



Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk

Halil Hasar*

Department of Environmental Engineering, Faculty of Engineering, Firat University, 23119 Elazig, Turkey

Received 18 February 2002; received in revised form 2 August 2002; accepted 2 August 2002

Abstract

Activated carbon was prepared from almond husk by activating without (MAC-I) and with (MAC-II) H_2SO_4 at different temperatures. The ability of the activated carbon to remove nickel(II) ions from aqueous solutions by adsorption has been investigated under several conditions such as pH, carbonisation temperature of husk, initial concentration of metal ions, contact time, and adsorbent concentration. Optimal conditions were pH 5.0, the carbonisation temperature of $700\text{ }^\circ\text{C}$, 50 min of contact time and adsorbent concentration of 5 g/l. The results indicate that the effective uptake of Ni(II) ions was obtained by activating the carbon, prepared from almond husk at $700\text{ }^\circ\text{C}$, through the addition of H_2SO_4 . The removal of Ni(II) were found to be 97.8% at initial concentration of 25 mg/l and the adsorbent concentration of 5 g/l. When the adsorbent concentration was increased up to 40 g/l, the adsorption density decreased from 4.89 to 0.616 mg/g for MAC-II. In the isotherm studies, the experimental adsorption data fitted reasonably well the Langmuir isotherm for both MAC-I and MAC-II.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nickel(II) uptake; Activated carbon; Almond husk; Adsorption isotherm

1. Introduction

Nickel is a toxic heavy metal that is widely used in silver refineries, electroplating, zinc base casting and storage battery industries [1]. The chronic toxicity of nickel to humans and the environment has been well documented. For example, high concentration of nickel(II) causes cancer of lungs, nose and bone. It is essential to remove Ni(II) from industrial wastewater before being discharged. For this reason, it is generally used the advanced treatment processes such as chemical reduction, ion exchange, reverse osmosis, electro dialysis, and activated carbon adsorption. Since the cost of these processes are rather expensive,

* Fax: +90-424-241-55-26.

E-mail address: hhasar@firat.edu.tr (H. Hasar).

the use of agricultural residues or industrial by-product having biological activities have been received with considerable attention [2]. Thus, many materials have been examined. In recent years, a number of agricultural material such as moss peat [3,4], coconut husk [5,6], chitosan [7], coirpith [1], rice husk [8,9], tea leaf [10] and almond husk [11] have been reported for the removal of toxic metals from aqueous solutions. Most of these materials contain functional groups associated with proteins, polysaccharides, lignin, and cellulose as major constituents. Metal uptake is believed to occur through sorption process involving the functional group mentioned above.

Almond husk is readily available in great abundance in Elazig, Turkey. It is generally discarded as a waste. The cell walls of almond husk consist of cellulose, silica, lignin, carbohydrates which have hydroxyl groups in their structures. This paper reports the effect of adsorption parameters such as pH, carbonisation temperature of husk, adsorbent concentration, contact time and initial concentration on nickel(II) uptake by using almond husk carbon as adsorbent material.

2. Experimental

2.1. Adsorbent preparation

In order to remove the trace amounts of metal ions present in almond husk, it was washed with 500 ml of deionised water and rinsed with 100 ml of 1% HCl. The almond husk was dried at 25 °C, room temperature, for 24 h and then ground using a grinder (ASTM E-11/BS-410). The powdered materials that remain between 50 and 100 mesh (150 µm) was divided to two portions. Steel tube was filled with the almond husk powder and placed into the oven. The N₂ gas was passed through the tube in order to prevent the burning of the almond husk.

In the first experimental series, husk samples were carbonised at different temperatures such as 300, 500, 600, 700, 800, 900, and 1000 °C under nitrogen atmosphere in an oven for 1 h (Fig. 1). They were activated by carbon dioxide gas for 1 h. Adsorbent obtained in this series is termed as 'Modified Activated Carbon-I, MAC-I'.

