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Thermodynamic Studies on the Removal of Metronidazole Antibiotic by Multi-Walled Carbon Nanotubes

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ABSTRACT

The adsorption of Metronidazole (MNZ) on Multi-Walled Carbon Nanotube (MWCNTs) samples of varying compositions was investigated using a batch adsorption technique. Adsorption studies were carried out for various parameters such as adsorbent dosage, ionic strength and contact time. Adsorption of MNZ onto MWCNTs increased with the increase in the adsorbent dosage and the optimum adsorbent dosage was found to be 0.1 g/L. The equilibrium between the MNZ and the adsorbent in the solution was established within 60 min. The negative value of ΔG◦ showed the spontaneous nature of MNZ adsorption onto MWCNTs. The standard enthalpy and the entropy changes were determined as 4.17 kJ mol^{-1} and 0.0165 kJ $mol^{-1}K^{-1}$ respectively. The positive value of ΔH◦ suggested the endothermic nature of adsorption, while positive values of ΔS◦ showed the increasing randomness at the MWCNTs-solution interface during the adsorption.

Keywords: $MWCNT_S$, Adsorption, Metronidazole, Thermodynamics

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INTRODUCTION

The problems of ecosystem are increasing with development technology[1, 2]. Pharmaceutical residues in the environment are received increasing attention as emerging contaminants[3, 4]. Antibiotics occupy an important place due to the high amounts consumed in both veterinary and human medicine[5-7]. Although the amount of these pharmaceuticals waste in the aquatic environment is low, the accumulation of pharmaceuticals waste constitutes a potential risk for the aquatic and terrestrial organisms at long-term[8-10].

Metronidazole (MNZ) with antibacterial and anti-inflammatory properties is a kind of nitroimidazole antibiotic, which is commonly used in clinical applications and widely used for the treatment of infectious diseases caused by anaerobic bacteria and protozoans, such as Giardia lamblia and Trichomonas vaginalis[11, 12]. Aside from being widel used as antibiotics for humans, MNZ is also abused as an additive in poultry and fish feed to eliminate parasites[13]. As a result, MNZ was accumulated in animals, fish farm water, and effluents from meat industries. Because of its low biodegradability and high solubility in water, MNZ is dif fi cult to be removed by traditional methods[14, 15]. Thus, it can be accumulated in the aquatic environment, causing adverse effects to humans and the ecological environment.

The conventional treatments of wastewaters containing antibiotics are considered incomplete and inefficient, thus there is a demand of development of new effective treatments technologies[16, 17]. Among several methods which have been studied, such as oxidation, electrodegradation, ozonation and biodegradation, and photocatalytic degradation, the adsorption is considered the most suitable treatment because it inhibits the toxic properties and restricts the transportation into water systems[18, 19]. Therefore, several adsorbents have been applied for antibiotics removal, such as, sludge-derived adsorbents, montmorillonite, graphene oxide, clay, and activated carbon[20, 21]. The activated carbons are adsorbents containing high surface area and an appreciable amount of active sites available for adsorption, i.e. which have sufficient affinity to retain certain pollutants[22, 23]. Due to these characteristics they are commonly employed in various processes for undesirable chemicals removal[24, 25]. Although efficient, the wastewater treatment by activated carbons is considered expensive due to its high production costs and restricted application[26, 27]. Therefore, many researches have been performed with the aim of obtaining low cost adsorbent.

Carbon nanotubes (CNTs) are new carbon materials and have found many applications in a wide areas such as adsorption, sepa-ration, catalysis, sensors, biomedicine and electronic devices[28, 29]. Due to their large specific surface area, small pore size, hollow and layered structures, carbon nanotubes have been proven to possess a great potential as superior adsorbents for removing many kinds of organic and inorganic contaminants from aqueous solution[30, 31]. The objective of this study is to investigate the capability of MWCNTs, for the removal of MNZ from aqueous solutions in batch system. The effects of different process parameters like biosorbent dose, initial MNZ concentration, Contact time and temperature on the biosorption of MNZ are studied. The equilibrium and kinetic data of biosorption studies are processed to understand the mechanism of MNZ onto MWCNTs.

