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Swelling properties of hydrogel networks of poly (methacrylic acid-cross-N-acrylate- N,N-dimethyl-N-dodecyl ammonium bromide). Application in the sorption of an industrial dye

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ABSTRACT

This paper deals with the study of the swelling and the sorption properties of new hydrogel networks of poly (methacrylic acid (MAA)-cross-dodécyle acrylate ammonium bromide (ADAB). The swelling properties of these hydrogels were achieved in distilled water at 25°C and expressed by the swelling ratios by weight, in order to evaluate their potential applications, particularly in the field of environment. Thus we have tried to take of these swelling properties by studying the sorption of an industrial dye, in this case, the red dye of bemacide. Prior to the study of the sorption, study of the swelling properties has shown a dependence of the swelling rate on the proportion of ADAB included in the hydrogel. The determination of the values of the capacities of sorption to the equilibrium of hydrogels enable us to trace the Freundlich and Langmuir isotherm and to show that these values are in a good correlation with the Lagmuir isotherm sorption

Keywords: Cationic dye, Hydrogel network, Red dye bemacide, Swelling properties, sorption.

INTRODUCTION

Technical Processing of wastewater by dyes by many adsorbents has been studied, including activated carbon, thus, activated carbon in granular or powder form was characterized and used as adsorbent for the effluent treatment. Composed of carbon atoms arranged in graphite [1] structure, the activated carbon is characterized by a high porosity which enables it to develop a large area of contact with the external environment. It was shown that the adsorption of organic molecules by activated carbon is governed by weak Van der Waals interactions between π electrons of grapheme structure of the carbon surface and electron clouds of solutes [2]. Among the polymeric materials, [3] hydrogels were investigated by environmental scientists, because of their characteristic properties, such as adsorption-regeneration, economic and environmental feasibility. These hydrogels are often porous structures and networks and allow the diffusion of solutes through these pores. In addition, some hydrogels have ionic functional groups which enable them to absorb the dye ion trap as in the case of methylene blue (MB). [4] has developed hydrogel of semi-interpenetrating polymer chains consisting of poly (acrylic acid-acrylamide-methacrylate) and amylose which has proven to be an effective adsorbent for dyes such as Crystal Violet (CV). The adsorption capacity of the hydrogel has been found to be very dependent on the length of the side of acrylic acid n-alkyl chains (AA) of the amylose content and pH of the solution. In this case, it was shown that the swelling, electrostatic interactions and hydrophobic interactions contribute to the sorption process.

MATERIALS AND METHODS

2.1 morphology of hydrogels

The detection of the morphology of these hydrogels was performed using the environmental scanning microscopy method.

2.2 Swelling properties

The swelling ratios by weight of hydrogels[5-6] in distilled water was determined according to equation (1)

$$SR = \frac{W_{hs}}{W_{hd}} \quad (1)$$

W_{hs} : Weight of the hydrogel in the swollen state in distilled water,

W_{hd} : Weight of the hydrogel in the dry state

2.3 Study of sorption

Swelling properties of these hydrogels were exploited to study the sorption of an industrial dye, namely, the red dye of bemacide.

For the sorption study, poly (methacrylic acid-cross- N-dimethyl dodecyl acrylate ammonium bromide or ADAB) hydrogel was immersed in 10 mL of 16–60 mg/L solution of red dye of bemacide. The test temperature was 25°C. During the sorption process, the samples were taken, over time, from the solution of red dye of bemacide in order to follow the change in its concentration until it reaches its equilibrium value by using a UV-visible spectrophotometer (λ_{max} 495 nm).

The amount of the red dye of bemacide absorbed by the hydrogel, at time t, which is corresponding to the sorption capacity q_t (mg/g dried hydrogel) was determined according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

Where, V is the solution volume (mL), m is the weight of dried hydrogel (g), C_0 and C_t is the dye concentration at the initial and indicated time (mg/mL), respectively.