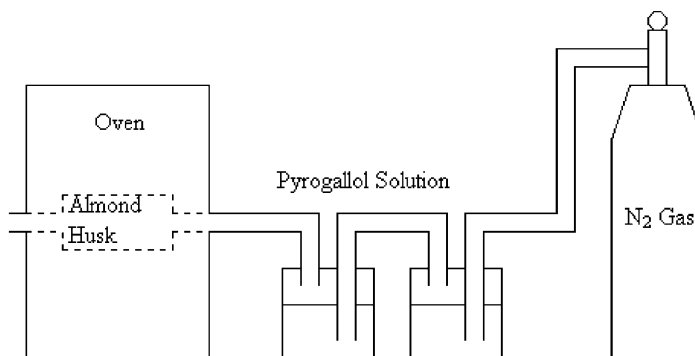


Fig. 1. Activated carbon preparation apparatus.

In second experimental series, a portion of the powdered material was chemically activated by washing 10% H_2SO_4 (in weight 1:1) for 6 h. Then, this material was carbonated at different temperatures under nitrogen atmosphere for 1 h, and it was again activated by carbon dioxide gas at 1 h. Adsorbent obtained in second experimental series is termed as 'Modified Activated Carbon-II, MAC-II'.

2.2. Adsorbate preparation

All reagents used are of analytical reagent grade. A stock solution of 1000 mg/l of Ni(II) was prepared by dissolving 4.4790 g of ultra pure nickel sulphate [$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$] in double distilled water, acidified with nitric acid to prevent hydrolysis. Adsorption experiments were conducted to investigate the influence of adsorption parameters such as pH, adsorbent concentration, activating temperature, contact time and initial concentration on Ni(II) uptake by using MAC-I and MAC-II as adsorbent.

2.3. Adsorption experiments

Batch adsorption experiments were carried out by shaking 0.125–10.0 g adsorbent with 250 ml of Ni(II) solutions of specified concentration in 500 ml flasks at incubator for 20 °C. Stuart Scientific (SF 1 Model) flask shaker was used for shaking. The samples were shaken at 1000 rpm for predetermined contact time. pH of the solutions was adjusted with NaOH and HCl solutions using a pH meter (Jenway 3015 model). Adsorbent concentration was varied from 0.5 to 40 g/l. Contact time was also varied from 10 to 100 min.

Lagmuir isotherm studies were carried out by using 25–250 mg/l Ni(II), pH 5.0 and 5 g adsorbent/l. Freundlich isotherm studies were conducted by using 25 mg/l Ni(II), pH 5.0 and 0.5–40 g adsorbent/l. At the end of predetermined contact period, the reaction mixture was centrifuged at 10,000 rpm for 10 min at 20 °C (SED 20R centrifugal). Nickel(II) in supernatants was analysed by using Unicam 929 Model Atomic Absorption Spectrometer. The percentage removal of Ni(II) was calculated from the differences between the concentrations of Ni(II) before and after adsorption.

After the adsorption was completed, 50 ml of 1% hydrochloric acid was applied to the adsorbent in order to elute the adsorbed metal ions. Then the adsorbent material was washed with 100 ml of deionised water and dried at 25 °C for 1 day, and thus could be reused.

3. Results and discussion

3.1. Effect of pH

It is well known that adsorption of heavy metal ions depends on pH the aqueous solution. Fig. 2 indicates the effect of pH on Ni(II) adsorption by the activated carbon prepared from almond husk under two different conditions. The pH of solution was varied from 2.0 to 7.0. While Ni(II) removal was 24.1 and 23% for MAC-I and MAC-II at pH 2.0, respectively, it

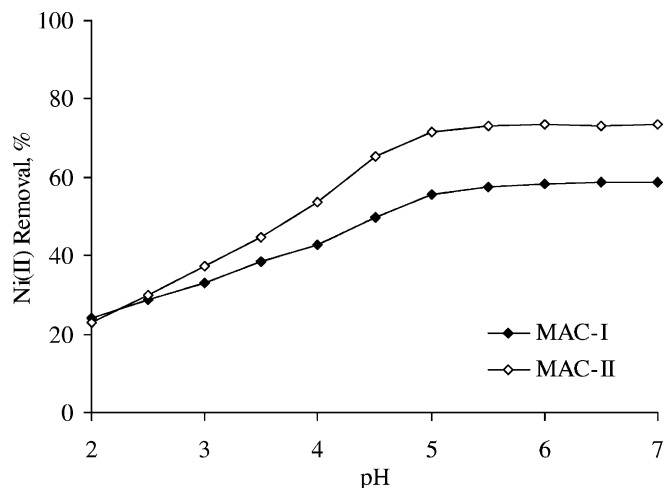


Fig. 2. Effect of pH on Ni(II) removal for MAC-I and MAC-II conditions: $T_{\text{carb}} = 600^{\circ}\text{C}$, $m = 1$ g adsorbent/l, $C_0 = 25$ mg/l, $t = 60$ min.

