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# Adsorption of Some Textile Dyes by Hexadecyltrimethylammonium Bentonite

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In this study, hexadecyltrimethylammonium (HDTMA) bentonite was synthesized by placing alkylammonium cation onto bentonite. Adsorption of some textile dyes such as Everdirect Supra Yellow PG, Everdirect Supra Orange 26 CG, Everdirect Supra Rubine BL, Everdirect Supra Blue 4BL and Everdirect Supra Red BWS on Na-bentonite and HDTMA-bentonite was investigated. While the Na-bentonite had no affinity for the dyes, the HDTMA-bentonite showed significant adsorption from aqueous solution. The Langmuir and Dubinin-Rasdushkevich (D-R) isotherm equations were applied to the data and values of parameters of these isotherm equations were evaluated. The mean energy of adsorption, E, was also calculated from the adsorption energy constant K' values determined from the D-R isotherm equation.

**Key Words:** Organoclay, Textile dyes, Adsorption isotherms, Langmuir equation, Dubinin-Rasdushkevich (D-R) equation

## Introduction

Widespread contamination of soil and groundwater by synthetic organic chemicals (e.g., dyes) has been recognized as an issue of growing importance in recent years. Most of these compounds are potential or known human carcinogens and are of considerable health concern, even at low concentrations. For this reason, the fate and transportation of these compounds have been the subject of much research.

Methods for decolorization have therefore become important in recent years. In principle, decoloration is possible with one or more of the following methods: adsorption, precipitation, chemical degradation, photodegradation and biodegradation[1].

The purification of waste waters contaminated by hazardous pollutants of inorganic and organic nature is among the serious problems of conservation, especially when such toxic materials, e.g., dyes, contaminating the environment even in insignificant concentrations, are involved. The elimination of such pollutants from aqueous solutions is an important problem not only from a technical but also from an economic point of view. Discoloration in drinking water may be due to the presence of coloured organic substances or highly coloured industrial wastes, of which pulp, paper and textile wastes are most common. Highly coloured, polluted water will frequently have an associated objectionable taste, but the degree to which this association is causative is not known. Synthetic dyes represent a relatively large group of organic chemicals which are encountered in practically all spheres of our daily life. It is therefore possible that such chemicals have undesirable effects not only on the environment, but also on humans. In order to minimize the possible damage to people and the environment arising from the production and application of dyes, several studies have been conducted around the world[2−5]. A number of researchers have used various organoclays for the removal of textile dyes from aqueous solutions[6,7].

The development of sorbents of different types is carried out by many research and commercial institutions. Active carbon, for example, is known as an effective sorbent of toxic materials from water solution. Its sorbent characteristics are regenerable by thermal desorption; however, a significant part of the sorbent is lost in each desorption cycle. This is the main reason for low economical efficiency in its application. Therefore, the interest in the development of sorbents of specific surface, e.g., organoclays, has significantly increased in recent years[8].

The aluminosilicate sheets of common clay minerals possess a net negative electrical charge compensated for by inorganic exchangable cations (e.g., $Na^+$ and $Ca^{2+}$), which are strongly hydrated in the presence of water. Surface properties of natural clays can be modified by simple ion exchange with organic cations. Bentonite and kaolinite clays are easily modified by exchanging their inorganic cations with quaternary ammonium cations[9−13]. This may result in an increase in the inter-lamellar spacing and exposure of new sorption sites of the clays. More importantly, the substituted organic cations are weakly hydrated. As the inorganic cations are progressively replaced by the organic cations, the surface properties of a clay may change considerably from highly hydrophilic to increasingly organophilic (hydrophobic).

The mechanisms controlling the sorption of compounds on organoclays are dependent on the type of organic cations forming organoclays. We used quaternary ammonium cations of the general form $[(CH_3)_3NR]^+$, where R is an aromatic or alkyl hydrocarbon group, to replace inorganic cations on clays. When R is a relatively small group (e.g., $R{=}{-}CH_3$, $-C_6H_5$) the organic cations in the interlamellar region of the clays are isolated from each other. Such organoclays have relatively high surface areas and display characteristics of surface adsorbents. Alternatively, when R is a large alkyl group [e.g., hexadecyltrimethylammonium (HDTMA), $R{=}{-}C_{16}H_{33}$], the resultant organoclays have low surface areas and act as partitioning media in the sorption[14−16].

Although the sorption of organic contaminants by soils is mainly controlled by the organic fraction, the increasing use of organoclays in environmental applications is making the organic-clay interactions of increasing importance.

