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Investigation of the Surface Adsorption of Cd^{2+} Ions on Modified Poly (Ethylene Terephthalate) by the Mixture of Methyl Methacrylate - Acrylic Acid Monomers

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ABSTRACT

In this study, graft copolymerization of methyl methacrylate (MMA), acrylic acid (AA) onto poly (ethylene terephthalate) (PET) fibers has been carried out in the presence of benzoyl peroxide (Bz_2O_2) as initiator. Reactive fibers have been used as a new adsorbent for removal of Cd^{2+} ions from aqueous solutions via adsorption. The effect of pH, adsorbate concentration, adsorbent dose, temperature and contact time were studied. The best conditions for removal of Cd^{2+} recorded (pH = 6.5, t=20 min, maximum adsorption capacity = 17.07 mg / g). The adsorption data's were fitted by Freundlich isotherm and Pseudo – second order kinetic model, as well. Thermodynamic parameters such as enthalpy (ΔH°), entropy (ΔS°) and gibbs free energy (ΔG°) have been determined, (0.0058 kJ/mol), (0.010 kJ/mol K) and (- 2.999 _ -3.301 kJ/mol), respectively. On the other hand, activation energy (E_a) has been recorded 1.90 kJ/ mol. These results emphasized that, the adsorption process was physisorption.

Keywords: Adsorption, Graft copolymerization, Isotherm models, Equilibrium and kinetics.

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INTRODUCTION

Water is one of the fundamental items needed for living beings for the perpetuity and growth. It also maintains ecological balance between different groups of organisms and their environment [1]. Heavy metals are very toxic and baneful and use in different industries [2-4]. Customary techniques for removal of heavy metals from wastewaters contain precipitation, adsorption, reverse osmosis, ion exchange, membrane separation, flocculation coagulation, ozonation, oxidation, evaporation and electrolysis [5-7].

Between the available physico-chemical treatment, adsorption has been found to be a sensational and economical method with high efficiency for the removal, recovery and recycling of heavy metals from wastewater. [8,9] Various sorbents such as fly ash, coconut shell, zeolite, perlite, manganese oxides, crab shell, activated carbon, bentonite, montmorillonite, chitosan, peanut shell have been studied for adsorption of metal ions. Reports show that, these adsorbents have inferior removal efficiencies for metal ions at low concentrations [10 – 15]. Recently polymer fibers have been used for removal of heavy metals and dyes from wastewater [16 – 19]. This is imputed to the relatively large specific area, fast kinetic adsorption, low activation energy and regenerable very easily. In this study, according to our previous works, grafted PET fibers with MMA – AA mixtures by the help of Bz_2O_2 for the removal of Cd^{2+} from aqueous solutions via batch adsorption method has been reported [20 , 21] .

MATERIALS AND METHODS

Experimental

In this study, MMA and AA as monomers were supplied by BDH Co of England. PET fibers (stretch ratio 2 , 30 filaments , 110 dTex) were provided from Amir Kabir University and Technology (Tehran) They were prepared as small hank (0.10 ± 0.01 g) soxhlet extracted for 6 hour with acetone and dried at ambient temperature . Bz_2O_2 (Aldrich) was recrystallized twice from the ethanol – chloroform (65% vol. ethanol) mixture and dried in vacuum desiccator. All of reagents such as HCL, NaOH, $CdCl_2$, acetone, and toluene were analytical grade, high purity and supplied by Merck Chemical Co.

Grafting procedure

The fiber specimen (0.10 ± 0.01) was placed in a 100 mL polymerization tube in 45 mL doubly distilled water. Then monomers (AA 30% + MMA 70 %) = 0.1 mol/ L) were added to the tube and containing took place in water bath (Lauda D 40 S, Germany) at desirable temperature (363 K). In order to providing different graft yields, procedure have been accomplished at 5 _ 60 min. After desirable time, removal of undesirable homopolymer is performed by doubly distilled water and soxhlet extracted with toluene for 8 h. Then, the samples were dried in vacuum at 323 K for 48 h and weighed .The percent increase in fibers determined by gravimetrically:

$$\text{Graft yield (\%)} = (W_2 - W_1 / W_1) \times 100$$

Where W_1 , W_2 were the weight of the ungrafted and grafted fibers, respectively.