MATERIALS AND METHODS

Chemicals and reagents

The multi-wall carbon nanotubes (MWCNTs) used in this study was of more than 98% purity and provided from Research Institute of Petroleum Industry (RIPI), Tehran, Iran). The size and morphology of SWCNTs were examined by scanning electron microscope (JEOL JSM 6500F) and transmission electron microscopy (TEM) (using a Philips XL30). Metronidazole (MNZ, $C_6H_9N_3O_3$) were purchased from the Sigma–Aldrich chemicals. The chemical and physical characteristics of MNZ are summarized in Table 1.

Bath adsorption experiments were carried out using 100 mL plastic flasks containing 100 mg of MWCNTs and 100 mL of MNZ solutions with different concentrations 10-100 mg/L. The plastic flasks were wrapped with aluminum foils to prevent light induced decomposition of the MNZ, and agitated at 220 rpm in a shaker at predetermined times. Then the mixtures were filtered using 0.45 lm membranes, and solutions were properly diluted with buffer solution of pH 7.0 for later analysis. The remaining concentrations of MNZ, C_e, were determined by high performance liquid chromatography (HPLC, Shimadzu, LC10A HPLC) equipped with a UV detector (SPD-10AV) at 318 nm. A Diamonsil (R) C18 column (5 µm, 250 mm long×4.6 mm) was used, and the mobile phase was composed of a mixture of acetonitrile and water (20/80, v/v). The fl ow speed was set at 1.0 mL min^{-1} , and 20 µL injections were used. The MNZ percentage removal was calculated according to Eq 1[32, 33]:

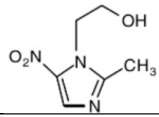
$$\%R = (C_o - C_e)/C_o \times 100 \qquad (1)$$

Where C_o corresponds to the initial concentration of MNZ ions and C_e is the residual concentration after stirring for a definite time. The metal uptake q_e (mg/g) was calculated as[34, 35]:

$$q = [(Co - Ce)/m].V \qquad (2)$$

Where m is the quantity of sorbent (mg) and V the volume of the suspension (mL).

Table 1: Physical and chemical characteristics of MNZ

Molecular formula	$C_6H_9N_3O_3$
Molecular weight (g mol^{-1})	171.2
Water solubility (g L^{-1})	9.5
pKa	2.55
Melting point (°C)	159–163
Molecular structure	

RESULTS AND DISCUSSION

TEM and SEM images (Fig. 1a and b) show the morphological structure of MWNTs. Images clearly suggests the crystalline tubular structure of nanotubes. The inner diameter and the outer diameter of the MWCNTs are in the ranges of 5–10 nm and 40–50 nm, respectively. Fig. 1c and d shows the TEM and SEM images of MNZ adsorbed MWNTs. Clusters of adsorbed MNZ over MWNTs surface can be seen from the images. The BET surface area determined by N_2 adsorption is 700 m^2/g.

