

## APPLICATION OF IMPREGNATED ALMOND SHELL ACTIVATED CARBON BY ZINC AND ZINC SULFATE FOR NITRATE REMOVAL FROM WATER

\* A. Rezaee, H. Godini, S. Dehestani, A. Khavanin

Department of Environmental Health, Medical Sciences Faculty, Tarbiat Modares University, Tehran, Iran

Received 4 December 2007; revised 8 February 2008; accepted 3 March 2008

### ABSTRACT

In this study impregnated almond shell activated carbon by  $Zn^0$  and  $ZnSO_4$  were used as adsorbent with a particle size of 10-20 mesh. The objective of this research was to determine the ability of impregnated activated carbon in nitrate removal. The modified activated carbon had 1mm effective size, with a uniformity coefficient of 1.18. Potassium nitrate solution was used in batch adsorption experiments for nitrate removal from water. The effects of nitrate concentration, activated carbon dosage and time of contact were studied. Experimental data showed that modified activated carbon by  $Zn^0$  and  $ZnSO_4$  was more effective than virgin almond activated carbon for nitrate removal. The maximum nitrate removal was 64%-80% and 5%-42% for modified activated carbon and virgin activated carbon, respectively. While virgin activated carbon used, nitrate-N decreased from 20 to 15mg/L in 30min reaction. The final nitrate concentration was not in the standard range of WHO recommendations for water quality; while impregnated activated carbons were used, nitrate decreased to <10mg/L. Maximum removal was over 16-17mg nitrate-N per 1g activated carbon for impregnated activated carbon. The experiments were conducted at pH=6.2, 20°C and initial concentrations of 20mg/L nitrate-N. Increase in modified activated carbon dosage increased the nitrate removal efficiency. The equilibrium time was found to be 45min for modified activated carbon.

**Key words:** Activated carbon, nitrate, adsorption, zinc, zinc sulfate

### INTRODUCTION

Nitrate is a wide spread contaminant in both ground and surface water due to excessive use of nitrogenous fertilizers in agricultural activities and disposal of untreated sanitary and industrial wastes (Hudak,2000 ; Almasri and Kaluarachchi,2004 ). Elevated nitrate concentrations in drinking water are linked to health problems such as methemoglobinemia in infants and stomach cancer in adults. Effluents with high concentrations of nitrate may also promote algal bloom in water reservoir (Zhi-Wei *et al.*, 2005). The maximum contaminant level (MCL) for nitrate set by the World Health Organization (WHO) and the US Environmental Protection Agency (EPA) for drinking water are 50 and 45mg/L of  $NO_3$  respectively (USEPA, 2000; WHO, 2004). Activated carbon (AC) adsorption is one of the

recommended technologies for nitrate removal from water (Mizuta *et al.*, 2004). Mizuta conducted nitrate removal with bamboo powder charcoal as adsorbent.

Activated Carbon mainly contains micropores and is efficient to remove some pollutants. In some cases, it needs mesopores to improve the adsorption velocity and mass transferring. Thus, it is necessary to increase the mesopore content in AC. One of the most effective approaches to increase mesopore and macropore volumes of AC is to catalyze the steam activation reaction of carbon by using the transition metals or rare earth metal compounds, which can promisingly promote the mesopore formation (Shen *et al.*, 2006). The generation mechanism of mesopore and macropore is the activation reaction taking place in the immediate vicinity of metal particles, leading to the formation of mesopore and macropores by

\*Corresponding author: [abbasrezaee@yahoo.com](mailto:abbasrezaee@yahoo.com)

Telefax: +98 21 8288 3575

pitting holes into the carbon matrix. The impregnation optimizes the existing properties of the AC giving a synergism between the chemicals and the carbon (Shen *et al.*, 2007; Namasivayam *et al.*, 2006). This facilitates the cost-effective removal of certain pollutant which would be impossible otherwise. The unique structure of AC produces a very large surface area. AC has an extraordinarily large surface area and pore volume that gives it a unique adsorption capacity (Baker *et al.*, 1992). It has both chemical and physical effects on substances where it is used as a treatment agent. Activity can be separated into (I) adsorption, (II) mechanical filtration; (III) ion exchange, and (IV) surface oxidation. Adsorption capacity depends on physical and chemical characteristics of the adsorbent, physical and chemical characteristics of the adsorbate, concentration of the adsorbate in liquid solution, characteristics of the liquid phase (e.g. pH, temperature) and the time the adsorbate is in contact with the adsorbent (Cheremishinoff *et al.*, 1978).