In our previous work, adsorption of phenol derivatives, cationic dyes and herbicides by organoclays have been investigated[12−13].

The present paper examines a convenient method for removing some textile dyes from water on a organoclay adsorbate such as hexadecyltrimethylammonium bentonite. Water soluble textile dyes such as Everdirect Supra Yellow PG, Everdirect Supra Orange 26 CG, Everdirect Supra Rubine BL, Everdirect Supra Blue 4BL and Everdirect Supra Red BWS resemble the dyes found in waste water.

## Materials and Methods

The bentonite clay used in this study was purchased from Sigma (USA). The $< 2\mu$m clay fractions were obtained by wet sedimentation and subsequently saturated with $Na^+$ cations by washing the clay repeatedly with NaCl solution (0.1 mole $L^{-1}$). A portion of clay suspension containing 20 g of bentonite was treated by adding the solution of hexadecyltrimethylammonium (HDTMA)-bromide in an amount just equal to the cation exchange capacity (79.5 meq/100g) of the clay. The mixture was agitated overnight on a magnetic stirrer at room temperature. The HDTMA-bentonite suspension was then washed with distilled water repeatedly until free of bromide ions as indicated by $AgNO_3$. The organoclay was dried at room temperature and stored in bottles for experimental use.

For XRD analysis, samples of the organoclays as oriented aggregates were used on glass slides. Basal X-ray diffraction spacings were then recorded using CuK$\mu$ radiation and a Rigaku DMAX III C X-Ray diffractometer.

Everdirect Supra Yellow PG, Everdirect Supra Orange 26 CG, Everdirect Supra Rubine BL, Everdirect Supra Blue 4BL and Everdirect Supra Red BWS were obtained from a local organization in Antalya-Turkey. They were used as received.

First, synthetic aqueous dye solutions of 250 mg $L^{-1}$ were prepared for adsorption studies. Then, the synthetic aqueous solutions of dyes were diluted to the concentrations ranging from 10 to 100 mg $L^{-1}$. HDTMA-bentonite amounts weighing 0.1 g were transferred into 50 mL of aqueous dye solution and allowed to equilibrate for 24 hours at 25°C in a water bath. Supernatants of these solutions were separated by centrifugation from organoclay. Dye concentrations of supernatants (equilibrium concentrations) were determined by spectrophotometry using a Shimadzu 160 A model UV-VIS spectrophotometer at ambient temperature. The wavelength for maximum absorbance ($\lambda_{\max}$) was 404 nm for Everdirect Supra Yellow PG, 417 nm for Everdirect Supra Orange 26 CG, 521 nm for Everdirect Supra Rubin BL, 595 nm for Everdirect Supra Blue 4BL and 517 nm for Everdirect Supra Red BWS. Distilled water was used as the reference. The equilibrium concentrations of the dye solutions were determined by means of a precalibrated scale.

## Results and Discussion

To observe the uptake of the textile dyes, the clays were placed in aqueous solutions of the textile dyes and allowed to equilibrate for one day. At the end of this time, HDTMA-bentonite in the aqueous solutions of the textile dyes showed the dark colorations of the original solutions. Na-bentonite had no affinity for the dyes. Na-clays carry a permanent negative charge in their structural framework. The hydration of $Na^+$ ions in clays and the nature of Si-O groups impart a hydrophilic nature to the mineral surfaces. Because of this property, water is preferentially adsorbed by these surfaces, and large organic compounds cannot compete with strongly held water for adsorption sites on the clay surfaces. Thus, Na-clays are ineffective sorbents for small organic molecules. However, it is possible to modify the surface properties of clays greatly by neutralizing the anionic framework of layer silicates by using positively charged organic species such as alkylammonim ions. In the modified form (HDTMA-bentonite), the clay surface may become organophilic and interact strongly with organic compounds. Textile dyes represent a relatively large group of organic chemicals. In an HDTMA-bentonite-dye system it is possible that adsorption may be enhanced by the hydrophobic interaction between the adsorbed dye molecule and HDTMA-bentonite. The interlamellar spacing of the HDTMA-bentonite was obtained by substracting the thickness of the clay layer from the experimentally determined basal spacing ($d_{001}$). The intercalation of the HDTMA cation increased the interlamellar distances from 13.2 Å (Na-bentonite) to 17.9 Å (HDTMA-bentonite). The larger basal spacing ($d_{001}$) of HDTMA-bentonite corresponds to the formation of bilayers in which the long-chained surfactant cations are in direct contact with each other[10], leading to the formation of organic phases consisting mostly of the $C_{16}$ hydrocarbon groups into which solutes are partitioned. Thus, the degree of sorption of dyes depends on the amount of the surfactant ions in the bentonite interlayer sites.