RESULTS AND DISCUSSION

3.1- Swelling properties

we studied the variation of the swelling ratios by weight of hydrogels of poly (MAA-cross-ADAB) according time in distilled water at 25°C. The results are illustrated in Fig.1

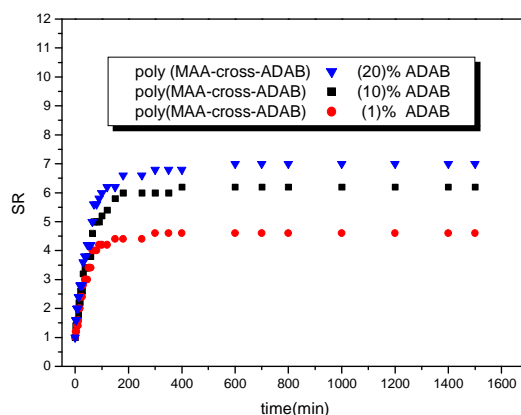


Fig.1: Variation of the swelling ratios by weight according time of hydrogels of poly (MAA-cross-ADAB) in distilled water at 25°C

We thus observe that the values of swelling ratios by weight in the equilibrium of hydrogels of poly (MAA-cross-ADAB) in distilled water at 25°C are proportional to the rate of ADAB incorporated in each hydrogel. This result

could be explained by the incorporation of more and more of the ADAB which, in this case, probably contributes to the increase of the swelling through electrostatic and hydrophobic interactions.

3.2- Morphology of the hydrogels

Photos provided by scanning electron microscopy allowed us to observe the morphology of the hydrogels we have prepared. This microscopy analysis aims to highlight the link between the morphology of these hydrogels and their swelling properties.

Photos provided by scanning electron microscopy are shown in Fig.2

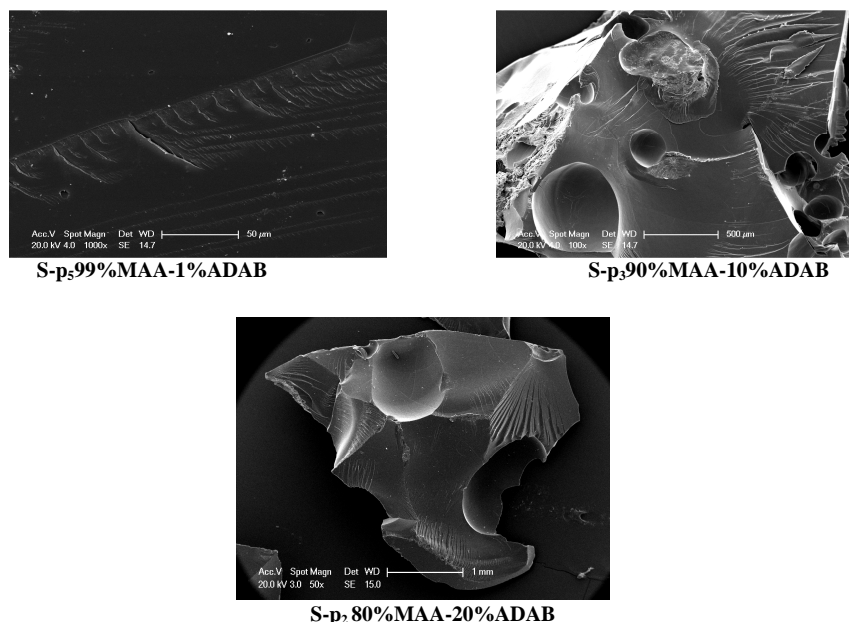


Fig.2: Photos supplied by the scanning electronic microscopy of hydrogels of poly (MAA-cross-ADAB)

According to the analysis by the scanning electron microscopy (SEM) we can see that the surface becomes more porous and filamentous gradually as the rate of ADAB incorporated into the network increases. These results are in agreement with those achieved by the swelling properties study.

3.3-Study of sorption

Sorption of the red dye of bemacide by hydrogel of poly (MAA-cross-ADAB) to 20% of ADAB is illustrated in the fig.3.

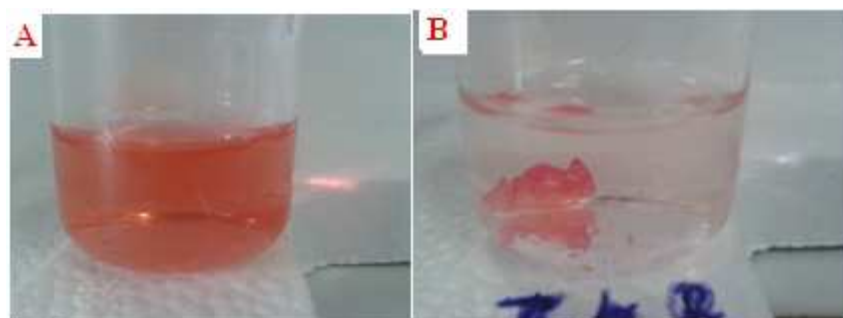


Figure3: Pictures of the solution of the red dye of bemacide and its sorption by the hydrogels: (A): poly (MAA-cross-ADAB) hydrogel before sorption; (B): before sorption; (T = 25 ° C, pH = 6.8, [ADAB] = 20 mol% and C₀ = 26 mg / L)

