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Adsorption, kinetic and thermodynamic studies of Hematoporphyrin IX on Clay Minerals

Mohamed Rashad^{1*}, Faiz F. Assaad²

¹Land and Water Technologies Department, Arid Lands Cultivation Research Institute, City of Scientific Research and Technological Applications (SRTA-City), New BorgEl-Arab21934, Alexandria, (EGYPT)

²Soil and Water Use Department, National Research Centre (NRC), Dokki, Cairo, (EGYPT)

E-mail : mrashad@mucsat.sci.eg; marashad1@yahoo.com

ABSTRACT

The adsorption behaviors of Hematoporphyrin-IX (HP-IX) on Kaolinite and Montmorillonite were studied. The adsorption behaviors differed noticeably according to the structure of the clay. The adsorption was more preferable on Montmorillonite than on Kaolinite.

HP-IX adsorption is affected by temperature and increased by increasing the dielectric constant of the used solvent. The adsorption capacity followed the order ethanol < methanol < water. Langmuir and Freundlich equations were used to analyze the adsorption behaviors and quantify the adsorption isotherms. The maximum adsorption showed a higher value for Montmorillonite than Kaolinite. The HP-IX adsorption on Kaolinite clay increased at acidic pH, while it decreased continuously in basic medium.

It was noticed that understanding HP-IX adsorption could be obtained by studying the relationship among HP-IX properties and the kinetic parameters of the reaction, taking into account the effect of experimental temperature and clay type on adsorption. Thermodynamic parameters of the kinetic reaction confirmed the adsorption isotherms data.

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KEYWORDS

Hematoporphyrin;
Adsorption;
Kaolinite;
Montmorillonite;
Polarity;
Langmuir;
Freundlich.

INTRODUCTION

The adsorption of Hematoporphyrin on clay surfaces is not only an academic interest, but also a basic phenomenon in many applied processes. For example the application in the remediation of contaminated ground water and industrial effluents as sorption technique produce high quality treated effluents. The sorption process has been investigated as a method to remove dye from waste water. In recent years, clays have

been accepted as one of the most appropriate low cost sorbent^[1].

Clay-Hematoporphyrin complex attracted much interest in the view point of materials chemistry as nanostructure; the lifetime of Hematoporphyrin on the clay surface is estimated to be in the order of nano second. These materials could be useful for electric and photo-responsible devices^[2].

Hematoporphyrins considered as an evidence for the biological source of petroleum and a variety of geo-

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logical and environmental research due to their extensive roles in both plant and animal biochemistry and as sorbed on the clay^[3].

The objective of the present work is to examine the adsorption process of HP-IX on two clay minerals (Kaolinite and Montmorillonite). Also the factors influencing the adsorption such as concentration, solvent dielectric constant, and temperature will be studied. Finally, kinetic reaction of this material will be examined to find out the thermodynamic parameters.

EXPERIMENTAL

The experiments were carried out using Na-saturated Kaolinite (Aswan, Egypt) and Na-saturated Montmorillonite (South Dakota, USA) as sorbents^[4] and HP-IX Figure 1 as adsorptive material.

The chemical analysis of Na-Kaolinite and Na-Montmorillonite was presented in TABLE 1. Cation exchange capacity (CEC) of Kaolinite and Montmorillonite clays was measured according to the standard method^[5].

TABLE 1 : Chemical analysis for Na-Kaolinite and Na-Montmorillonite

Parameter	Na-Kaolinite	Na-Montmorillonite
Ignition loss	13.20	8.44
SiO ₂	45.60	52.52
Al ₂ O ₃	39.20	23.66
TiO ₂	1.10	1.54
Fe ₂ O ₃	0.87	10.72
CaO	0.20	0.42
MgO	0.08	3.23
Na ₂ O	0.01	0.82
K ₂ O	0.01	0.40
P ₂ O ₅	0.00	0.10

Adsorption isotherms were determined by shaking 0.05g of Kaolinite or Montmorillonite in dark 100 mL vessels with HP-IX solutions containing 1, 5, 10, 15, 20, 25, 30, 40, 50 and 70 μmol. The pH of these suspensions was adjusted at 7.0±0.05. After 24 hours the vessels were centrifuged. The remaining HP-IX in the supernatant was measured by UV-VIS spectrophotometry^[6]. The amount of adsorbed HP-IX was calculated from the difference between the initial and the final equilibrium concentrations. The adsorption isotherms were

constructed at two temperatures 5 °C and 25 °C. The experiments were carried out by using three different solvents (methanol, ethanol, and water) to prepare the HP-IX solutions.