Electrical forces between the AC surface and some contaminants may result in adsorption or ion exchange. Adsorption is affected by the chemical nature of the adsorbing surface (Saswati and Kumar, 2005). The chemical properties of the adsorbing surface are determined to a large extent by the activation process. AC materials formed from different activation processes will have chemical properties that make them more or less attractive to various contaminants. For example, chloroform is adsorbed more efficiently by AC that has the least amount of oxygen associated with the pore surfaces (Bakasiet *al.*, 2003). A general rule of thumb is that similar materials tend to associate. Organic molecules and AC are similar materials; therefore there is a stronger tendency for most organic chemicals to associate with the AC rather than dissolved solute in water. Generally, the least soluble organic molecules are most strongly adsorbed. Often the smaller organic molecules are held the tightest, because they fit into the smaller pores (Bakasi *et al.*, 2003).

Adsorption usually increases as pH and temperature decrease. Chemical reactions and forms of chemicals are closely related to pH and

temperature. When pH and temperature are decreased, many organic chemicals become more adsorbable (Bakasi *et al.*, 2003). The AC is not widely used in practice for nitrate control due to low capacities and slow adsorption kinetics of nitrate by commercially available activated carbons. In the present work, nitrate removal was carried out for treatment of water by a series of modified and well characterized almond shell-based activated carbon with Zn<sup>o</sup> and ZnSO<sub>4</sub>.

## MATERIALS AND METHODS

### *Impregnated activated carbon modification*

Almond shell-based activated carbon was supplied from Kimia Carbon Co., Arak, Iran. The AC was then modified using the surface modification pathway as follows:

Almond activated carbon was stirred in a boiling solution containing, Zn<sup>o</sup> and ZnSO<sub>4</sub> (5wt.% based on AC) at room temperature, filtered and dried at 120°C (Cheremishinoff *et al.*, 1978). The modified activated carbon (MAC) was then extensively washed with normal perchloride acid and deionized water. After washing, the AC was dried at 90°C in a drying oven and stored in a desiccator until use. The AC particles between 10 and 20 mesh sizes with 1mm effective size and 1.18 uniformity coefficient were used in all experiments.

### *Experimental design*

Batch adsorption experiments were carried out by taking various dosages (1.5, 3, 4.5 and 6g AC/ 50mL water) of adsorbent, nitrate concentration (10, 20, 30, 40 and 50mg/L NO<sub>3</sub>-N) and contact time variations (10, 20, 30, 40, 50, 60, 90 and 120min), with 50mL of nitrate solution of known initial concentration in different conical glass flasks in a shaking thermostat with a constant speed of 120rpm. All experiments were conducted in triplicate and average values are presented in subsequent sections.

Potassium nitrate was used as the source of nitrate in all the experiments (Merck). Percentage of nitrate removed was measured calorimetrically using a UV/visible spectrophotometer (Philips PU 8700 Series model). The experiments were conducted at 20°C for the impregnated AC and AC. The effect of pH was evaluated by adjusting pH using HCl and NaOH. Distilled water prepared

in the laboratory was used for preparation of all reagents and all experimental works.

*Analytical procedures*

pH was monitored by a digital pH meter (Sens Ion 387, HACH model). Nitrate was analyzed using UV-visible spectrophotometer. Ammonia was estimated by phenate method at wavelength of 640nm after removing divalent magnesium ion at higher pH, and nitrite was analyzed by sulphanimide method at 543nm. Zn and sulfate measurements were regularly checked for the untreated and treated effluents according to the Standard Methods (APHA, 1995). AC properties such as apparent and bulk densities, iodine adsorption test, moisture content (%) and particle size were analyzed according to ASTM D2854, ASTM D4607, ASTM D2867 and ASTM D5158, respectively. Surface morphology of AC was estimated by scanning microscopy (XL30 Philips

model). The metals on AC were demonstrated by SEM equipped by EDX (Energy Dispersive X-ray microanalysis) and analysis system of ZAF software. For preparation of SEM, AC was dried in a CO<sub>2</sub> atmosphere under critical conditions.