was 28.6 and 30.1% for above adsorbents at pH 2.5. This situation indicates that MAC-II is not very different from MAC-I for Ni(II) removal at low pH values. At $\text{pH} > 4.0$, the differences in removal by MAC-I and MAC-II are obvious. The removal of Ni(II) increased rapidly at pH values between 3.0–5.0 and reached up to 55.6 and 71.7% at pH 5.0 for MAC-I and MAC-II, respectively. At $\text{pH} < 3.0$, H^+ ions compete with Ni(II) ions for the surface of the adsorbent which would hinder Ni(II) ions from reaching the binding sites of the sorbent caused by the repulsive forces. However, the metal removal is minimum presumably due to the enhanced competition of proton with nickel ions for ligand binding sites and complex formation. At $\text{pH} > 5.0$, the Ni(II) ions get precipitated due to hydroxide anions forming a nickel hydroxide precipitate. For this reason, the optimal pH value was selected to be 5.0.

3.2. Effect of carbonisation temperature

Fig. 3 indicates the effect of carbonisation temperature of husk on the adsorption of Ni(II) ions by MAC-I and MAC-II. It was shown that the Ni(II) uptake increased with increasing temperature up to 700°C , and then decreased at higher temperatures. In the adsorption experiments carried out by MAC-I and MAC-II prepared at 300°C , the removal was, respectively, 18.2 and 21.6%. At 700°C , the removal by MAC-II and MAC-I increased up to 77.6 and 53.2%, respectively. The best results have been obtained with activated carbon modified MAC-II by adding 10% H_2SO_4 at the carbonisation temperature of 700°C . This can be partially attributable to the transition of amorphous silica to crystalline form occurred at this temperature. In addition, a maximum porous structure develops in the material at this temperature, and creates a larger internal surface area. Therefore the optimum carbonisation temperature was selected to be 700°C .

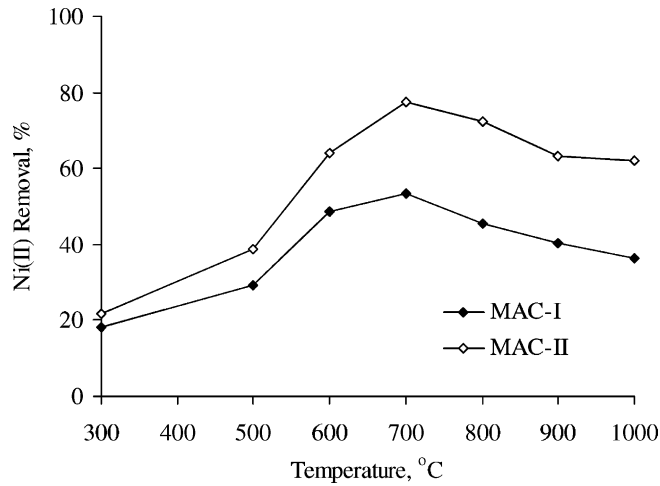


Fig. 3. Effect of carbonisation temperature on metal removal for MAC-I and MAC-II conditions: pH = 5.0, $m = 1$ g adsorbent/l, $C_0 = 25$ mg/l, $t = 60$ min.

3.3. Effect of contact time

The effect of contact time on the adsorption of Ni(II) ions by MAC-II and MAC-I can be seen in Fig. 4. The removal of Ni(II) ions increased rapidly with time up to 50 min and thereafter increased slowly. The uptake of Ni(II) ions was 77.0 and 49.7% at 50 min and 83.0 and 54.4% at 100 min by MAC-II and MAC-I, respectively. According to the results, the equilibrium reached at 50 min and was taken as the optimal contact time for the subsequent experiments.