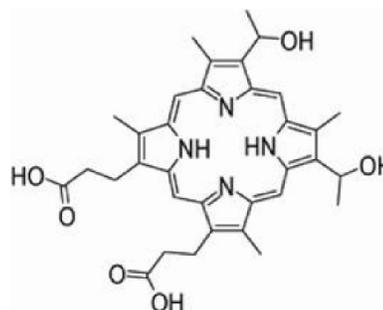


Figure 1 : Structure of Hematoporphyrin IX

A kinetic study of the adsorption process was followed up by monitoring the progress of the adsorption process at different time intervals. For these purpose two identical sets of a certain concentration (the concentration at maximum adsorbed amount) of HP-IX in methanol, ethanol and water were run simultaneously at two different temperatures (5 °C and 25 °C). The adsorbed amount of HP-IX was estimated at different time intervals.

RESULTS

The results were examined by using the Freundlich equation that is expressed by:

$$\log x/m = \log K + 1/n \log C \quad (1)$$

Where x/m is adsorbed porphyrin μmol/g, C is equilibrium concentration of HP-IX, μmol/mL, K is the index for classifying the degree of adsorption, and $1/n$ is the intensity of adsorption.

If $1/n < 1$, bond energies increase with the surface density; if $1/n > 1$, bond energies decrease with the surface density and when $1/n = 1$, all the surface sites are equivalent. The $1/n$ is often to be less than one and it varies with the degree of heterogeneity.

The verification of the Freundlich equations was done by calculating the standard error of the estimates (S.E.), given by:

$$S E = \Sigma (q^* - q / n)^{1/2} \quad (2)$$

Where q measured HP-IX adsorption, q^* is the predicted HP-IX adsorption, and n is the number of isotherm points

Adsorption behavior of HP-IX on Kaolinite and Montmorillonite

The adsorption of porphyrin by heterogeneous surfaces such as clays are usually follows a complex isotherm which may represent a combination of adsorptive mechanism^[7]. The complete isotherm obtained throughout this study didn't confirm to a single isotherm type (Figure 2 and Figure 3). Since Langumir isotherms are valid up to the formation of monolayer and characteristic of molecules that adsorb flat on substrate, the obtained data couldn't be explained by using this equation. The adsorption isotherms as shown in Figure 2 and Figure 3 have been divided into three distinct regions. These three regions were obtained for HP-IX adsorption on both of Kaolinite and Montmorillonite surfaces^[8]. The results revealed the following observations:

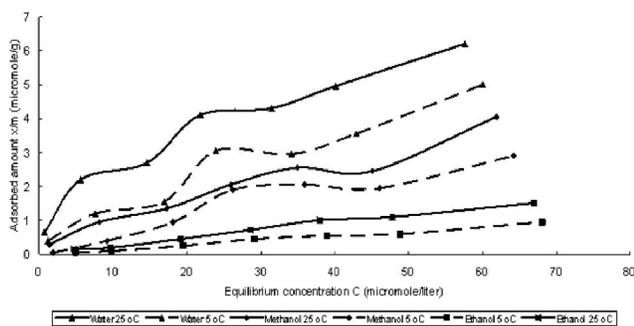


Figure 2 : Adsorption isotherm of HP-IX on Kaolinite clay in three different solvents at two temperatures

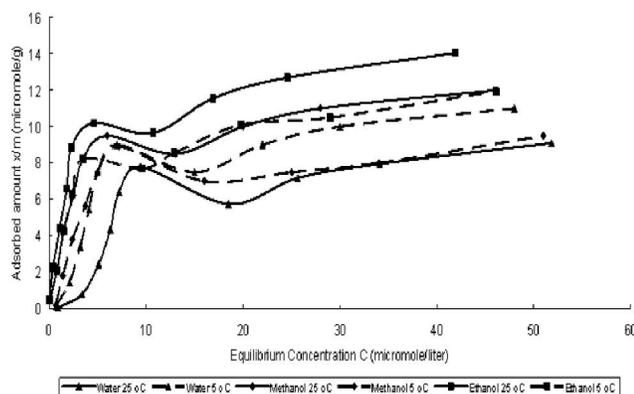


Figure 3 : Adsorption isotherm of HP-IX on Montmorillonite clay in three different solvents at two temperatures

1. At low HP-IX concentration, the adsorption isotherm rises very steeply, remaining close to the y-axis.
2. The region in which the isotherm becomes convex to the x-axis.