**RESULTS**

After modification of activated carbon, physicochemical characteristics were determined. Physicochemical characteristics of almond shell AC and impregnated AC are shown in Table 1. The results were obtained from the mean of triplicate samples for every variable. The SEM micrographs of AC and impregnated AC were displayed in Fig. 1. The x-ray microanalysis of AC is demonstrated by Fig. 2. The almond shell activated carbon has not Zn of total elements (carbon exception) on the surface while in the impregnated ACs, the Zn increased at surface by

Table 1: Physicochemical characteristics of AC and impregnated ACs with Zn<sup>o</sup> and ZnSO<sub>4</sub>

Parameters	AC	AC-Zn	AC-ZnSO <sub>4</sub>
Apparent density (g/cm <sup>3</sup> )	0.29611	0.30026	0.29895
Bulk density (g/cm <sup>3</sup> )	0.25983	0.2717	0.26893
Average pore diameter (nm)	41.269	45.562	45.326
Total cumulative volume(mL/g)	0.24716	0.3493	.33897
Total porosity (%)	12.2527	9.4901	9.3895
Iodine adsorption test	375	260	298.62
Moisture content (%)	3.3	6.26	6.73

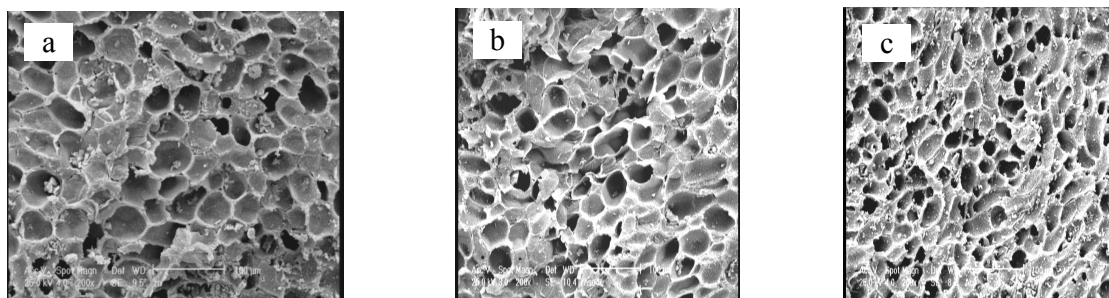


Fig. 1: SEM micrographs of a: AC; b: AC-Zn and c: AC-ZnSO<sub>4</sub>

80.67 of total elements composition (carbon exception). The form of Zn<sup>o</sup> on the AC was zinc oxide. The effects of contact time on the removal of nitrate by AC, AC-Zn<sup>o</sup> and AC-ZnSO<sub>4</sub> with the initial concentration of 20mg/L NO<sub>3</sub>-N, 20°C temprature and pH=6.2 are shown in Figs. 3 and 4. Adsorption of nitrate ions onto

the adsorbent was studied by batch experiments. The effect of carbon dosages for the adsorption process is shown in Fig. 5. Nitrate isotherms of diferent type of activated carbons (AC-0, AC-ZnSO<sub>4</sub> and AC-Zn<sup>o</sup>) in mass basis are shown in Fig. 6. Water quality after ACs treatment is shown in Table 2.