The amount of dye adsorbed per unit weight of an adsorbent, $q$, was calculated using the following formula:

$$q = \frac{(C_o - C)V}{m} \tag{1}$$

where, $C_o$ is the initial concentration of dye (mg $L^{-1}$), C is the equilibrium concentration of dye in solution (mg $L^{-1}$), m is the mass of the clay (mg) and V is the volume of solution (L).

The results concerning dye adsorption for HDTMA-bentonite are presented in Figs. 1-5. Together with experimental data, the corresponding theoretical adjustment of experimental determinations by the Langmuir equation was also plotted.

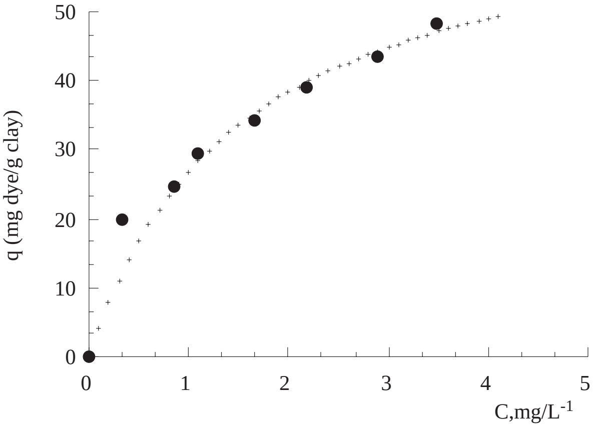

**Figure 1.** Adsorption isotherm of Yellow PG on HDTMA-bentonite. •: Experimental +: Langmuir isotherm

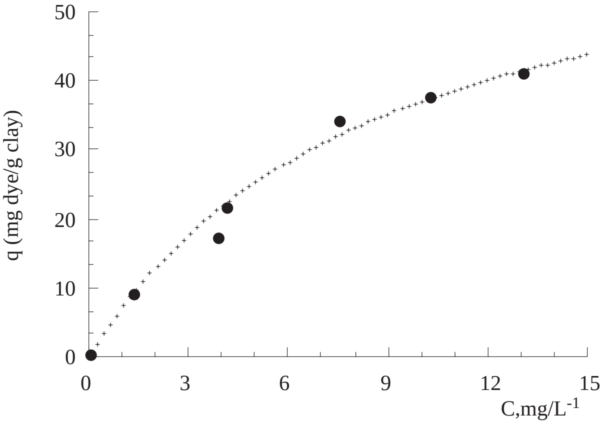

**Figure 2.** Adsorption isotherm of Orange 26 CG on HDTMA-bentonite. •: Experimental +: Langmuir isotherm

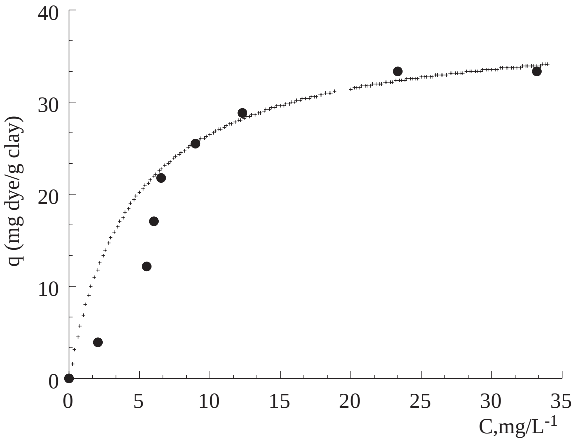

**Figure 3.** Adsorption isotherm of Rubine BL on HDTMA-bentonite. •: Experimental +: Langmuir isotherm

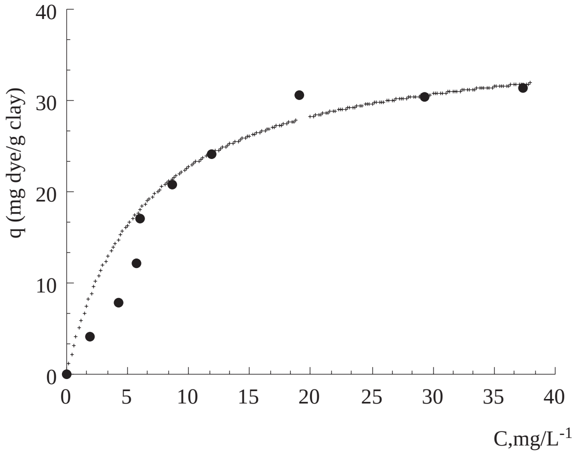

**Figure 4.** Adsorption isotherm of Red BWS on HDTMA-bentonite. •: Experimental +: Langmuir isotherm

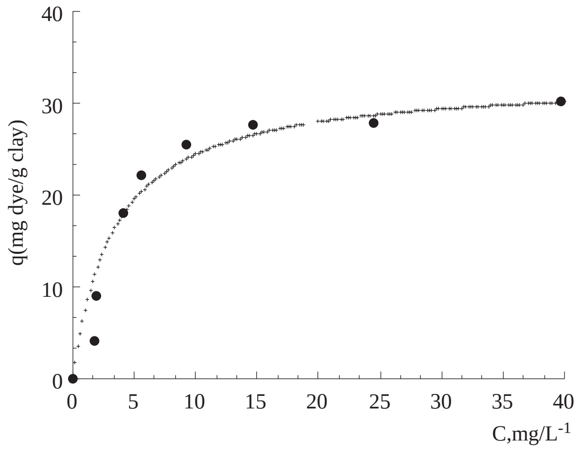

**Figure 5.** Adsorption isotherm of Blue 4BL on HDTMA-bentonite. ●: Experimental +: Langmuir isotherm

It is obvious from Figs. 1-5 that the adsorption isotherms of dyes on HDTMA-bentonite are L-type according to the Giles classification[17]. In this type of isotherm, the initial portion provides information about the availability of the active sites to the adsorbate and the plateau signifies the monolayer formation. The initial curvature indicates that a large amount of dye is adsorbed at a lower concentration as more active sites of HDTMA-bentonite are available. As the concentration increases, it becomes difficult