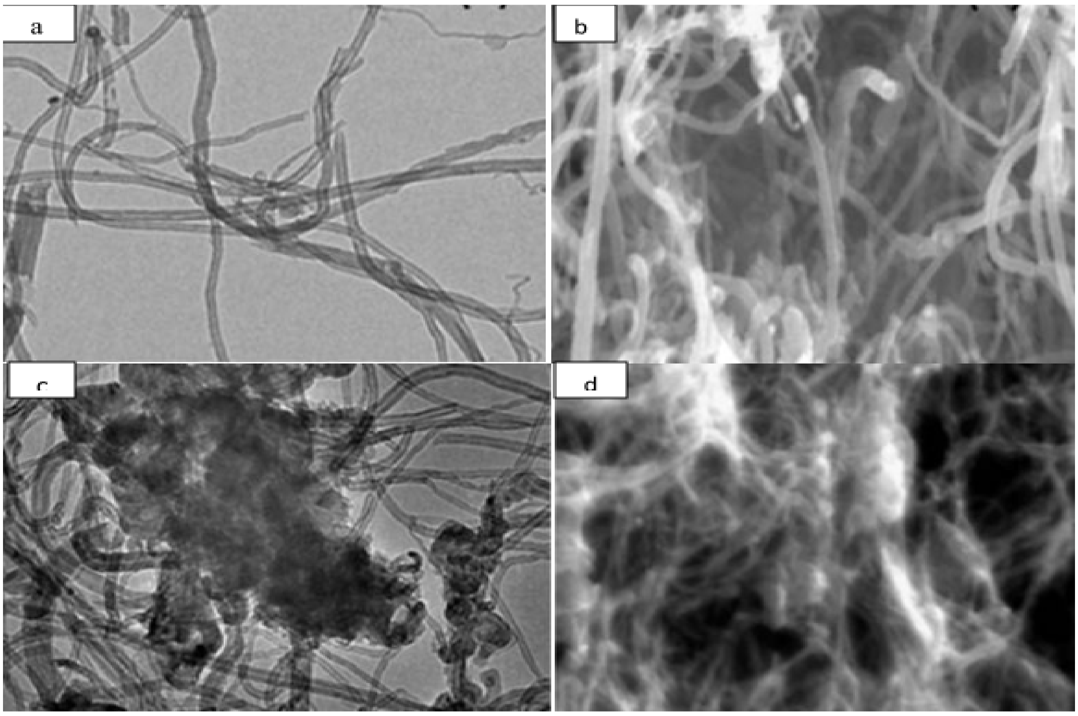


Fig. 1. TEM and SEM images of (a and b) MWNTs and (c and d) MNZ adsorbed MWNTs

Effect of MWCNTs Dosage: The effect of biosorbent dose on biosorption of MNZ on to MWCNTs was studied to determine an optimum biosorbent dosage. The tested biosorbent dosages varied from 0.01 to 0.2 g/L using an initial MNZ concentration of 100 mg/L and contact time of 60 min. As shown in Fig. 2, the biosorption capacity of MNZ on the SWCNTs decreased from 3580 to 427.5 mg/g, while the MNZ removal percent increased from 35.8% to 85.5% when biosorbent dosage increased from 0.01 to 0.2 g/L. Lower biosorption capacity of MNZ at a higher dosage of biosorbent is probably due to the decrease of the surface area of the biosorbent by the overlapping or aggregation during the sorption[36, 37]. However, the higher the dosage of the biosorbent in the solution, the greater the availability of active sites for MNZ, leading to the higher MNZ removal[38, 39].

Effect of Contact Time: Contact time studies are helpful in understanding the amount of MNZ adsorbed at various time intervals by a fixed amount of the adsorbent (0.1 g) nad temperatures (30℃) . Fig. 3 clearly indicates a rapid increase in the amount of adsorption with increase in time initially, gradually leading to equilibrium. Although at higher contact time, the rate of adsorption decreased and a saturation stage was attained due to the accumulation of the adsorption sites by the MNZ ions. This decline is due to decrease in total adsorbent surface area and increased diffusion pathway[40, 41].

Effect of ionic strength

MNZ adsorption data under three ionic strengths (0.02 and 1 and 0.2 mol/L as NaCl) and initial MNZ concentration 50 mg/L are given in Fig. 4. The MNZ adsorption data under two ionic strengths overlapped, indicating that ionic strength can hardly impact the adsorption of MNZ onto MWCNT. Furthermore, this result again confirmed that the surface electrostatic effect had no influence on the overall adsorption of MNZ on MWCNT[42, 43].

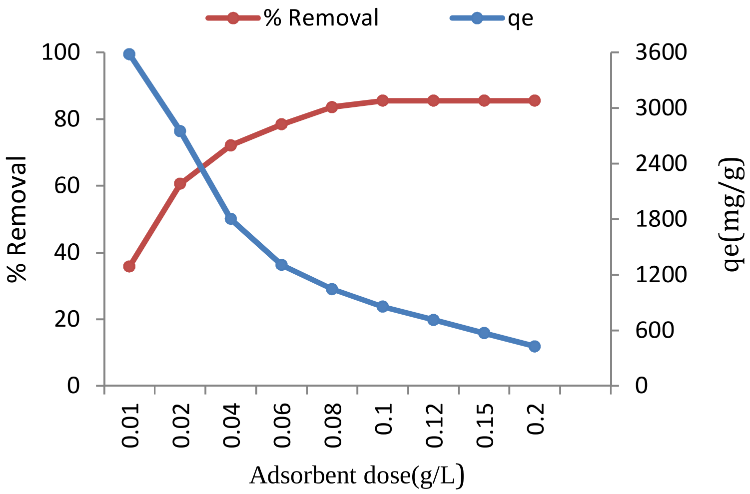


Fig 2: Effect of adsorbent dosage on MNZ adsorption. (C_0 = 100 mg/L, Contact time = 60 min, pH = 7, temperature = 30 ± 2°C)