Adsorption studies

Adsorption experiments were achieved using 0.1 g of the reactive fibers with 20 mL solution of Cd^{2+} (100 g/mL) in 250 mL Erlenmeyer flasks as functions of pH, concentration and temperature. In all experiments agitation speed was 150 rpm. The concentration of unadsorbed Cd^{2+} in the solution after filtration by filter paper (Whatman No. 40) was calculated by using an AAS with an air acetylene flame with hollow cathode lamp according to this equation:

$$q = (C^0 - C) \times V / m$$

Here, C^0 and C being the initial Cd^{2+} concentration and equilibrium concentration (mg / L), respectively V is the total volume of the solution (L), m is the adsorbent amount (g) and q is the amount of the adsorbed Cd^{2+} at the definite time (mg / g).

RESULTS AND DISCUSSION

Effect of pH

The best pH was determined 6.50 for adsorbent. At pH 1.50, the adsorption observed 5.4 mg / g and at pH 9.0 it was 8.5 mg / g. While at pH 6.50, maximum removal has been observed. It was 12.88 mg / g. These results showed that at acidic environment, the hydrogen and cadmium ions on the sorption sites have been competed to each other. At alkaline pH, insoluble cadmium hydroxide has been caused decreasing in adsorption. This is attributed to precipitation of hydroxyl complexes. Fig .1 [22, 23]

Effect of adsorbent

By increasing of the reactive fibers ($G \% = 75 \%$) from 0.05 g to 0.20 g , the adsorption amount increased from 10.6 mg / g to 13.85 mg / g , respectively . This is related to increasing in adsorbent surface area and more available adsorption sites . Results have been shown in Fig. 2

Effect of contact time

The effect of contact time on adsorption was investigated from 5 to 75 min at the fixation condition of other variables (pH = 6.50, $T = 298 \text{ K}$, solution volume = 20 mL, adsorbent = 0.10 g, adsorbate = 100 mg / L, graft yield = 75 % and shaking rate = 150 rpm). As shown in Fig .3, a rapid adsorption occurred in 5 min and completed for 20 min. By increasing in the time, the amount of Cd^{2+} adsorbed did not change. Therefore, the best time for removal of Cd^{2+} ascertained 20 min for all experiments. [23, 24]

Effect of adsorbate concentration

Effect of Cd²⁺ ions on adsorption has been investigated at different concentrations of 50, 75, 100, 120, 140, 150 mg / L at 298 K and pH 6.50. Maximum removal has been attained 17.07 mg / g for 140 mg / L and 16.95 mg / g for 150 mg / L, respectively. Therefore, the CEC (cation exchange capacity) recorded 17.07 mg / g. Fig. 4

Effect of grafting yield

By increasing of the grafting yield 17% , 60 % and 75 % , the amount of 100 mg / L Cd²⁺ ions adsorbed per unit of fibers recorded 10.6 , 12.88 and 14.22 mg / g , respectively . This is ascribed to a higher surface area and more active sites. [16, 17]

Adsorption isotherm

According to three isotherm, Langmuir, Freundlich and Temkin - Pyozhev, the adsorption equilibrium data have been studied. These equations are given as follows:

$$\text{Langmuir equation: } C_e / q_e = 1 / q_m \cdot b + C_e / q_m$$

$$\text{Freunlich equation: } \ln q_e = \ln K_F + 1 / n \ln C_e$$

$$\text{Temkin-Pyozhev equation: } q_e = B \ln A + B \ln C_e$$

As shown in Fig 5-13 experiments have been accomplished at different temperatures (298, 313 and 328 K). The R² values show that Freundlich model fits well with experimental data in all temperatures. These results identify that the surfaces of reactive fibers are rough and heterogeneous and can be efficient on multilayer adsorption. [26]

Adsorption kinetics

Three models have been investigated to elucidate the adsorption mechanism of Cd²⁺ onto adsorbent [27 – 29].

$$\text{Lagergren's pseudo-first order: } \ln (q_e - q_t) = \ln q_e - K_a t$$

$$\text{Ho's pseudo-second order: } t / q_t = 1 / K_2 q_e^2 + t / q_e$$

$$\text{Intra-particle diffusion: } q = K_{id} \cdot t^{1/2} + I$$

Results have been shown in Fig 14 – 16. The best compatibility observed by pseudo-second order equation. According to this model the correlation coefficient was found very high (R² = 0.994), and can be practiced for the adsorption process. [30]