3.3.1- Sorption capacities of the red dye of bemacide of hydrogels of poly (MAA-cross-ADAB)

Values of the sorption capacity of the red dye of bemacide of hydrogels of poly (MAA-cross-ADAB) were calculated for different concentrations of the dye according to equation (2).

The figure 4 shows the variations of the sorption capacities of the red dye of bemacide of hydrogels of poly (MAA-cross-ADAB) according to time, at different molar rates of ADAB (1, 10 and 20%), from an initial concentration of 26 mg / L of ADAB.

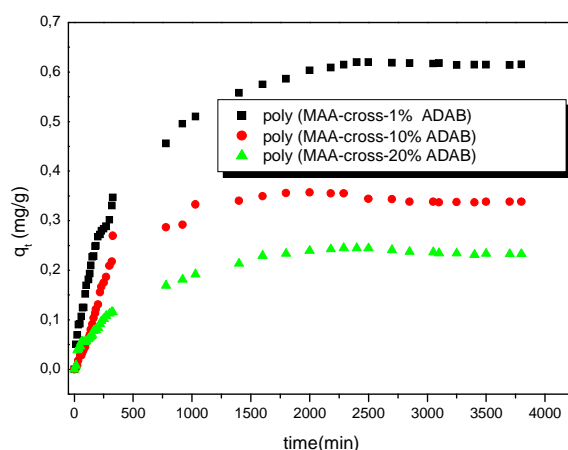
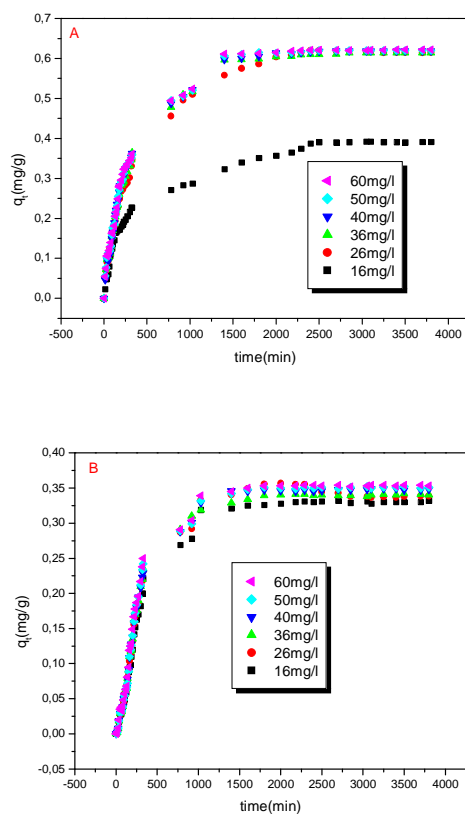


Fig.4: Variations of the sorption Capacity of the red dye of bemacide of hydrogels of poly (MAA-cross-ADAB) according to time at different rates of ADAB

From examination of the curves we can make the following observations:

-the time of arrival to the equilibrium of sorption of the red dye of bemacide by hydrogels of poly (MAA-cross-ADAB) is practically the same one. the sorption capacity of the red dye of bemacide is inversely proportional to the rate of ADAB incorporated into hydrogels of poly (MAA-cross-ADAB).

-introduction of more and more of amounts of ADAB in the hydrogels of poly(MAA-cross-ADAB) creates probably electrostatic interactions due to quaternary ammonium sites which prevent the sorption of the cationic dye.



