mol} - CH_2 - \text{grup},$$

This value for free energy contribution per CH_2 group {-1 kT) is in good agreement with the values reported by Fuerstenau and his associates for alumina/alkylsulfonate (Somasundaran and Fuerstenau 1966, Wakamatsu and Fuerstenau 1968). These results clearly demonstrate that, regardless of die mechanism in Region 1, the chains of the molecules associate in Region II and enhance the adsorption process depending on the chain length.

749

3.2 Effect of Heat Treatment on Surfactant Adsorption

The adsorption isotherms of heat-treated sepiolite at 300°C with an increased specific surface area of 235.5 m^2/g'a for DTAB and HTAB surfactants at 25°C are illustrated in Figures 2a and 2b. As is evident from the figure, the adsorption of heat-treated sepiolite exhibits a definite reduction at all concentrations due to the loss of zeolitic and adsorbed water molecules upon heat treatment and the inability of amine molecules to form mainly hydrogen bonding. It is to be noted that while the adsorption densities between the original and heat-treated sepiolites in M/g exhibit marginal differences, those in M/ro show considerable differences because there is more than a four-fold increase in surface area upon heat treatment, but there İs no extra adsorption. Although the increase in surface area upon increasing the temperature is in line with the data in the literature (Jimenez-Lopez et al. 1978, Hibino et al. 1995), the decrease seen in adsorption needs to be elaborated further.

It is also evident mat the residual concentrations in the plateau region are almost the same, indicating that the saturation adsorption is possibly governed by the formation of CMC. The CMC values in water for DTAB and HTAB are 1.56x1 (T^2 M (Ottewil 1967) and lxlO"^{3} M (Okuda et al. 1987). However, it is well known that in the presence of mono- and multivalent ions, CMC values undergo significant reduction (Shinoda 1963). In a typical sepiolite supernatant, about 20 ppm of Mg and 40 ppm of calcium is released into the solution. It appears that the Cr values of about 3.9x1O"^{2} M obtained at the plateau values in Figure 2 are close to the CMC of the system and in line with the above explanation.

The parking areas of DTAB and HTAB molecules on heat-activated sepiolite respectively yield 96 Â^2 and 75 Â^2. The surface coverage of DTAB on heat-activated sepiolite gives a surface coverage of 0 = 0.26, whereas that of HTAB yields 0 = 0.30. These values indicate that both amines adsorb onto die surface and channels of the heat-activated sepiolite in the form of patches and islands, but not of layers.

4 CONCLUSIONS

Examination of the slopes of adsorption isotherms for both DTAB and HTAB/original sepiolite systems at 25°C reveals that adsorption densities are high even at low concentrations. This shows that adsorption of amine molecules not only occurs in the external surfaces but also in the internal channels depending upon the position of water molecules, i.e., in die edges and corners of the sepiolite.

The adsorption isotherms of DTAB and HTAB/original sepiolite systems at 25°C show that HTAB with 16 CH$_2$ groups exhibits higher adsorption densities than DTAB with 12 CHi groups. This finding is particularly pronounced in the region of hemimicelle formation where the curves become steeper. Moreover, despite considerable differences in the rising part of the adsorption isotherms for two surfactants of different chain length onto a sepiolite adsorbent, the adsorption densities almost coincide at the onset of plateau (Region III), where the solution concentration reaches saturation. This emphasizes the crucial finding that it is adsorption and not absorption that is the driving force in the uptake of surfactant molecules.

In spite of a several-fold increase in the specific surface area of sepiolite upon heat activation, the adsorption in M/g was found to remain almost constant, whereas in M/m^2 it was found to decrease significantly. This was attributed to the increase in the number of micropores which exclude the cationic surfactant and lead to the partial collapse of the magnesium layer in the octahedral sheet. The removal of zeolitic water upon heat treatment is also instrumental in the loss of hydrogen bonds for primary amines. In conclusion, heat activation of sepiolite appears to be detrimental as far as cationic surfactants are concerned. The question of whether this can be extended to all organic compounds requires further studies a other organic compounds.

REFERENCES

Alvarez, A. 1984. Sepiolite: Properties and Uses. In: A.Singer and E. Galan, eds. Palygorskite-Sepiolite. Occurrences. Genesis and Uses. *Developments in Sedimentology 37:* 253-287.

Çetişli, H. 1989. Eskişehir sepİyolitinin yüzey asit-baz özellileri. *TÜBİTAK Doğa TU Mühendislik ve Çevre Debisi.* 13(2): 213-227.

Del Hoyo, C. Rives, V. & Vicente, M.A. 1993. Interaction of N-metly 8-hydroxy quinoline methyl sulphate with sepiolite. *Applied Clay Science.* 3: 37-51.

Harkins, W.D. & Florence, R.T. 1938. Interactions in mixed monolayers on aqueous solutions. *Journal of Chemical Physic.* 6: 847-854.