for a dye molecule to find vacant sites, and so monolayer formation occurs. The types of system which give this curve do in fact fulfil these conditions. Thus they have one of the following characteristics: (i) the adsorbed molecules are most likely to be adsorbed flat or (ii) if adsorbed end-on, they suffer little solvent competition. Examples of (ii) are: (a) systems with highly polar solute and adsorbent, and a nonpolar solvent; and (b) systems with monofunctional ionic subtances with very strong intermolecular attraction. It is possible that in the system (b) cases the adsorbed ions may have become associated into very large clusters and just adsorption takes place. Where the sites are few and widely separated, the surface has large hydrophobic regions[18].

Solid-liquid equilibrium can be easily described by adsorption isotherms. The Langmuir equation is the mathematical function most commonly used to describe this process.

The Langmuir isotherm can be expressed as

$$q = \frac{X_m kC}{1 + kC} \tag{2}$$

where $q$ =amount of dye adsorbed per unit weight of adsorbent (mgg$^{-1}$), $C$ =concentration of dye remaining in solution at equilibrium (mgL$^{-1}$), $Xm$ =amount of dye adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface (mgg$^{-1}$) and $k = a$ constant related to the energy or net enthalpy ($k$). By plotting $q$ versus $C$, a curve is obtained which is linear at low equilibrium concentrations, followed by a curvature (concave to the x-axis), and with an asymptotic tendency to saturation corresponding to a monolayer covering.

The linear form of the Langmuir isotherm equation is represented in equation (3).

$$\frac{C}{q} = \frac{1}{kX_m} + \frac{C}{X_m} \tag{3}$$

Straight lines were obtained by plotting $C/q$ against $C$ for the adsorption of dye onto HDTMA-bentonite as shown in Figure 6.