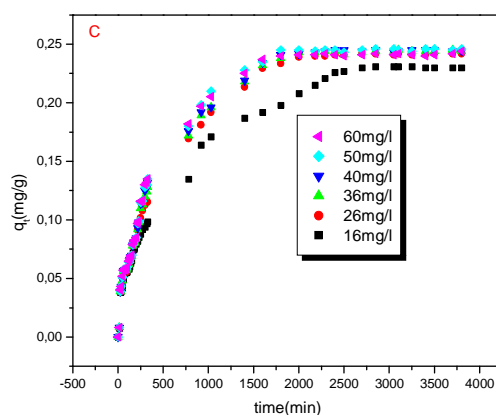


Fig.5: Variations of the sorption capacity of the dye, according to time, of hydrogels for solutions containing the dye at different initial concentrations:

($m_{\text{hydrogel}} = 80 \text{ mg}$, $T = 25^\circ \text{C}$, $\text{pH} = 6.8$)

- (A) poly (MAA-1% cross-ADAB)
- (B) poly (MAA-cross -10% ADAB)
- (C) poly (MAA-cross -20% ADAB)

We observe that the sorption capacity values of all the hydrogels increases with the initial concentrations of the dye until equilibrium of saturation

Time arrival of the equilibrium of saturation is not dependant on the initial concentration of the dye.

Starting from the concentration of 26mg/ L of the dye, the sorption capacity increases and reaches a maximum value that remains substantially constant regardless of the initial concentration of the dye. These results mean that there is probably a concentration the shold value of the dye for which the sorption capacity is maximal.

4.1.2 Study of sorption isotherm models

With the aim of knowing in which model of sorption isotherm obeys the sorption of the dye, we were interested in the study of two models of sorption isotherm: Langmuir model [7-8] and Freundlich model [9-10].

In addition, there are other complex isotherm models that take into account specific conditions such as changes in ionic strength, electrostatic forces[11] or interactions between functional groups of adsorbat.

The values of the sorption capacities of the red dye of bemacide of the hydrogels at equilibrium time allowed us to plot the curves related to the sorption isotherms.

4.1.2.1 Model Langmuir

Langmuir model is given by the following equations:

$$q_e = \frac{q_0 \times k_L \times c_e}{1 + k_L \times c_e} \quad (3) \Rightarrow \frac{c_e}{q_e} = \frac{1}{k_L \times q_0} + \frac{c_e}{q_0} \quad (4)$$

q_e is the sorption capacity at the equilibrium, c_e is the concentration at the equilibrium, q_0 : maximum sorption capacity (mg / g), k_L : Langmuir adsorption isotherm ($\text{L} \cdot \text{mg}^{-1}$).

The results are illustrated by **Fig.6**

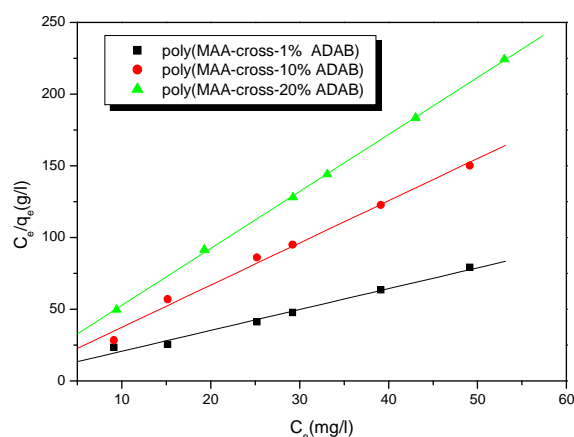


Fig.6: Langmuir sorption isotherms of the dye by the hydrogels of poly (MAA-cross-ADAB) at 25°C

According to the Langmuir model we observe that the plotted curves are linear. Using extrapolation and the slopes of the curves, we determined the parameter values of this model which are mentioned in table 1

Table1: Parameter values of Langmuir sorption isotherms of the red dye of bemacide by the hydrogels of poly (MAA-cross-ADAB)

Hydrogels	ADAB (% mol)	k_L (L.mg ⁻¹)	q_0 (mg/g)	R^2
Poly (MAA-cross-ADAB)	1	1.44	0.7	0.987
	10	1.08	0.36	0.999
	20	0.55	0.25	0.999

We observe that the capacity and the constant of isothermal sorption and desorption are inversely proportional to the rate of ADAB.

The essential characteristic of the Langmuir isotherm is the separation factor [12] R_L given by equation (5).

$$R_L = \frac{1}{1 + k_L \times C_0} \quad (5)$$

k_L is Langmuir adsorption isotherm (L.mg⁻¹) and C_0 is the initial concentration of the dye (mg / L).

The sorption process of the Langmuir isotherm can be interpreted with reference to the values of R_L reported in Table2.