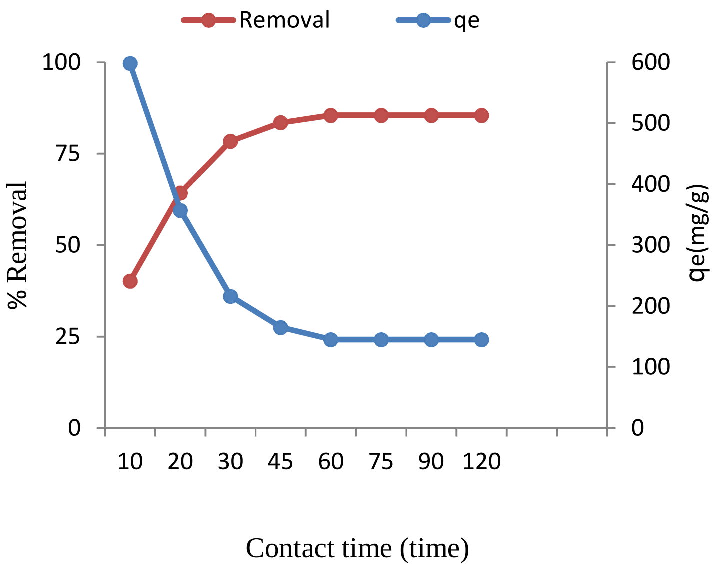


Fig 3. Effect of contact time and initial MNZ concentration (C_0 = 100 mg/L, pH =7, Adsorbent dosage 0.1 g/L and temperature = 30 ± 2°C)

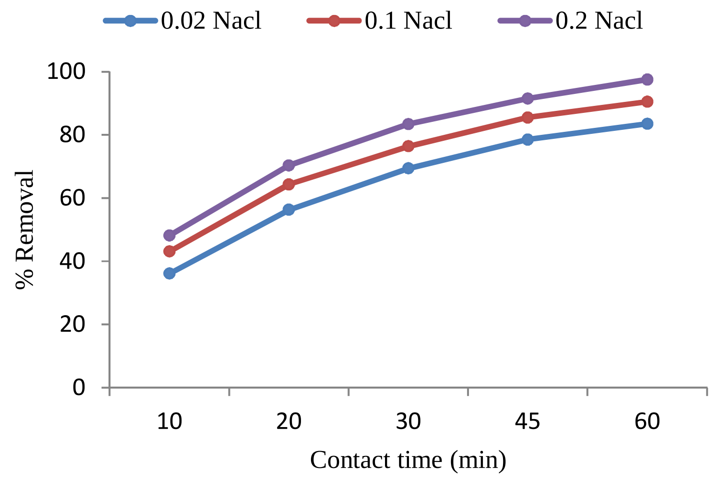


Fig 4: Effect of ionic strength on MNZ adsorption. (C0 = 100 mg/L, Contact time = 60 min, pH = 7, temperature = 30 ± 2°C and Adsorbent dosage 0.1 g/L)

Thermodynamic studies

The sorption behaviors of different concentrations MNZ onto MWCNT were critically investigated at 273, 293, 313 and 333 K, respectively. Thermodynamic parameters were calculated from following equations[34, 45]:

$\Delta G^{\circ} = -RT \ln K$

Where R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$), T is the temperature (K) and K is the distribution coefficient. Gibbs free energy change of adsorption (ΔG°) was calculated using ln K values for different temperatures. The K value was calculated using following equation[46, 47]:

$K = \frac{C_e}{q_e}$

Where C_e is the equilibrium concentration of MNZ and q_e is the amount of MNZ adsorbed per unit weight of MWCNT at equilibrium concentration (mg/g).

The enthalpy change (ΔH°) and entropy change (ΔS°) of adsorption were estimated from the following equation[48, 49]:

$\mathrm{Ln}\ K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$

The ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of lnK versus 1/T, respectively. The thermodynamic parameters were summarized in Table 2. The positive values of ΔH° and the negative values of ΔG° are showed the endothermic and spontaneous nature of sorption process.