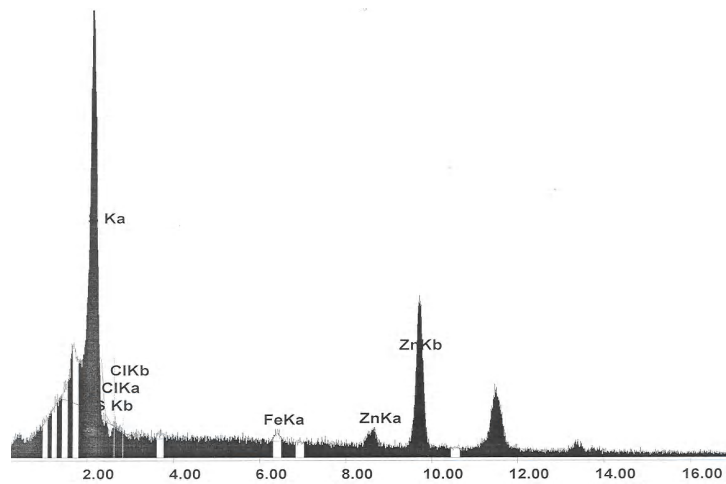


Fig. 2: The x-ray microanalysis of impregnated AC with Zn

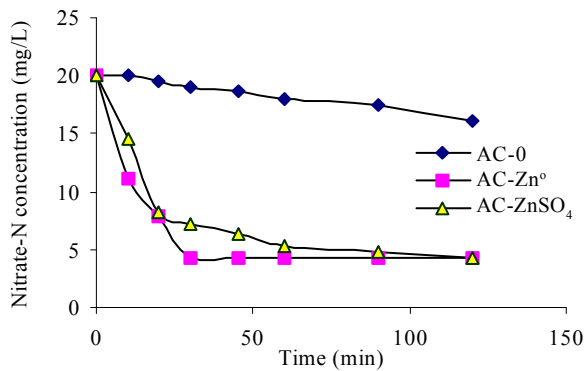


Fig. 3: Effect of different ACs on nitrate removal (T=20°C, C<sub>0</sub>=20mg/L and pH=6.2)

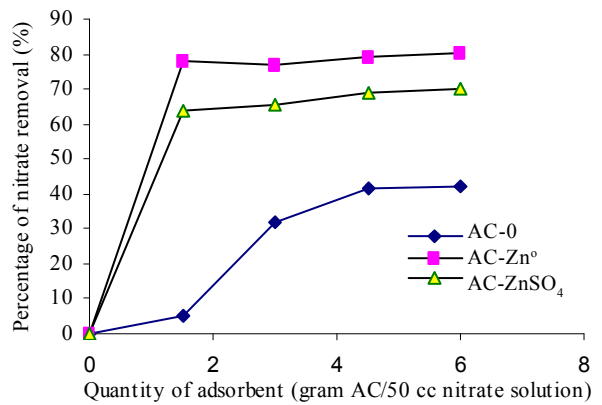


Fig. 5: Effect of adsorbent dosage on the percentage of nitrate-N removal (T=20°C, C<sub>0</sub>=20 mg/L and pH=6.2)

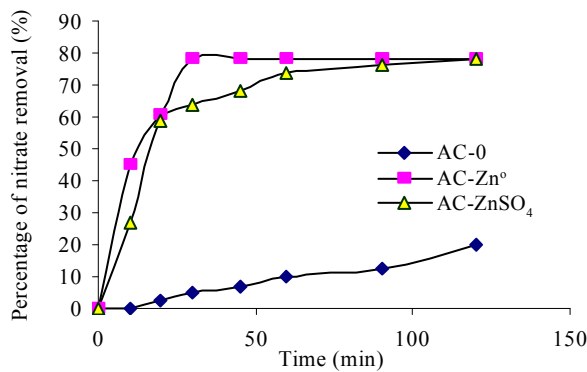


Fig. 4: Percentage of nitrate removal for different ACs (T=20°C, C<sub>0</sub>=20mg/L and pH=6.2)

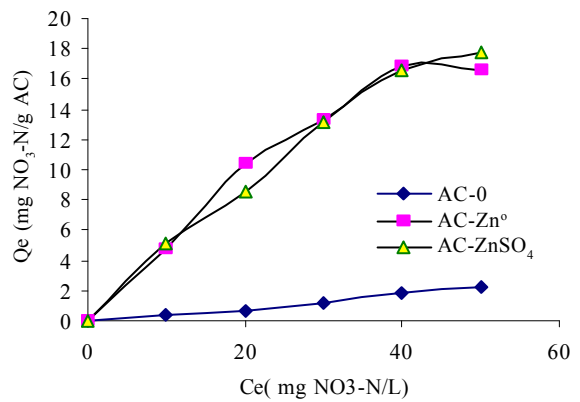


Fig. 6: Nitrate-N isotherms of all types of activated carbon in mass basis (T=20°C and pH=6.2)

Table 2: Water quality after treatment with ACs

	pH	Nitrite-N (mg/L)	Ammonia (mg/L)	Sulfate (mg/L)	Zn (mg/L)
AC	6.71	0.017	0.72	0	0
AC - Zn	5.39	0	0.65	0	1.4
AC - ZnSO <sub>4</sub>	5.9	0.012	0.5	0	1.8