Jones, B.F. *&* Galan, E. 1988. Hydrous phyllosilicates (exclusive of micas). In: S.W. Bailey (Ed.), Sepiolite and Palygorskite. *Reviews in Mineralogy.* 19, *Mineralogical Society of America.* 16:631-667.

Klevens,H.B. 1948.7. *Phys. Coll. Chem.* 52:130.

Okuda, H. Imae, T, *&.* Dceda, S. 1987. The adsorption of cetlytriemethyl ammonium bromide on aqueous surfaces of sodium bromide solutions. *Colloids and Surfaces.* 27.

Ottewil, R.H. 1967. *In* "AU*iionic Surfactants".* Dekker, New York: (M.J. Schick, Ed.;.

Powers, G.W. 1970. *The volumetric determination of organic sulfates or sulfonates by the double indicator method.* Tulsa, USA; Communication C-225, Amoco Production Co.

Reid, B.E & Aninachalam, S. 1994. Use of granular activated carbon columns for lead removal *J. Environmental Engineerin*. 120'416-436

Sabah, E. Sağlam, H. Kara, M. & Çelik, M.S 1997. Uptake of cationic surfactants by a clay absorbent' Sepiolite, *5"" Southern Hemisphere Meeting on Mineral Technology* 277-270.

Sema, C. & Van Scoyoc, G.E. 1978. Infrared study of sepiolite and palygorskite surfaces *Proc 1978 Int. Clay Conf.* 197-206.

Shinoda, K.J. 1963 *Surfactants and interfacial phenomena* New York: Wiley Interscience Publication.

Singer, A & Huang, P.M. 1989 Adsorption of humic acid by palygorskite and sepiolite, *Clay Minerals. 24:* 561-564.

Somasundaran, P. & Fuerstenau, D.W. 1966. Mechanism of alky] sulfonate adsorption at the alumina-water interface. *J Phys.Chem.* 70'90

Wakamatsu, T. & Fuerstenau, D.W. 1968. The effect of hydrocarbon chain length on the adsorption of sulfonates at the water- sol id interface. *Advan Chem.Ser* 79 161
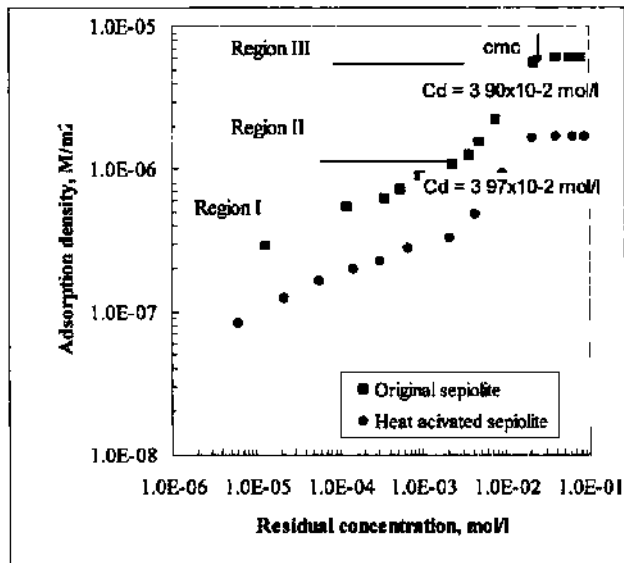
(a)
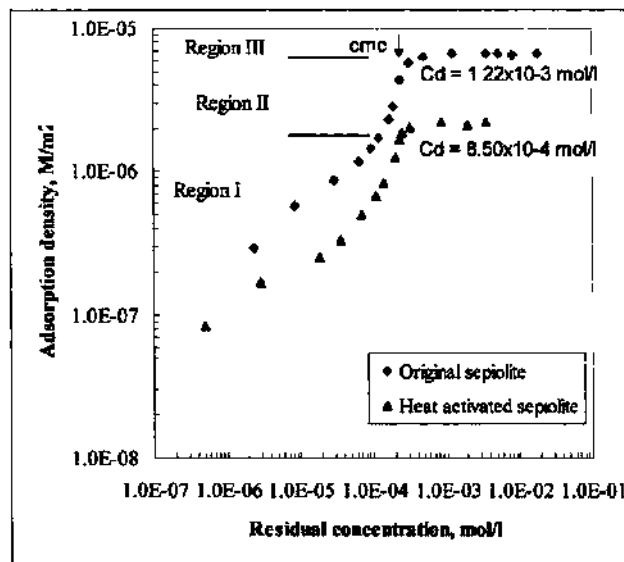
(b)

Figure 2. Adsorption isotherms of DTAB (a) and HTAB (b) on original and heat-activated sepiolite (Natural pH of 8.5, solution temperature 25°C, S/L=0.05, Cond. Time: 2h).