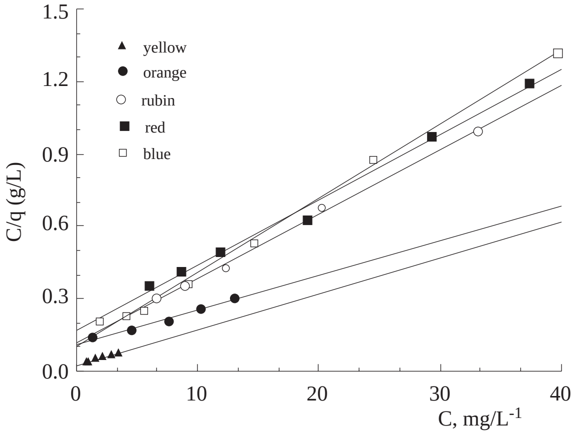

**Figure 6.** Langmuir plots HDTMA-bentonite/ dye systems.

The values of $X_m$ and $k$ calculated from the slopes and intercepts of the Langmuir plots and correlation coefficients $r$, are reported in Table 1. As it can be seen most of the adsorption isotherms fitted the Langmuir equation with correlation coeffiecints $r > 0.99$. Many experimental isotherms conforming to a Langmuir isotherm involve monolayer coverage. The value of monolayer coverages of HDTMA-bentonite by these dyes increased in the order Everdirect Supra Yellow PG> Everdirect Supra Orange 26 CG> Everdirect Supra Rubine BL> Everdirect Supra Red BWS>Everdirect Supra Blue 4BL.

**Table 1.** Langmuir isotherms constants for the adsorption of dyes

| DYE | Xm (mg $g^{-1}$) | k (L $mg^{-1}$) | $r$ |
|---|---|---|---|
| Yellow Pg | 67.71 | 0.654 | 0.995 |
| Orange CG | 52.36 | 0.177 | 0.997 |
| Rubine BL | 38.67 | 0.218 | 0.998 |
| Red BWS | 37.18 | 0.147 | 1.000 |
| Blue 4BL | 32.65 | 0.295 | 0.998 |

The adsorption data were also tested for another adsorption isotherm, the Dubinin-Radushkevich (D-R)[19]. The relationship between D-R and other types of adsorption isotherm is shown by Polyzpoulos et al. This isotherm is more general than the Langmuir isotherm since it does not assume a homogenous surface or constant sorption potential. The D-R equation is

$$q = X'_m \exp(-K'\epsilon^2)$$

where $\epsilon$ (polanyi potential)= RT ln (1+1/C), q is the amount of dye adsorbed per unit weight of HDTMA-bentonite (mg $g^{-1}$), $X'_m$ is the adsorption capacity (mg $g^{-1}$), C is the equilibrium concentration of dye in solution (mg $L^{-1}$), $K'$ is the constant related to the adsorption energy ($mol^2$ $kJ^{-2}$), R is the gas constant (kJ. $deg^{-1}$ $mol^{-1}$) and T is the temperature (K).

The D-R isotherm can be linearized as

$$\ln q = \ln X'_m - K'\epsilon^2 \tag{4}$$

The plots of ln $q$ against $\epsilon^2$ are shown in Figure 7.

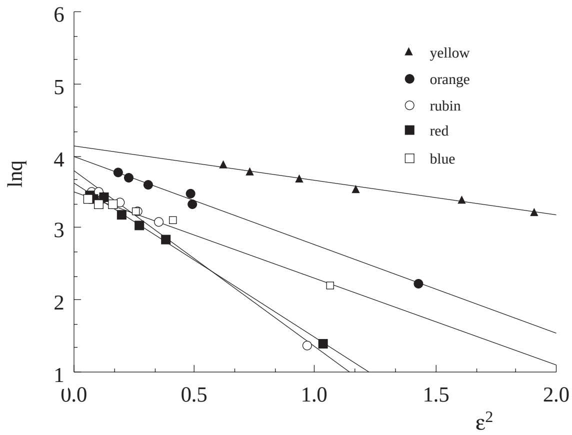

**Figure 7.** D-R plots HDTMA-bentonite / dye systems.

The parameters $X_m$ and $K'$ obtained from the intercepts and slopes of these plots are given in Table 2.

**Table 2.** D-R isotherm parameters and mean energy of the adsorption of dyes.

| DYE | $X'_m$(mg g$^{-1}$) | $K'_m$ (mol$^2$ kJ$^{-2}$) | E (kJ mol$^{-1}$) | $r$ |
|---|---|---|---|---|
| Yellow Pg | 63.07 | 0.491 | 1.010 | 0.993 |
| Orange CG | 53.67 | 1.218 | 0.641 | 0.996 |
| Rubine BL | 44.02 | 2.430 | 0.454 | 0.992 |
| Red BWS | 37.52 | 2.153 | 0.482 | 0.998 |
| Blue 4BL | 33.39 | 1.195 | 0.647 | 0.993 |