Thermodynamic studies

The thermodynamic parameters of the adsorption process have been calculated from the experimental data by the use of the following equation:

$$\Delta G^\circ = -RT \ln K_d, \ln K_d = \Delta S^\circ / R - \Delta H^\circ / RT, K_d = q_e / C_e$$

Where, K_d is the distribution coefficient, ΔS° , ΔH° and ΔG° are the changes of entropy, enthalpy and Gibbs free energy, respectively. R is the ideal gas constant (8.314 J / mol. K) and T is the absolute temperature (K). By the use of the plot of K_d versus $1 / T$ the values of ΔH and ΔS have been determined. Results tabulated in Table 1. and Fig .17

Table 1. Thermodynamic Parameters at Different Temperatures

T (K)	ΔH° (kJ / mol)	ΔS° (kJ/mol .K)	ΔG° (kJ/mol)
298	0.0058	0.010	-2.999
313			-3.150
328			-3.301

The positive value of ΔH° proposes endothermic reaction and also emphasizes the possibility of physical adsorption. The positive value of ΔS° , identify increased disorder at the adsorbent – solution interface during the adsorption of Cd^{2+} . On the other hand, the freedom degrees increased at the adsorbent – liquid interface during the adsorption process. [31, 32] The ΔG° values are negative at all of experiments. These results identify the adsorption of Cd^{2+} ions onto fibers are thermodynamically favorable and spontaneous. By increasing of temperature from 298 to 328 K, the values of ΔG become high negative. This fact shows that adsorption is more spontaneous at high temperature. Usually, ΔG° for physisorption is between -20.0 to 0.0 kJ / mol. Thus, the results of ΔG° mention that physisorption might dominate the adsorption process. [33]

Effect of temperature on adsorption

According to Arrhenius plot of $\ln q$ versus $1 / T$ the activation energy for adsorption was computed (1.90 kJ/mol). Fig 18. E_a 's quantity is very low and suggests the adsorption of Cd^{2+} ions onto reactive fibers are so easy. [34] The desorption activation energy can be determined using this equation:

$$E_d = \Delta H + E_a$$

The calculated value (1.906 kJ / mol) is approximately equal to E_a . Therefore, desorption can be occurred easily.