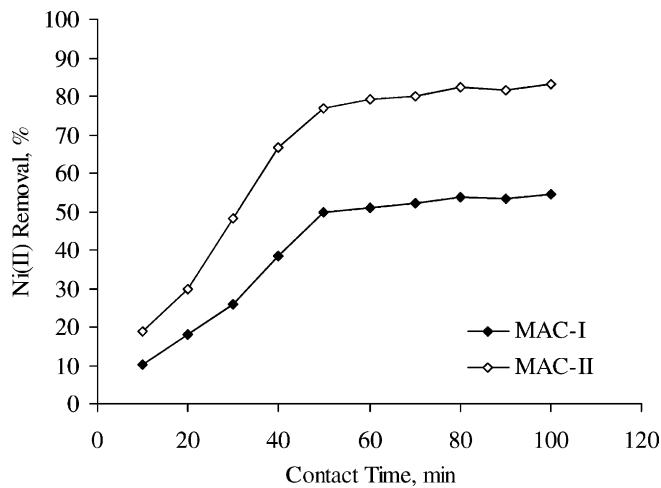


Fig. 4. Effect of contact time on metal removal for MAC-I and MAC-II conditions: pH = 5.0, $T_{\text{carb}} = 700$ °C, $m = 1$ g adsorbent/l, $C_0 = 25$ mg/l.

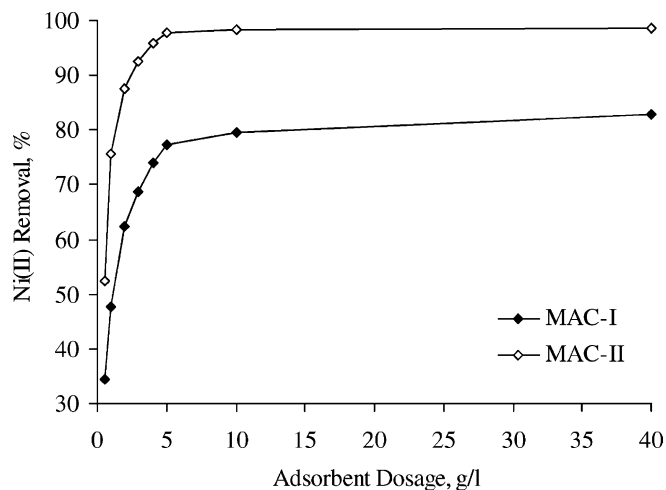


Fig. 5. Effect of adsorbent concentration on metal removal for MAC-I and MAC-II conditions: pH = 5.0, $t = 50$ min., $T_{\text{carb}} = 700$ °C, $C_0 = 25$ mg/l.

3.4. Effect of adsorbent concentration

Fig. 5 indicates the effect of adsorbent concentration on Ni(II) uptake for both MAC-I and MAC-II. The removal increased by MAC-II and MAC-I, respectively, from 52.4 and 34.3% at 0.5 g/l to 97.8 and 77.4% at 5.0 g/l. The removal reached up to 98.6 and 82.8% at 40.0 g/l by MAC-II and MAC-I, respectively. However, while the adsorption density was 4.89 mg/g for MAC-II and 3.87 mg/g for MAC-I at the adsorbent concentration of 5 g/l, it decreased to 0.616 mg/g for MAC-II and 0.518 mg/g for MAC-I at the adsorbent concentration of 40 g/l. This means that, at >5 g/l adsorbent concentration, adsorption density got lowered. Hence, optimal adsorbent concentration was selected to be 5 g/l.

3.5. Effect of initial Ni(II) concentration

Fig. 6 indicates the effect of initial metal concentration on the adsorption of Ni(II) by both MAC-I and MAC-II. When the initial Ni(II) concentration of sample was increased from 25 to 250 mg/l, the removal decreased from 97.4 to 68.6% for MAC-II and from 75.9 to 45.9% for MAC-I. For example, while the adsorption density was 4.87 mg/g at the initial Ni(II) concentration of 25 mg/l, it increased to 34.3 mg/g at the initial Ni(II) concentration of 250 mg/l for MAC-II.