3. The linear area of the isotherm at medium to high concentrations.

For that reasons the results of the HP-IX adsorption on the two studied clays were represented well by using Freundlich equation.

(a) Adsorption isotherm of HP-IX on Kaolinite

Freundlich's equation was used to analyze the adsorption behavior, to quantify the adsorption isotherms, where it fits the sub-monolayer range, especially if the adsorbent surface possesses heterogeneous structure^[9].

Figure 4 showed that all the adsorption isotherms of HP-IX on Kaolinite in the different solvents obeyed Freundlich's equation. The adsorption isotherms had identical forms for all solvents. This indicated that the mechanism of the adsorption is similar, which fits the physical adsorption in sub monolayer range especially if the adsorbent surface posses heterogeneous structure. The data of TABLE 2 and Figure 4 of the isotherms indicated two-step mechanisms, as the isotherm is split into two straight line parts.

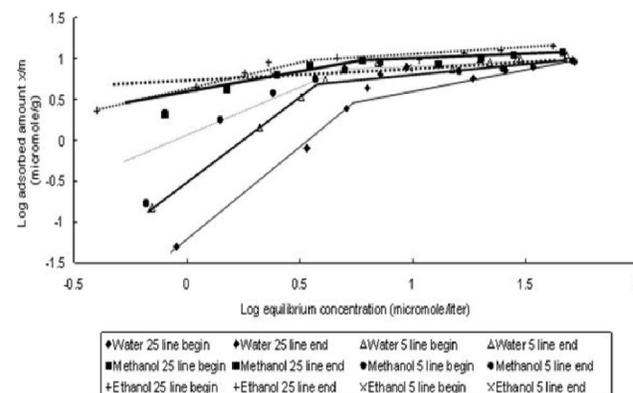


Figure 4 : Freundlich adsorption isotherm of HP-IX on Kaolinite clay in three different solvents at two temperatures

This indicated that two adsorption mechanisms are involved throughout these isotherms. There is a change from one type to another with increasing HP-IX concentration. As the Freundlich constants are different, TABLE 2, so there should be a significant difference between these two parts. This would be possibly due to that Kaolinite clay contains specific sites having different binding characteristic and the adsorption would depend on the occupation of these sites^[10]. Freundlich $1/n$ parameter, related to the adsorption affinity for the first and second linear parts, TABLE 2, proved again that there is a significant difference between the two parts of these adsorption isotherms. Such phenomenon

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was discussed^[11] and postulated that, Kaolinite clay contains specific sites of different binding characteristics and adsorption would thus depend on the percent loading i.e., the occupation of these sites. The increase in prophyrin concentration and the change from one

type of energy level of Kaolinite binding sites to another is probably responsible for the variation among Freundlich 1/n parameter values obtained from these isotherms TABLE 2.

It was noticed from these values that:

TABLE 2 : Freundlich isotherm constants of Hematoporphyrin IX adsorption on Kaolinite and Montmorillonite

Type of clay	Type of solvent	Na-Kaolinite			Na-Montmorillonite		
		Methanol	Ethanol	Water	Methanol	Ethanol	Water
1/n	Temperature 25 °C	First = 0.65	First = 1.16	First = 0.51	0.69	0.93	0.51
		Second = 0.27	Second = 0.33	Second = 0.27			
	Temperature 5 °C	First = 1.6	First = 0.9	First = 0.59	1.13	0.67	0.63
		Second = 0.26	Second = 0.21	Second = 0.21			
K	Temperature 25 °C	First = 3.15	First = 0.34	First = 4.69	0.21	0.03	0.79
		Second = 4.33	Second = 3.19	Second = 5.21			
	Temperature 5 °C	First = 0.61	First = 0.12	First = 2.96	0.03	0.01	0.34
		Second = 3.33	Second = 2.19	Second = 5.88			

- 1/n values of the second linear parts for the three solvents are lower than the first parts which means these parts of isotherms represent specific sites with higher binding energies than what are represented by the first parts. For that reason the adsorption of the prophyrin on Kaolinite could not be represented by using Langmuir equation.
- The values of 1/n in the two parts are lower for Water than Methanol and Ethanol. It means that the affinity increases by increasing the dielectric constant of the solvent.
- The K, predicted quantity of adsorption, is higher for the second linear parts than the first parts. The lowest value was for Ethanol at the two linear parts. This is again could be attributed to the dielectric constant of Ethanol.