Table 2: Thermodynamic parameters for the adsorption of MNZ on MWCNT

C_0 (mg/L)	ΔH° (Kj/mol)	ΔS° (kJ/molK)	ΔG° (kJ/mol)			
			273 K	293 K	313 K	333 K
100 mg/L	4.17	0.0165	-2.876	-3.659	-4.534	-5.451

CONCLUSION

The adsorption of Metronidazole from aqueous solution onto MWCNT has been studied. Adsorption tests were carried out as a function of contact time, adsorbent dosage and ionic strength. The percentage of removal increased with the increasing adsorbent dosage and ionic strength. The negative value of ΔG◦ confirmed the spontaneous nature adsorption process. The positive value of ΔS◦ showed the increased randomness at the solid–solution interface during adsorption and the positive value of ΔH◦ indicated the adsorption process was endothermic. The adsorption experiments indicated that MWCNT was effective in removing antibiotics such as MNZ from aqueous solution.

REFERENCES

[1] Zazouli MA, Mahdavi Y, Bazrafshan E, Balarak D. *Journal of Environmental Health Science & Engineering* **2014**;12(66):1-5.
[2] Diyanati RA, Yazdani J, Balarak D. *Mazandaran university of medical science*. **2013**;22(87):58-64.
[3] Zhang L , Song X, Liu X,Yang L,Pan F. *Chem. Eng*. J.**2011**; 178 ; 26– 33.
[4] Gulkowsk A, Leung HW, So MK, Taniyasu S, Yamashita N. *Water research*. **2008**;42:395-403.
[5] Aksu Z, Tunc O. *Process Biochemistry*. **2005**;40(2):831-47.
[6] Rivera-Utrilla J, Prados-Joya G, Sánchez-Polo M. *Journal of Hazardous Materials*. **2009**;170:298–305.
[7] Malakootian M,Balarak D, Mahdavi Y, Sadeghi SH, Amirmahani N. *IJAPBS*.**2015**;4(7);105-113.
[8] Balarak D,Kord Mostafapour F, Joghataei A. *British Journal of Pharmaceutical Research*.**2016**; 10(2): 1-11.
[9] Balarak D, Mahdavi Y, Azadi NA, Sadeghi SH. *International Journal of Analytical, Pharmaceutical and Biomedical Sciences*.**2016**;5(3);8-14.
[10] Xu WH, Zhang G, Zou SC, Li XD, Liu YC. *Environ. Pollut*. **2007**;145, 672-679.
[11] Gulkowsk A, Leung HW, So MK, Taniyasu S, Yamashita N. *Water research*. **2008**;42:395-403.
[12] Bendesky A, Menendez D, Ostrosky-Wegman P. *Mutat. Res*. **2002**; 511;133–144.
[13] Lanzky PF, Haning-Snrensen B. *Chemosphere*.**1997**; 35; 2553–2561.
[14] Johnson MB, Mehrvar M. *Eng. Chem. Res*.**2008**; 47; 6525–6537.
[15] Alexy R, Kumpel T, Kummerer K. *Chemosphere*; **2004** ; 57, 505–512.
[16] Zhang W, He G, Gao P, Chen G: *Sep Purif Technol* **2003**, 30:27–35.
[17] Choi KJ, Kim SG, Kim SH. *J. Hazard. Mater*.**2008**; 151;38–43.
[18] Zhang L, Song X, Liu X, Yang L, Pan F, Lv J. *Chem. Eng. J.* **2011**; 178;26–33.
[19] Zhu XD, Wang YJ, Sun RJ, Zhou DM. *Chemosphere*. **2013**; 92; 925–932.
[20] Su YF, Wang GB, Kuo DTF, Chang ML. *Applied Catalysis B: Environmental*. **2016**; 186;184-192.
[21] Ji K, Kim S, Han S, Seo J, Lee S, Y. *Ecotoxicology*;**2012**; 21;2031-2050.
[22] Gómez-Pacheco CV, Sánchez-Polo M, Rivera-Utrilla J, López-Peñalver J. *Chem. Eng. J.* **2011**; 178 ;115–121.