3.6. Adsorption isotherms

The distribution of metal ions between the liquid phase and the solid phase can be described by several mathematical model equations such as the standard Langmuir isotherm model and the Freundlich isotherm model [12]. The Langmuir model assumes that the

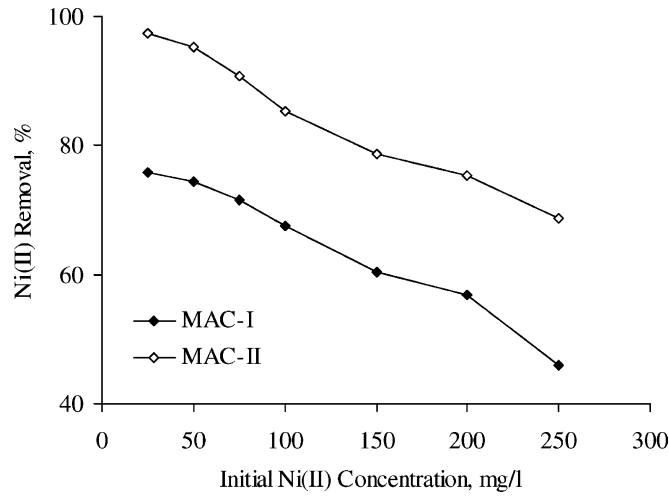


Fig. 6. Effect of initial concentration on metal removal for MAC-I and MAC-II conditions: pH = 5.0, $t = 50$ min., $T_{\text{carb}} = 700$ °C, $m = 5$ g adsorbent/l.

uptake of metal ions occur on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The model takes the following form:

$$\frac{C_e}{A_m} = \frac{1}{k} \frac{1}{b} + \frac{C_e}{b} \quad (1)$$

where C_e is the equilibrium concentration (mg/l), A_m the amount adsorbed per specified amount of adsorbent (mg/g), k the equilibrium constant (l/mg) and b is the amount of adsorbate required to form a monolayer (mg/g).

The Freundlich model assumes that the uptake of metal ions occur on a heterogeneous surface by monolayer adsorption. The model is described by the following equation:

$$A_m = k_f C_e^{1/n} \quad (2)$$

or

$$\log(A_m) = \log(k_f) + \frac{1}{n} \log(C_e) \quad (3)$$

The common terms in Eqs. (1) and (2) are described above and k_f and n are Freundlich constant.

Langmuir isotherm plots were obtained by using initial concentration effect-data on Fig. 6. Freundlich isotherm plots were also obtained by using adsorbent concentration effect-data on Fig. 5. Figs. 7 and 8 indicate the Freundlich and the Langmuir isotherms for both adsorbents prepared from almond husk, respectively. The plots of $\log(A_m)$ against $\log(C_e)$ give the line (Fig. 7) showing the Freundlich isotherm. The values of k_f and $1/n$ for the uptake of Ni(II) ions by MAC-I and MAC-II were determined from the slopes and intercepts of these lines. Plots of C_e/A_m against C_e are linear (Fig. 8) showing the applicability of Langmuir isotherm. The values of k and b for the removal of Ni(II) ions by MAC-II and MAC-I

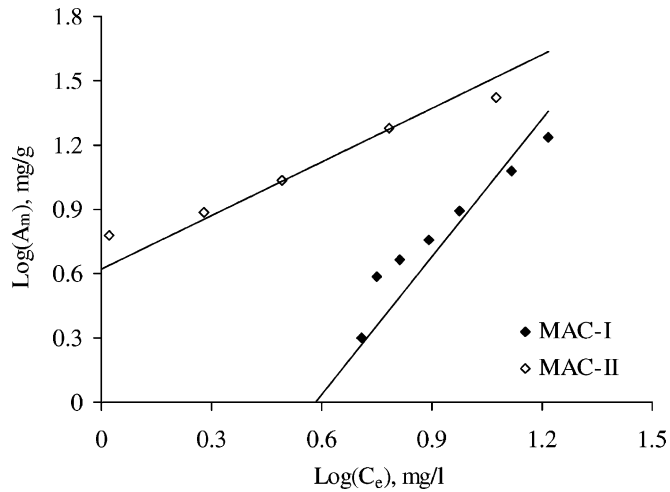


Fig. 7. The Freundlich isotherms for MAC-I and MAC-II conditions: pH = 5.0, $t = 50$ min., $T_{\text{carb}} = 700^\circ\text{C}$, $C_0 = 25$ mg/l.

were determined from the slopes and intercepts of these lines, and are given in Table 1. When the Freundlich isotherm was applied to data obtained from Fig. 5, it was shown that the correlation coefficient (r) was approximately 0.91 for both MAC-I and MAC-II. The Langmuir correlation coefficients were found to be higher than 0.99 for MAC-I, and nearly 0.98 for MAC-II. According to the results, the data fitted reasonably well the Langmuir isotherm in the adsorption studies carried out by the MAC-I and MAC-II. The Langmuir