As shown previously in Figure 2 the HP-IX adsorption was influenced by changing the solvent. In suspensions containing charged macromolecules and a charged surface, the interaction between both is substantially affected by the polarity of the medium. Obviously, a high dielectric permittivity of the solvent causes a greater unfolding of the HP-IX molecules due to electrostatic repulsion arising from the partial ionization of the residues originally buried in the folded HP-IX in the non-ionized form. Therefore, the adsorption increases with increasing dielectric constant because of the unfolding of HP-IX molecules. Under this condition the degree of HP-IX exposure to the sorbent surface in-

creases^[12].

The magnitude of adsorption had the order: water > methanol > Ethanol, although in the case of water there will be a little aggregation of the HP-IX which may decrease the adsorption. The high dielectric constant of water and its smaller molecular volume comparing with the alcohols, there would be no competition between water and the HP-IX molecules. This may cause increasing in the adsorption process. These results clearly implies that the adsorbed amount constantly decrease with an increase in the number of carbon atoms so the order of adsorbed amount was as follows: Ethanol < Methanol. This result can be explained that upon addition of aliphatic alcohol to the suspension there may be interaction between alcohol and clay and it may get adsorbed on the active sites of the clay. With increasing the number of carbon atoms there will be more effective sites to be adsorbed on the clay. This would increase the competition between HP-IX and ethanol molecules to be adsorbed on the clay, resulting in the decreasing the adsorbed amount of HP-IX.

As shown in Figure 2 and Figure 4 the adsorption was greater at 25 °C than at 5 °C, this means that the adsorption is an endothermic reaction process^[12]. This can be explained that at higher temperature the HP-IX unfold and agglomerated, so that its hydrophobic part interacted with the hydrophobic part of the clay. In addition the mobility of the HP-IX increased which re-

sulted in increasing the adsorption by raising the thermal energy.

(b) Adsorption isotherm of HP-IX on Montmorillonite

As illustrated in Figure 3 the adsorption isotherms of HP-IX on Montmorillonite showed a turning point of the curve which indicate the completion of the first layer and the subsequent rise represents the development of a second layer of adsorption. This development can be treated as that, for the first with the difference in the place of the substrate surface, the adsorbate is attracted by a layer of its own molecule in a particular orientation. The forces generated for the second are weaker than those generated the first. This means that the second rising portion of the isotherm is likely to be S – shape^[13].

As shown in Figure 3, the adsorbed amount increased with increasing the temperature and the dielectric constant of the solvent taking the same behavior as in Kaolinite clay. As illustrated in Figure 3 and Figure 5 the adsorption of HP-IX on Montmorillonite is much higher than on Kaolinite. This result can be attributed to the fact that each clay contains specific sites of different binding characteristic specific for its own. It is also due to the difference in surface area, cation exchange capacity and structure of the clay. Kaolinite and Montmorillonite clays represent two different families of clays. Montmorillonite clay, has a much higher available surface for adsorption than Kaolinite clay, and this is probably responsible for the larger amount of HP-IX adsorbed on Montmorillonite as compared with Kaolinite^[14].

Figure 5 showed that the adsorption isotherm of HP-IX on Montmorillonite can be represented by Freundlich equation. The data was represented without using the splitting technique. By comparing the values of $1/n$ in Freundlich equation of the three solvents, they had the same order of Kaolinite and followed the sequence of water methanol ethanol. It means that, the binding of HP-IX on Montmorillonite depends on the dielectric constant of the solvent. Beside that the K values followed the same sequence. From the data of $1/n$ and its relation with temperature it can be declared that the affinity for HP-IX adsorption into the three solvents increased by increasing temperature. This behavior can

be explained again through the effect of the adsorbant/adsorbate interaction.

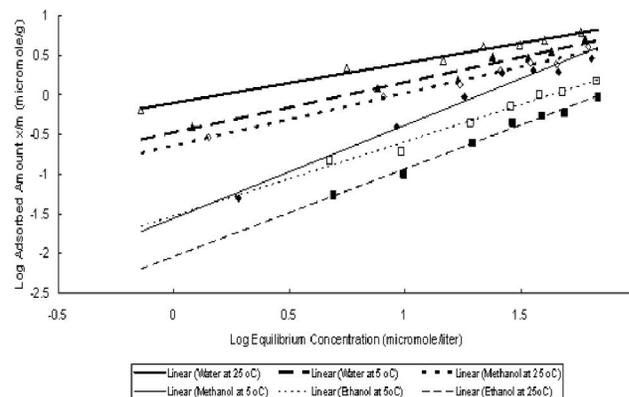


Figure 5 : Freundlich adsorption isotherm of HP-IX on Montmorillonite clay in different solvents at different temperatures