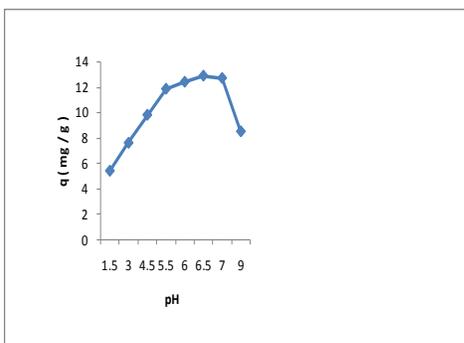


Fig 1. Effect of pH on the adsorption

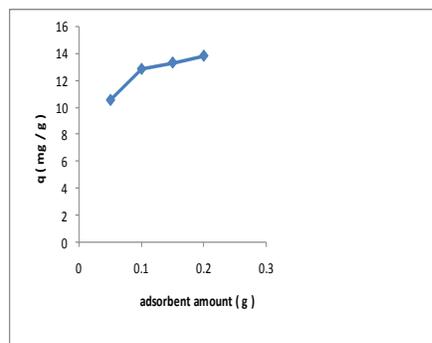


Fig 2. Effect of adsorbent amount on the adsorption

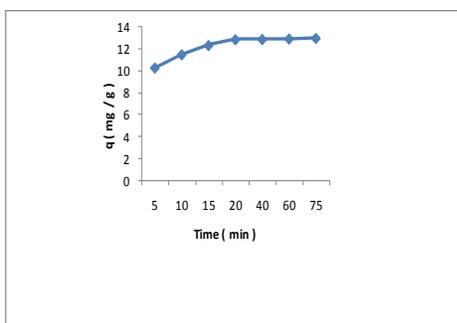


Fig 3. Effect of time on the adsorption

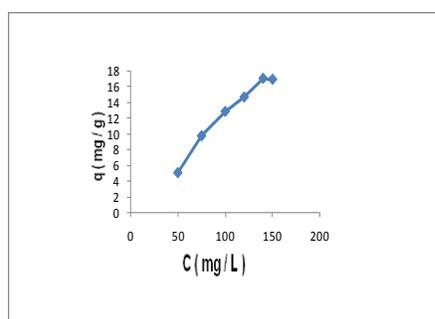


Fig 4. Effect of adsorbate on the adsorption

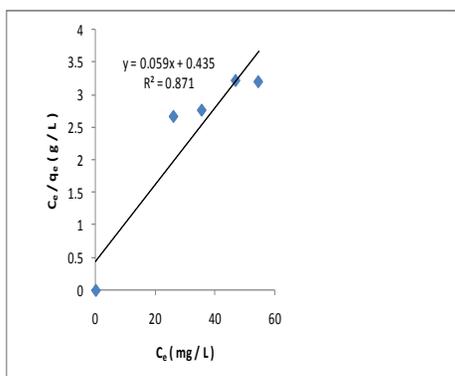


Fig 5. Langmuir isotherm (T= 298 K)

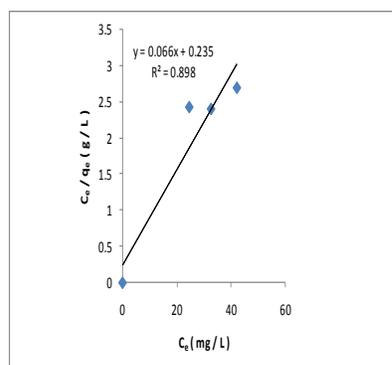


Fig 6. Langmuir isotherm (T= 313 K)

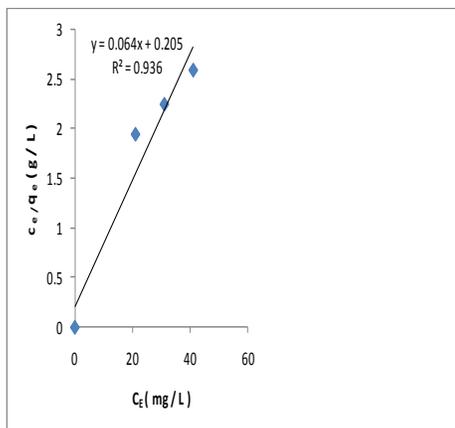


Fig 7. Langmuir isotherm (T = 328 K)

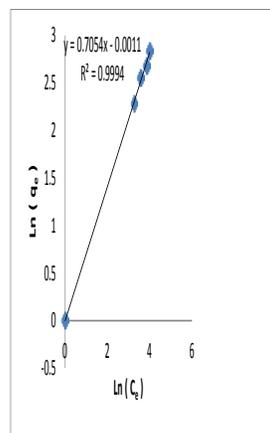


Fig 8. Freundlich isotherm (T = 298 K)

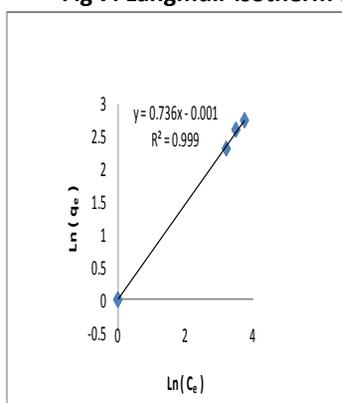


Fig 9. Freundlich isotherm (T = 313 K)

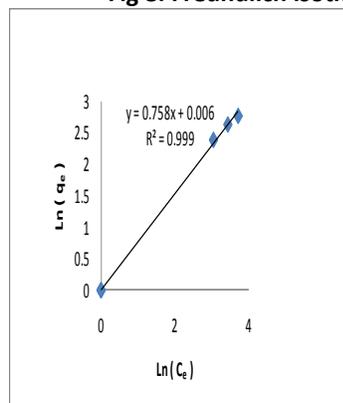


Fig 10. Freundlich isotherm (T = 328 K)

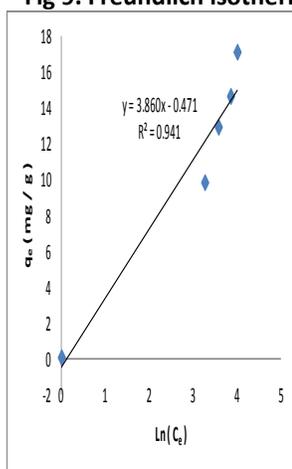


Fig 11. Temkin – Pyozhev isotherm (T = 298 K)