## DISCUSSION

The nitrate could be effectively removed by AC that was impregnated in the presence of Zn<sup>0</sup> and ZnSO<sub>4</sub>. Bulk density and apparent density increased by modification of almond shell AC (Table 1). The SEM micrographs of AC<sub>s</sub> (Fig. 1) shows that original AC (a) was dark after modification (b and c); surface of modified AC lost the metallic glaze and the color of the surface also turned black. Comparing Fig. 1 a, b and c show that by modification of AC, macropores were filled by Zn<sup>0</sup> and ZnSO<sub>4</sub> and micropores were formed. Also, zinc presented at carbon surface as ZnO and increased positive charge of AC. This phenomenon increased ions adsorption such as nitrate. The SEM micrographs and energy dispersive x-ray microanalysis of ACs (Fig. 2) supports this subject. It was show that the AC-0 had 0% Zn of total elements (carbon exception) on the surface (Fig. 2), while with modification by Zn<sup>0</sup> and ZnSO<sub>4</sub>, Zn increased at surface by 80.67% and 34.89% of total elements composition (carbon exception). The studies conducted by Shen *et al.*, (2004) and Namasivayan *et al.*, (2006) supports this subject.

Figs. 3 and 4 show the effect of different ACs on nitrate removal from solution with 20mg/L nitrate-N concentration. While AC was used, the amount of nitrate removal reached 15mg/L as nitrate in 30min reaction. The final nitrate concentration was not in the standard range of WHO recommendation for water quality; while AC-Zn<sup>0</sup> and AC-ZnSO<sub>4</sub> were used, nitrate removal was lower than 10mg/L as nitrate-N. It was obvious that the modification of AC with Zn<sup>0</sup> and ZnSO<sub>4</sub> greatly enhanced the nitrate removal. This phenomenon may be caused by adsorption and chemical reactions. As for the AC-0, AC-Zn<sup>0</sup> and AC-ZnSO<sub>4</sub> at AC series, the AC-ZnSO<sub>4</sub> and AC-Zn<sup>0</sup> showed the highest removal capacity for nitrate, which was near to 60-80% in 30min

reaction. The equilibrium time was found to be 45 min for impregnated ACs. (Namasivayam *et al.*, 2006) experimented removal of anions, heavy metals, organics and dyes from water by adsorption on to ZnCl<sub>2</sub> activated coir pith carbon. Results showed that nitrate was removed as 95% by ZnCl<sub>2</sub> coir pith carbon at initial concentration of 20mg/L, temperature of 35°C, 200rpm and agitation time of 3h, while this reduction for coir pith carbon without ZnCl<sub>2</sub> modification was found to be negligible.

The mechanisms of nitrate removal included adsorption and chemical reactions with lower performance of chemical reactions. In the modification process, after impregnation of AC with Zn<sup>0</sup> and ZnSO<sub>4</sub>, micropores were formed. The SEM micrographs showed that MAC had a superior micropore content than its parent sample (Fig. 1).

The other advantage of impregnation by Zn<sup>0</sup> and ZnSO<sub>4</sub> is increasing of AC positive charges. This phenomenon increased anions adsorption such as nitrate. The studies conducted by the same experiments confirmed the results (Mizuta *et al.*, 2004; Cheng *et al.*, 2005; Shen *et al.*, 2006) studied removal of nitrate from drinking water using bamboo powder charcoal. Adsorption isotherm of nitrate-nitrogen onto commercial AC at 10°C showed that maximum amount of nitrate adsorption was 1.17 and 0.93 for bamboo powder charcoal and AC, respectively. Shen *et al.*, (2006) studied the effect of AC fiber structure and loaded metals on the adsorption of dichloroethylene. In their work, the AC was modified and impregnated with copper, which was transformed to metal oxides and reduced to elemental substance; the adsorption properties of dichloroethylene on the AC fiber was investigated. The results showed that both the pore structure of AC fiber and metal/oxide loading affected the adsorption capacity of dichloroethylene. The amount of AC adsorption increased with the increase in carbon dosage and reached a maximum value after a particular dosage. Effect of quantity of adsorbent AC and variation of percentage of nitrate removal with weight of adsorbent on nitrate removal is shown in Fig. 5. Study conducted in the same experiments showed that an increase in adsorbent dosage

increased the percent removal of nitrate and reached a maximum value after a particular dosage and our results were the same (Ozturk and Bektas, 2004).

Nitrate isotherms of all AC in mass basis are shown in Fig. 6. Ozturk (2004) and Bektas (2003) studied nitrate removal from aqueous solution by adsorption into various materials. The equilibrium time was found to be 45min for AC. Maximum amount removal by time was 4mg NO<sub>3</sub> per gram of AC while in this paper; maximum removal was more than 16 and 17mg nitrate-N per 1g AC for AC-Zn<sup>o</sup> and AC-ZnSO<sub>4</sub>, respectively.