[23] Parolo ME, Savini MC, Vallés JM, Baschini MT, Avena MJ. *Appl. Clay Sci*. 208;40;179–186.
[24] Ocampo-Pérez R, Rivera-Utrilla J, Gómez-Pacheco C, Sánchez-Polo M, López-Peñalver JJ. *Chem. Eng. J.* **2012**; 213; 88–96.
[25] Putra EK, Pranowoa R, Sunarsob J, Indraswatia N, Ismadjia S. *Water Res*. **2009**; 43, 2419-2430.
[26] Balarak D, Mahdavi Y, Maleki A, Daraei H and Sadeghi S. *British Journal of Pharmaceutical Research*. **2016**;10(4): 1-9.
[27] Balarak D, Mahdavi Y and Mostafapour FK. *British Journal of Pharmaceutical Research*.**2016**; 12(1): 1-11.
[28] Yu JG, Zhao XH, Yang H, Chen XH, Yang Q, Yu LY, et al. *Science of the Total Environment* .**2014**. 482-483; 241–251.
[29] Chen GC, Shan XQ, Wang YS, Wen B, Pei ZG, Xie YN, et al. *water research*. **2009**. 43; 2409-2418.
[30] Li X, Zhao H, Quan X, Chen S, Zhang Y, Yu H. *Journal of Hazardous Materials*. **2011** 186; 407–415.
[31] Sun WL, Xia J, Shan YC. *Chemical Engineering Journal*. **2014**. 250;119–127.
[32] Zazouli MA, Mahvi AH, Mahdavi Y, Balarak D. *Fluoride*. **2015**;48(1):15-22.
[33] Zazouli MA, Yazdani J, Balarak D, Ebrahimi M, Mahdavi Y. *Journal of Mazandaran University Medical Science*. **2013**;23(2):73-81.
[34] Balarak D, Joghataei A. *Der Pharma Chemica*, **2016**, 8(6):96-103.
[35] Balarak D, Mahdavi Y, Bazrafshan E, Mahvi AH, Esfandyari Y. *Flouride*. **2016**;49(1):35-42.
[36] Diyanati RA, Yousefi Z, Cherati JY, Balarak D. *J Mazandaran Uni Med Sci*. **2013**; 23(106).17-23.
[37] Zazouli MA, Mahvi AH, Dobaradaran S, Barafrashtehpour M, Mahdavi Y, Balarak D. *Fluoride*. **2014**;47(4):349-58.
[38] Balarak D, Mahdavi Y , Bazrafshan E , Mahvi AH. *Fresenius Environmental Bulletin*.**2016**;25(5); 1321-1330.
[39] Mane VS ,Mall ID. J. *Environ. Manage*.**2007**: 84 ;390–400.
[40] Zazouli MA, Balarak D, Karimnezhad F, Khosravi F. *Journal of Mazandaran University Medical Sciences* **2014**;23(109):208-17.
[41] Yang K, Wu W, Jing Q, Zhu L. *Environ Sci Technol*. **2008**;42:7931-6.

[42] Tor A, Cengeloglu Y. *Journal of Hazardous Materials*. **2006**;138(2):409-15.
[43] Diyanati RA, Yousefi Z, Cherati JY, Balarak D. *Journal of Mazandaran University of Medical Science*. **2013**; 22(2);13-21.
[44] Balarak D, Mostafapour FK, Joghataei A. *Der Pharma Chemica*, **2016**, 8(8):138-145.
[45] Balarak D, Jaafari J, Hassani G, Mahdavi Y, Tyagi I, Agarwal S, Gupta VK. The use of low-cost adsorbent (Canola residues) for the adsorption of methylene blue from aqueous solution: Isotherm, kinetic and thermodynamic studies. Colloids and Interface Science Communications. Colloids and Interface Science Communications. **2015**;7:16–19.
[46] Balarak D, Joghataei A. *Der Pharma Chemica*, **2016**, 8(6):96-103.
[47] Balarak D. Kinetics, *International Journal of ChemTech Research*.**2016**;9(5);681-690.
[48] Garg VK, Gupta R, Yadav AB, et al. *Bioresource Technology*. **2003**; 89(1): 121–4.
[49] Ferdag C, Necip AO. *Chemical Engineering Journal*. **2009**;150(1):122-30.