Table2: Values of separation factor [13] in the Langmuir isotherm

hydrogels	ADAB (% mol)	k_L (L.mg ⁻¹)	c_0 (mg/L)	R_L
Poly (MAA-cross-ADAB)	1	1.24	16	0.05
			26	0.03
			36	0.02
			40	0.02
			50	0.02
			60	0.02
			60	0.02
Poly (MAA-cross-ADAB)	10	1.08	16	0.05
			26	0.03
			36	0.03
			40	0.02
			50	0.02
			60	0.02
			60	0.02
Poly (MAA-cross-ADAB)	20	0.55	16	0.10
			26	0.07
			36	0.05
			40	0.04
			50	0.04
			60	0.04
			60	0.03

Thus we have calculated the separation factor values which are reported in table3.

Table3: Values of the separation factor relating to the dye sorption by the hydrogels of poly(MAA-cross-ADAB)

RL value	type isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

We observe that the separation factor values are inversely proportional to the initial concentrations of the dye and proportional to the rate of ADAB included in the hydrogel network.

We note that the sorption of the dye obeys the isotherm of Langmuir since the separation factor values are between 0 and 1.

To verify the spontaneity of sorption process, we determined the values of the changes in free energy ΔG sorption hydrogels of poly (MAA-cross-ADAB).

Thus the variation of the free enthalpy (ΔG) of sorption [14] at 25°C was calculated starting from the equation 6.

$$\Delta G = -RT \ln K_L \quad (6)$$

Where T is the Kelvin temperature, R is the gas constant

The calculated values of (ΔG) are reported in table4.

Table4: values of free enthalpy ΔG of sorption of the dye by hydrogels of poly (MAA-cross-ADAB)

Hydrogels	ADAB (%mol)	ΔG (KJ.mol ⁻¹)
Poly (MAA-cross-ADAB)	1	-05.25
	10	-01.88
	20	14.60

Negative values of changes in the free energy of sorption of the dye by hydrogels poly (MAA-cross-ADAB) indicating the nature of spontaneous sorption which confirms the affinity of the sorbent for the dye. We note that ΔG has a negative value only in the case of hydrogel containing 1% and 10% of ADAB and this one increases with the rate of ADAB. Positive ΔG values observed in the case of poly (MAA-cross-ADAB) (20% in ADAB) show probably that the desorption process seems to be more important than that of the sorption with the increase of the ADAB rate. These results are in good agreement with those obtained in the determination of the sorption capacity values.

4.1.2.2 Freundlich model

The sorption isotherm of Freundlich, is given by the following equations:

$$\ln q_e = \frac{1}{n_F} \times \ln C_e + \ln k_F \quad (7)$$

$$\ln q_e = n \times \ln C_e + \ln k_F \quad (8)$$

Where n or $1/n_F$ and k_F (L / g) respectively represent the type of interaction or factor of heterogeneity and Freundlich constant.

This model does not take into account the sites number of sorption at the equilibrium in the solid, but it admits that the sorption may proceed through the formation of multiple layers.

Tracing of the sorption isotherms curves of the dye by the hydrogels of poly(MAA-cross-ADAB), according to the Freundlich model after linearization of the latter, gives the results reported in figure 7.

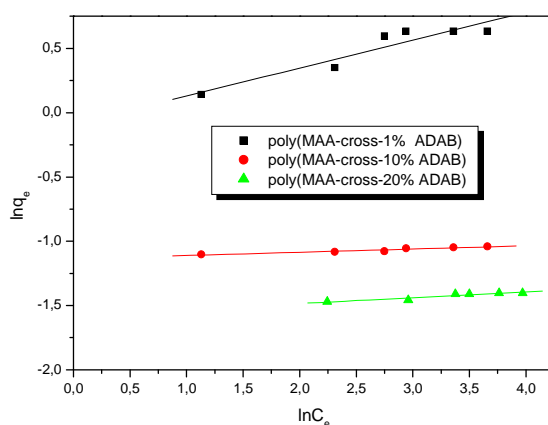


Fig.7: Sorption isotherms of the dye by hydrogels of poly (MAA-cross-ADAB) according to the Freundlich model at T = 25°C

Starting from the isotherm curves, we determined the values of the Freundlich isotherm parameters which are given in table 5.