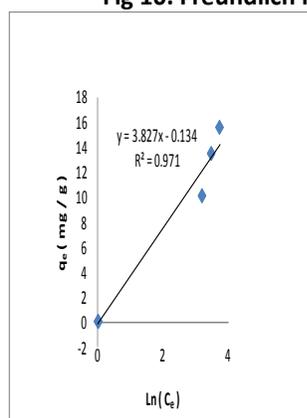


Fig 12. Temkin – Pyozhev isotherm (T = 313 K)

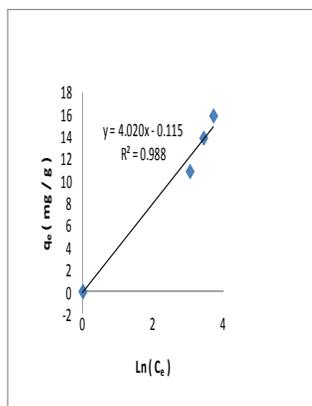


Fig 13. Temkin – Pyozhev isotherm (T = 328 K)

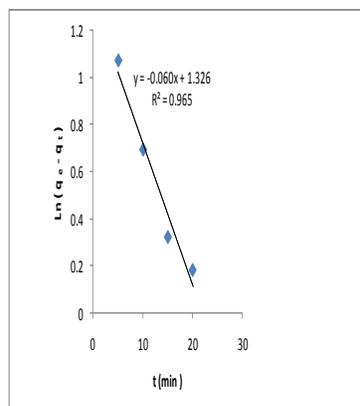


Fig 14. Pseudo - first order kinetics

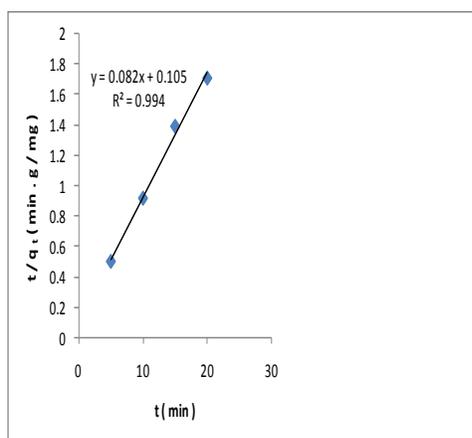


Fig 15. Pseudo - second order kinetics

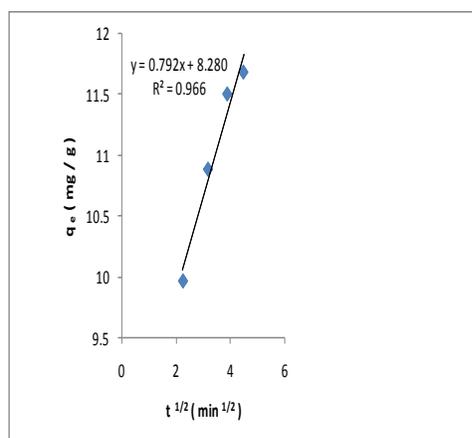


Fig 16. Intra - particle diffusion kinetics

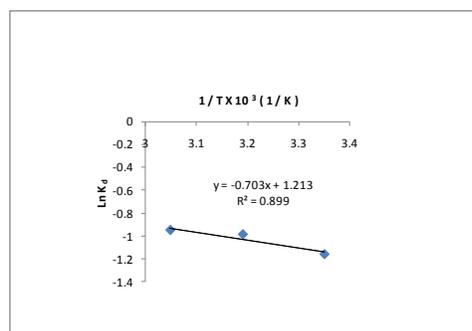


Fig 17. Van't Hoff plot for thermodynamic

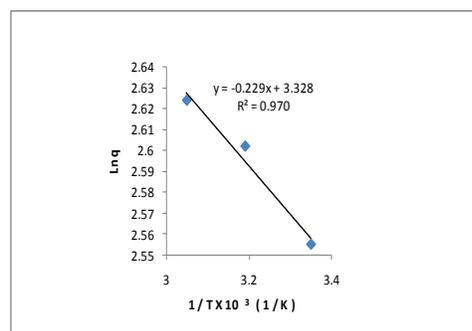


Fig 18. Plot of Ln q - 1/T

CONCLUSION

The results of present study showed that the PET – g – MMA/AA is a drastic adsorbent for the removal of Cd²⁺ ions from aqueous solutions. The adsorption of Cd²⁺ ions are correlated on pH, contact time, adsorbent dose and concentration of the metal ions. The isotherm and kinetic studies showed that Freundlich and Pseudo-second order models well explained the adsorption equilibrium of Cd²⁺ ions onto reactive fibers. Thermodynamic studies showed that

the adsorption of Cd^{2+} onto fibers was endothermic and spontaneous. Meanwhile, the adsorption of Cd^{2+} ions was through a physisorption process.