Kinetic and thermodynamic studies

Studying HP-IX kinetic of adsorption process onto clay-liquid interface is one of fundamental importance for complete understanding interfacial phenomena. Normally, the adsorption of HP-IX molecule from a bulk solution onto clay is considered to occur in the following three steps:

- Diffusion of HP-IX molecule from the bulk of the interface.
- Attachment of HP-IX molecule to active sites of the surface.
- Reconfirmation of the structure of the HP-IX molecule after adsorption.

Of these three steps, the last one is not only controlling the adsorption kinetics of HP-IX, but also it modifying the surface properties of the substrate^[15].

The rate of HP-IX adsorption on the clay can be calculated by using multiple-order kinetic equation

$$\frac{dC}{dt} = K_a C^{n_a} \quad (3)$$

Where C is the HP-IX concentration in solution, t is the reaction time, K_a is the rate of HP-IX adsorption and n_a is the order of the reaction.

Integration of this equation gives, in its simplified logarithmic form:

$$\log C = \frac{1}{1-n_a} \log(n_a - 1)K_a + \frac{1}{1-n_a} \log t \quad (4)$$

Thus, plotting $\log C$ as a function of $\log t$ according to (Eq. (4)) will give a straight line. The rate of adsorp-

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tion; K_a can be calculated from the intercept of the line, while the order of the reaction; n_a can be calculated from its slope^[16].

The standard enthalpy change of adsorption " H_a " can be determined through Van't Hoff relationship:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (5)$$

In terms of absolute reaction rate theory, the reaction rate constant K_a at two temperatures T_1 and T_2 for adsorption can be expressed as:

$$K_a = \frac{K^* T}{h} \exp(\Delta S_a) / R \cdot \exp\left(\frac{\Delta H_a}{RT}\right) \quad (6)$$

Where K_a is the rate constant, K^* is Boltzman constant, h is Plank's constant, T is the temperature, and ΔH_a , ΔS_a is the enthalpy and entropy energy respectively.

Eq. (6) would enable the calculation of ΔS_a since ΔH_a is found from Eq. (5).

The activation energy E_a and the change in the free energy ΔG_a can be calculated using the following relationships:

$$\Delta H_a = E_a - RT \quad (7)$$

$$\Delta G_a = \Delta H_a - T\Delta S_a \quad (8)$$

The thermodynamic parameters calculated from the adsorption kinetic data of HP-IX on Kaolinite and Montmorillonite clays at 5 °C and 25 °C are presented in TABLE 3. The effect of temperature showed that the process is an endothermic reaction process which was proved by the positive values of ΔH_a ^[17].

The absolute rate constant of HP-IX adsorption K_a increased with increasing the temperature. This is in agreement with the data obtained from the adsorption isotherms. Also the values of this parameter were higher for water than methanol, which noticed in the adsorption experiments. Beside that the rate constant K_a in the case of Montmorillonite is lower than in the case of Kaolinite which means that the HP-IX molecule is easily adsorbed on Kaolinite rather than on Montmorillonite. This is due to that Kolinite is 1:1 clay mineral type, therefore its available exposed surfaces for adsorption is much more accessible than Montmorillonite^[18]. These observations are further supported by the magnitude of the activation energy E_a values. Hence at adsorption process on the Kaolinite clay the E_a was lower than in

the case of Montmorillonite clay means that the rate of adsorption in the first case should be larger than the second one. The low values of the activation energy under different conditions indicated that the type of HP-IX adsorption is physical in nature on these two clays.

TABLE 3 : Kinetic and thermodynamic parameters of Hematoporphyrin adsorption on Kaolinite and Montmorillonite