As can be seen in this table, most of the adsorption isotherms fitted the D-R equation with correlation coefficients $r > 0.99$. By making certain assumptions, the mean energy of adsorption, E, can be calculated from the K$'$ values (20) using the relation

$$E = (-2K')^{-0.5} \tag{5}$$

The determined values of E are presented in Table 2. The Langmuir isotherm constants do not give any information concerning the chemical or physical properties of the sorption. But the calculated mean energy of adsorption, E, from the D-R isotherm, gives information about the chemical or physical properties of the sorption. The calculated mean energy values of adsorption of the textile dyes by HDTMA-bentonite are very small and this implies that the type of adsorption is physical. There was a good fit between the Xm data for HDTMA-bentonite and the Langmuir and D-R model (Tables 1-2).

# Conclusion

We investigated the sorption of textile dyes such as Everdirect Supra Yellow PG, Everdirect Supra Orange 26 CG, Everdirect Supra Rubine BL, Everdirect Supra Blue 4BL and Everdirect Supra Red BWS on bentonites with and without quaternary ammonium salt (HDTMA). The bentonite was modified with HDTMA, rendering it organophilic. Whilst no sorption of textile dyes occurred on Na-bentonite, the textile dyes were strongly sorbed on HDTMA-bentonite. This could be explained by adsorption interaction between the adsorbed dye molecules and hydrophobic alkyl group on HDTMA-bentonite, which should enhance the adsorptive capacity of the bentonite.

The values of adsorption of dyes ranged from 60.3 to 99.2%.

There was a good fit between the experimental data for HDTMA-bentonite the Langmuir and D-R models.

At the end of the adsorption studies, it can be said that HDTMA-bentonite may be used as an adsorbent for adsorption or decolorization of some textile dyes from waste water solutions. The usability of HDTMA-bentonites in industrial waste water requires further investigations.

## References

1. H. Zollinger, **Color Chemistry,** VCH Publishers Inc. New York, (1991).
2. R. Deoraj, R.D. Guy, **Clays and Clay Miner., 29,** 3, 205-212 (1981).
3. G.S. Gupta, S.P. Shuckla, G. Prasad, V.N. Singh, **Environ. Tech., 13,** 925-936 (1992).
4. J. Cenens and A. Schoonheydt, **Proceedings of the 9th International Clay Conference, Strasbourg,** 85, 15-23 (1990).
5. L. Margulies, H. Rozen, S. Nir, **Clays and Clay Miner. 36,** 3, 270-276 (1988).
6. B.J. Bhalala, J. Bhatt, P.V. Pandya, **I. J. Environ. Prot., 16,** 186-188 (1996).
7. M.M. Socias, M.C. Hermosin, J. Cornejo, **Chemosphere, 37**, 289-300 (1998).
8. M. Kowalska, H. Güler, D.L. Cocke, **The Science of The Total Environment, 141,** 223-240 (1994).
9. S.A. Boyd, J.F. Lee, M.M. Mortland, **Nature 333,** 345-347 (1988).
10. S.A. Boyd, M.M. Mortland, C.T. Chiou, **Soil Sci. Soc. Am. J., 52,** 652-657 (1988).
11. W.F. Jaynes, S.A. Boyd, **J. Air Waste Manage, 40,** 1649-1653 (1990).
12. Ö. Ceyhan, H. Güler, R. Güler, **Adsorp. Science Techno., 17,** 469-477 (1999).
13. Ö. Ceyhan, H. Güler, C.Ü. **Fen Bilim. Der., 21,** 105-116 (1999).
14. W.F. Jaynes, S.A. Boyd., **Soil Sci. Soc. Am. J., 55,** 43-48 (1991).
15. J.A. Smith, R.R. Jafte, C.T. Chiou,**Environ. Sci. Technol., 24,** 1167-1172 (1990).
16. M.M. Mortland, **Soil Science of America, 677,** 59-76 (1986).
17. C. H. Giles, T.H. MacEwan, S.N. Nakhwa, D. Smith, **J. Chem. Soc,** 3973-3993 (1960).
18. C.H. Giles, A.P. D'Silva, I.A. Easton, **J. Colloid and Interface Soc., 47,** 3, 766-778 (1974).
19. N.A. Polyzpoulos, V.Z. Keramidas, H. Kiosse, **Soil Sci. Soc. Am. J. 49,** 81-84 (1985)
20. R. Qaderr, J. Hanif, **Jour. Chem. Soc. Pak. 15,** 4,227-230 (1993).