REFERENCES

- [1] Kumar S. Water Supply Engineering, Khanna Publishers, New Delhi, 1984.
- [2] Eren E, Afsin B. J Hazard Mater 2008; 151: 682-688.
- [3] Bhattacharya KG, Gupta SS. Chem Eng J 2008; 136: 1-9.
- [4] Tofan L, Paduraru C, Beilba D, Rotariu M. J Hazard Mater 2008; 156: 1-10.
- [5] Cabuk A, Akar T, Tunali S, Tabak O. J Hazard Mater 2006; 136: 317-323.
- [6] Zouboulis AI, Loukidou M, Matis KA. Process Biochem 2004; 39: 909-914.
- [7] Tewari M, Vasudevan P, Guha BK. Biochem Eng J 2005; 23: 185-192.
- [8] Bhattacharya KG, Gupta SS. Separ Purific Technol 2006; 50: 388-395.
- [9] Bhattacharya KG, Gupta SS. Adv Colloid Interface Sci 2008; 140: 114-120.
- [10] Bailey SE, Olin TJ, Bricka RM, Adrian DD. Wat Res 1999; 33: 2469-2479.
- [11] Srivastava VC, Mall ID, Mishra IM. Chem Eng J 2007; 132: 267-278.
- [12] Babel S, Kurniawan TA. J Hazard Mater 2003; 97: 219-243.
- [13] Kurniawan TA, Chan GYS, Lo W, Babel S. Sci Total Environ 2006; 366: 409-426.
- [14] Singh V, Sharma AK, Sanghi R. J Hazard Mater 2009; 161: 955-962.
- [15] Wang L, Wang A. J Hazard Mater 2008; 160: 173-181.
- [16] Coskun R. J Appl Polym Sci 2000; 75: 766-772.
- [17] Coskun R, Soykan C. J Polym Res 2006; 13: 1-8.
- [18] Arslan M. Fibers Polym 2010; 11: 325-330.
- [19] Arslan M. Fibers Polym 2010; 11: 177-184.
- [20] Azizinejad F, Talu M, Abdouss M, Shabani M. Iran Polym J 2005; 14: 33-38.
- [21] Azizinezhad F, Harutyunyan R, Abdouss M. Asian J Chem 2010; 22: 7803-7809.
- [22] Sakalar N, Bilir M H, Acemioglu B, Alma M H. Asian J Chem 2010; 22: 5649-5662.
- [23] Abdelwaheb O. Egypt J Aquatic Res 2007; 33: 125-143.
- [24] Nagashanmugam KB, Srinivasan K. Asian J Chem 2010; 22: 5447-5462.
- [25] Mall DI, Srivastava VC, Agarwal NK. Dyes Pigments 2006; 69: 210-223.
- [26] Masel RI. Principle of Adsorption and Reaction on Solid Surfaces, Wiley , New York , 1996.
- [27] Lagergren S. Theory of so-called Adsorption of Soluble Substances 1898.
- [28] Ho YS, McKay G. Chem Eng J 1998; 70: 115-127.
- [29] Weber WJ, Morris JC. J Sanit Eng Div 1963; 89: 31-45.
- [30] Aksu Z, Isoglu IA. J Process Biochem 2005; 40: 3031-3044.
- [31] Krishna DG, Bhattacharyya G. Appl Clay Sci 2002; 20: 295-306.
- [32] Arivoli, Ph D Thesis, Gandhigram Rural University 2007.
- [33] Jaycock MJ, Parfitt GD. Chemistry of Interfaces, Ellis Horwood Ltd, Onichester 1981, 12-13.
- [34] Benefield J, Judkins P, Wend BL. Process Chemistry for Water and Waste water Treatment , Prentice Hall, Englewood Cliffs, N J 1982.