### ACKNOWLEDGMENTS

This research was supported by the Department of Environmental Health, Tarbiat Modares University of Iran. Authors are also grateful to Mr. A. Rezaee, Tarbiat Modarres University, For providing SEM photographs.

### REFERENCES

- Almasri, M. N., Kaluarachchi, J. J., (2004). Assessment and management of long-term nitrate pollution of ground water in agriculture-dominated water-sheds. *J. Hydrol.*, **295**: 225-245.
- APHA, AWWA, WEF., (1995). Standard methods for the examination of water and wastewater, 20<sup>th</sup> Ed., Washington DC, USA.
- ASTM, D2854., (2002). Standard test method for apparent density of activated carbon. American Society for Testing and Materials, 15.01, D2854, West Conshohcken, PA., USA. p. 759-761.
- ASTM, (2002). Standard test method for determination of iodine number of activated carbon. American Society for Testing and Materials, 15.01, D4607, West Conshohcken, PA., USA. p. 814-818. West Conshohcken, PA., USA. p. 814-818.
- ASTM, (2002). Standard test method for moisture content of activated carbon. American Society for Testing and Materials, 15.01, D2867, West Conshohcken, PA., USA. p. 769-771.
- ASTM, (2002). Standard test method for particle size analyzed of Activated Carbon. American Society for Testing and Materials, 15.01, D2854, West Conshohcken, PA., USA. p. 821-822.
- Bakasi, S., Biswas, S., Mahjan, S., (2003). Activated carbon from bamboo-technol. Develop. toward commercialization. *BAMTECH.*, **3**: 14-19.
- Baker, F. S., Miller, C. E., Repik, A. J., Tolles, E. D., (1992). Activated carbon, *Encyl. Chem. technol.*, **4**: 1015-1037.
- Cheng, W., Dasgheib, S. A., Karanfill, T., (2005). Adsorption of dissolved natural organic matter by modified activated carbons. *Water. Res.*, **39**: 2281-2290.
- Cheremishinoff, N. P., Moressi A. C., Lund, H. F., (1978). Carbon adsorption handbook: Ann Arbor mich: 1-53.
- Hudak, P. F., (2000). Regional trends in nitrate content of texas groundwater. *J. Hydrol.*, **228**: 37-47.
- Mizuta, K., Matsumoto, T., Hatate, Y., Nishihara, K., Nakanishi, T., (2004). Removal of Nitrate - nitrogen from drinking water using bamboo powder charcoal. *Biores Technol.*, **95**: 255-257.
- Namasivayam, C., Sangeetha, D., Cherif, T., (2006). Recycling of agricultural solid waste, Coir pith, Removal of anions, heavy metals, organics and dyes from, water by adsorption onto ZnCl<sub>2</sub> activated coir pith carbon. *J. Hazard. Mater.*, **136**: 449-52.
- Oztürk, N. S., Bekta, T. E., (2004). Nitrate removal from aqueous solution by adsorption onto various materials. *J. Hazard. Mater.*, **B112**:155-162.
- Saswati, C., Kumar, M., (2005). Chemical denitrification of water by zero-valent magnesium powder. *J. Hazard. Mater.*, **135**: 112-21.
- Shen, W., Guo, Q., Yashu, Z., Liu, Y., Zheng, J., Cheng, J., Fan, J., (2006). The effect of activated carbon fiber structure and loaded copper, cobalt, silver on the adsorption of dichloroethylene, *Colloids and surf A: Physicochem. Eng.*, **273**:147-153.
- Shen, W., Parette, R., Zou, J., Cannon, F. S., Dempsey, B. A., (2007). Arsenic removal by iron-modified activated carbon. *Water. Res.*, **41**: 1851-1858.
- USEPA., (2000). Drinking water standards and health advisories, Office of Water., 822 B-00-001.
- Wisniewski, C., Persin, F., Cherif, T., Sandeaux, R., Grasmick, A., Gavach, C., Lutin, F., (2002). Use of a membrane bioreactor for denitrification of brine from an electro dialysis process. *Desalination.*, **149**: 331-336.
- WHO (2004). Guidelines for drinking water quality, 3<sup>rd</sup> Ed. Geneva., **1**: 417-420.
- Zhi-wei, H., Xin-hua, X. U., Da-hui, W., (2005). Reductive denitrifications of nitrate by scrap iron fillings. *J. zhejiang. Uni. sci.*, **6** (3): 182-186.