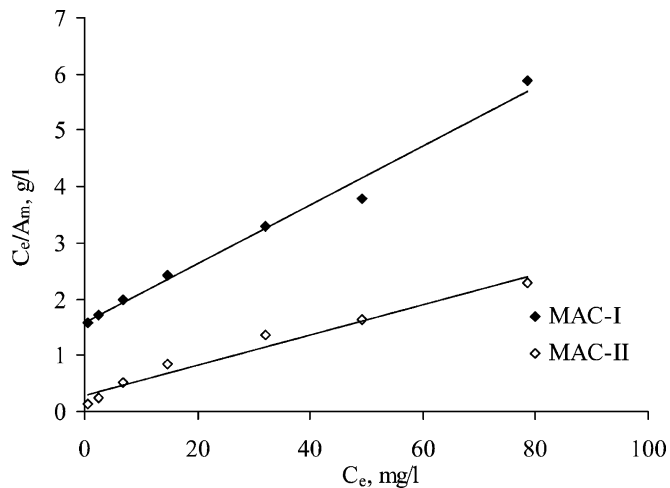


Fig. 8. The Langmuir isotherms for MAC-I and MAC-II conditions: pH = 5.0, $t = 50$ min., $T_{\text{carb}} = 700^\circ\text{C}$, $m = 5$ g adsorbent/l.

Table 1
Isotherm constants of the Freundlich and Langmuir models for Ni(II) ions uptake by MAC-I and MAC-II

	Freundlich isotherm			Langmuir isotherm		
	r	k_f (mg/g)	$1/n$	r	k (l/mg)	b (mg/g)
MAC-I	0.911	4.203	2.141	0.995	0.025	30.769
MAC-II	0.909	0.057	0.832	0.983	0.091	37.175

type isotherm hints towards surface homogeneity of the adsorbent [13]. This leads to the conclusion that the surfaces of MAC-I and MAC-II prepared from the almond husk is made up of small homogeneous adsorption patches.

4. Conclusion

The activated carbon prepared from almond husk which is an agricultural waste could be used as a potential adsorbent for the removal of Ni(II) ions from aqueous solution and is inexpensive material for treating the industrial wastewater. It was searched the optimal conditions for an effective treatment of Ni(II) by almond husk and found that the best removal occurred by MAC-II, which was modified by adding H₂SO₄, at pH 5.0, 50 min of contact time, carbonisation temperature of 700 °C and 5.0 g/l of adsorbent concentration. The adsorption data fitted reasonably well the Langmuir isotherm for both activated carbon types prepared from almond husk under different conditions.

References

- [1] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Sep. Pur. Technol. 24 (2001) 497.
- [2] H. Hasar, Y. Cuci, Anadolu Univ. J. Sci. Technol. 1 (2000) 201.
- [3] C.K. Lee, K.S. Low, Environ. Technol. 10 (1989) 395.
- [4] D.C. Sharma, C.F. Forster, Water Res. 27 (1993) 1201.
- [5] W.T. Tan, S.T. Ooi, C.K. Lee, Env. Technol. 14 (1993) 277.
- [6] K.S. Low, C.K. Lee, S.L. Wong, Env. Technol. 16 (1995) 877.
- [7] I. Saucedo, E. Guibal, C.H. Roulph, P. Cloirec, Env. Technol. 13 (1992) 1101.
- [8] R. Suemitsu, R. Uenishi, I. Akashi, M. Nakano, J. Apply. Polym. Sci. 31 (1986) 75.
- [9] E. Munah, R. Zein, Env. Technol. 18 (1997) 359.
- [10] T.W. Tee, A.R.M. Khan, Env. Technol. Lett. 9 (1988) 1223.
- [11] H. Hasar, Y. Cuci, Env. Technol. 21 (2000) 1337.
- [12] R. Chakravarty, G. Prasad, D.C. Raupainwar, Env. Technol. 19 (1998) 315.
- [13] M. Ajmal, A.H. Khan, S. Ahmad, A. Ahmad, Water Res. 32 (1998) 3085.