Table 5: sorption parameter values of the dye by the hydrogels poly(MAA-cross-ADAB) in the Freundlich model

Hydrogels	ADAB (mole%)	k_F ($L \cdot g^{-1}$)	n	n_F	R^2
poly (MAA-cross-ADAB)	1	0.27	0.230	4.34	0.89
	10	0.20	0.045	22.22	0.88
	20	0.30	0.040	25.00	0.90

The values of the interaction parameters of Freundlich n are inversely proportional to the ADAB rates. The low values of n observed in the case of the hydrogels of poly (MAA-cross-ADAB) with 10% and 20% of ADAB probably state that the process of sorption is controlled by [15] van der Waals interactions and / or hydrophobic interaction.

Values of the correlation factor R are lower than those which were calculated for the isotherm of Langmuir, which shows that sorption does not obey the isotherm of Freundlich.

CONCLUSION

The swelling ratios by weight, at equilibrium, of hydrogels are proportional to the rate of ADAB. This result can be probably explained by contribution of electrostatic and hydrophobic interactions of the ADAB.

The sorption capacity values of red dye of bemacide by hydrogels of poly (MAA-cross-ADAB) are inversely proportional to the rate of ADAB. The presence of ADAB in the hydrogels of poly (MAA-cross-ADAB) creates probably electrostatic interactions due to quaternary ammonium sites which prevent the sorption of the cationic dye. We observe that the sorption capacity values of all the hydrogels increase with the initial concentrations of the dye until equilibrium of saturation. Time of arrival to the equilibrium of saturation is not dependant on the initial concentration of the dye. Starting from the concentration of 26 mg/L of the dye, the sorption capacity increases and reaches a maximum value that remains substantially constant regardless of the initial concentration of the dye.

These results mean that there is probably a threshold value of the dye initial concentration for which the sorption capacity is maximal.

The analysis of equilibrium using the Langmuir and Freundlich isotherms shows that they are in a good correlation with the Langmuir sorption isotherm.

To highlight the spontaneous nature of the dye sorption, we proceeded to determine variations in the free energy of sorption. Free energy negative value calculated for the hydrogel of poly(MAA-cross-ADAB) with 1% of ADAB indicates spontaneous sorption of the dye. The positive values of ΔG observed in the case of hydrogel (with 10% and 20% of ADAB) probably mean that the process of desorption is more important than that of sorption with the increase of the ADAB rate.

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REFERENCES

- [1] F.Villacañas, M.Pereira, R. Fernando R, Órfão. José, J. M.José, L.Figueiredo, *Journal of Colloid and Interface Science.*, **2006**, 293, 128-136
- [2] N.Ahmed Shmroukh, H.Ahmed, , H. Ali, K.Ali *International. Journal of Chemical, Nuclear, Materials and Metallurgical Engineerin.*, **2013**, 7, 461-467
- [3] Li.Shengfang, Xianli. Liu, *Polymer for Adversed Technologies*, **2008**, 19, 371-376
- [4] Li.Shengfang *Bioresource Technology*, **2010**, 101, 2197–2202
- [5] Zhang. Xian-Zheng, Zhang.Jian-Tao, Zhuo.Ren-Xi, Chu. Chih-Chang *Polymer*, **2002**, 43, 4823-4827
- [6] T.Inoue, Guohua.Chen, Katsuhiko.Nakamae, Allan S. Hoffman *Journal of Controlled Release*, **1997**, 49, 167–176
- [7] I.Langmuir *Journal of American Chemical Society*, **1916**, 38, 2221-2295
- [8] I.Langmuir *Journal of American Chemical Society*, **1918**, 40, 1361-1403
- [9] U.Freundlich *Zeitschrift fur Physikalische Chemie*, **1906**, 57, 385-470
- [10] Wang.Jianquan, Wu.Wenhui, Lin.Zhihui *Journal of Applied Polymer Science*, **2008**, 109, 3018–3023
- [11] S.Schiewer, B. Volesky *Environmental Science & Technology*, **1997**, 31, 2478–2485
- [12] K R.Hall, L C. Eagleton, Acrivos. *Andreas Industrial and Engineering Chemistry Fundamentals*, **1966**, 5, 212-223
- [13] W.Weber, W.J.Morris *Journal of Sanitary Engineering Division–ASCE*, **1963**, 89, 31-60
- [14] Y.Liu, C.Ying i, Y.Guoqiang, M.Hanchong *Iranian Polymer Journal*, **2009**, 18, 339-348
- [15] F.Lulu, Ying. Zhang, Chuannan. Luo, Fuguang. Lua, Huamin. Qiu, Min. *Suna International Journal of Biological Macromolecules*, **2012**, 50, 444– 450