Type of Clay	Na-Kaolinite		Na-Montmorillonite		
Type of Solvent	Methanol	Water	Methanol	Water	
n_a	Temperature 5 °C	2.12	1.88	12.04	8.898
	Temperature 25 °C	1.94	1.77	10.18	6.51
K_a	Temperature 5 °C	2.13×10^{-3}	6.7×10^{-3}	7.3×10^{-21}	1.4×10^{-15}
	Temperature 25 °C	4.89×10^{-3}	11.7×10^{-3}	9.14×10^{-18}	1.48×10^{-11}
E_a (Kcal/ μ mole)	2.88×10^4	1.93×10^4	24.6×10^4	32.1×10^4	
ΔH_a (Kcal/ μ mole)	2.6×10^4	1.68×10^4	24.43×10^3	31.8×10^3	
ΔS_a (esu)	-133.64	-157.4	-317.06	-683.2	
ΔG_a (Kcal/ μ mole)	6.18×10^4	6.371×10^4	14.98×10^3	11.45×10^3	

n_a is the order of reaction and K_a is the rate of Hematoporphrin adsorption

The positive values of ΔH_a as expected; proved again that the reaction is endothermic and agreed with the adsorption isotherms experiments. Also it is in agreement with the Hemoglobin adsorption on the clay minerals^[19].

The negative ΔS values indicated that the HP-IX molecules become more ordered after their adsorption on the clay surfaces. The values of ΔS were more negative in the case of Montmorillonite than Kaolinite means that the arrangement of the HP-IX molecule on the Montmorillonite surface is more ordered as it has more surfaces to accommodate HP-IX molecules.

The free energy of adsorption ΔG had lower positive values for Montmorillonite than for Kaolinite. The low positive values of ΔG means that HP-IX molecules can approach the surface more closely, resulting in stronger adsorptive forces with more ordering. As the value of ΔG becomes low the adsorption increases, this explains the reason for more adsorbed HP-IX on Montmorillonite than Kaolinite. This is agreed with all the previous kinetic parameters and the reasons that have been mentioned earlier^[20].

CONCLUSION

Adsorption and kinetics of Hematoporphrin were

significantly depending on the status of surface sites available on the clay minerals, dielectric constant of the solvent, pH and temperature of the media. For thermodynamic parameters especially ΔS ; it can be concluded that the type of the clay surface and its ordering oriented ΔS values toward more negativity. These parameters should be considered during the application of Hematoporphrin in fields such as nanostructure, search of petroleum and diagnosis of animals and plants biochemical properties.

REFERENCES

- [1] E.Tannenbaum, B.J.Huizinga, H.Perzerate; The American Association of Petroleum Geologists Bulletin, **70**, 1156 (1986).
- [2] W.J.Bowden, A.D.M.Bolland, M.A.Posner, P.J.Quirk; Natural of Physics Sci., **81**, 245 (1973).
- [3] R.D.Kosiur; Clay and Clay Minerals, **53**, 65 (1997).
- [4] F.F.Assaad, W.K.Mekhamer; Applied Polymer Sci., **73**, 659 (1999).
- [5] C.A.Black; Methods of Soil Analysis, Part 1, Chap., **57**, 891 (1965).
- [6] K.Ma, A.C.Pierre; Clay and Clay Minerals, **40**, 586 (1992).
- [7] K.A.Bajpai, R.Sachdeva; Applied Polymer Science, **85**, 1607 (2002).
- [8] S.Takagi, D.A.Tyrke, H.Inoue; Journal of Phys.Chem., **106**, 5455 (2002).
- [9] Z.Bouberka, S.Kacha, M.Kameche, S.Elmaleh, Z.Derrich; Journal of Hazardous Materials, **119**, 117 (2005).
- [10] T.Shichi, S.Takagi; Photochemistry and photobiology C: Photochemistry Reviews, **1**, 113 (2000).
- [11] M.F.Brigatti, S.Colona, D.Malferrari, L.Medici, L.Poppi; Journal of Applied Clay Sci., **28**, 1 (2005).
- [12] A.M.Machado, D.F.Wypych, S.M.Nakagaki; Colloid and Interface Sci., **254**, 158 (2002).
- [13] S.Takagi, T.Shimada, M.Eguchi, T.Yui; Langmuir, **18**, 2265, (2002).
- [14] K.Takagi, T.Shichi; Solid State and Surface Photochemistry, **5**, 31 (2000).
- [15] J.L.Keith; Kinetic Chemistry, University of Ottawa, Ontario, Canada, (2001).
- [16] T.Saito, K.Fukui, J.Kodra; J.Dyes and Pigment, **65**, 21 (2005).
- [17] W.Tasai, M.Change, W.Lai; J.App.Clay Sci., **29**, 149 (2005).
- [18] J.Barthel, R.Neueder; Chemical Thermodynamics, University of Regensburg, Germany, (2001).
- [19] S.Glastone; Text of physical chemistry, Macmillan India press, Madras, 2nd Edition, (1976).
- [20] R.M.Douglas; Engineering Chemistry, University of Maine, Maine, USA, (2001).