Wat. Res. Vol. 34, No. 1, pp. 185–190, 2000

Printed in Great Britain
0043-1354/99/$ - see front matter
PII: S0043-1354(99)00122-0
PERGAMON
www.elsevier.com/locate/watres

NITROGEN REMOVAL FROM FERTILIZER WASTEWATER BY ION EXCHANGE

S. LEAKOVIĆ[1]*, I. MIJATOVIĆ[2M], Š. CERJAN-STEFANOVIĆ[3M] and E. HODŽIĆ[3]

[1]Petrokemija, Aleja Vukovar 4, 44320 Kutina, Croatia; [2]Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, 10000 Zagreb, Croatia and [3]Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 20, 10000 Zagreb, Croatia

(First received 1 March 1998; accepted in revised form 1 March 1999)

Abstract—The wastewater treatment in the fertilizer factory in Kutina (Croatia) is carried out by an ion exchange process using strong acid cation and weak basic anion ion exchangers. The regeneration of cation exchange resin is performed by 56% HNO_3 while the anion resin regeneration is done by 16% ammonium hydroxide as an external regeneration process.

The wastewater in the investigation period contained a high content of nitrogen in ammonium form (with an average of 325 mg l^{-1} N-NH_4^+) as well as nitrogen in nitrate form (with an average of 201 mg l^{-1} N-NO_3). After treatment, the wastewater contained 8.7 mg l^{-1} of ammonium nitrogen and 7.0 mg l^{-1} of nitrate nitrogen and with the conductivity of 150 μS cm^{-1} it is added into the cooling water system.

As the nitrogen in collected wastewater is very high, the dilution is done prior to the ion exchange processing. The treated wastewater is a better choice for dilution process than decarbonisated water. In this case the exchange capacity of cation resin is higher by 9.3%.

Four types of anion resin were used at the wastewater treatment plant. The influence of 2% HNO_3 on LEWATIT S 4428 ion exchange resin was examined under laboratory conditions. Due to the effect of 2% HNO_3 on LEWATIT S 4428 anion resin during 24 days the exchange capacity decreased from the initial 1.19 mol l^{-1} to a final 0.71 mol l^{-1}.

The dynamic contact of 2% HNO_3 with the same anion resin in the column results also in a decrease of the exchange capacity by 32%.This confirms the harmful influence of nitrogen acid on the nitrate binding capacity and resin stability.

Four types of anion resins were used under industrial conditions. Under dynamic equilibrium the best results were obtained with the LEWATIT S 4428 resin.

Key words—ammonium, fertilizer factory, ion exchangers, nitrate, nitrogen, wastewater

INTRODUCTION

The production of mineral fertilizers belongs to industrial processes during which wastewater with a high quantity of pollutants is produced. Because of this, and for environmental protection reasons, the wastewater has to be purified. The wastewater from fertilizer production has a significant quantity of nitrogen in the ammonium and nitrate form. This wastewater also contains a certain extent of fluoride, nitrate, phosphate, silica and suspended matters.

There are many different processes and methods which are used for industrial wastewater treatment (Davis, 1994; Kroiss, 1994; Belhateche, 1995). Several well known methods for nitrogen removal can be satisfactorily used (Halling-Sørensten and Jørensten, 1993) specifically denitrification (Mijatović, 1992) and physicochemical processes (Matsumoto *et al.*, 1992). One of the common processes for wastewater treatment, recently used, is the ion exchange process (Philipot and De Laminat, 1988; Kataoka and Muto, 1991; Clifford and Xiaosha, 1993).

The ion exchange process was satisfactorily used for the treatment of municipal water (Andrews and Harward, 1994) and fertilizer wastewater (Arion *et al.*, 1986). Arion described the overloading of anion resin by the 3rd fraction of cation resin regeneration, as an activity which increases the working capacity of anion resin. However, the nitric acid contained in the 3rd fraction is a very strong oxidant and can have a harmful effect on the stability of anion resin. However, the wastewater treatment by ion exchange can also be dangerous if a high concentration of HNO_3 is used for the regeneration of cation resin at working conditions above 40°C (Davies, 1994).

*Author to whom all correspondence should be addressed. Tel.: +385-44-647-240; fax: +385-44-680-773; e-mail: razvoj1@petrokemija.tel.hr

This paper presents the experience of wastewater treatment by an exchange process in a fertilizer factory in Kutina (Croatia).

The wastewater was treated with strong acid cation resin and weak base anion resin. The cation resin regeneration is provided by nitric acid (56%) and anion resin by ammonium hydroxide (16%) applying the external regeneration process. It has a pretreatment program with sand filter and activated carbon filter. It also dilutes wastewater before the ion exchange process. The wastewater treatment plant which operates by ion exchange is shown in Fig. 1.

There are four fractions in the regeneration process. Fractions 1 and 4 return to the wastewater storage. Fraction 2 is the final product of regeneration. This is ammonium nitrate solution. After utilization to a 50% concentration it is used in NPK (nitrogen–phosphorus–potassium complex fertilizer) production. The conductivity of treated wastewater is up to 150 μS cm^{-1} and is used as additional water in cooling water system. Fraction 3 is used for subsequent saturation of the resins. The 3rd fraction from the cation exchanger regeneration is used for overloading of the anion resin. This part of the fraction contains 0.5–2.0% HNO_3.

The fertilizer wastewater treatment by ion exchange process has the following advantages:

1. Own chemical production for the regeneration of the ion resins.
2. Reuse of treated wastewater.
3. Utilization of product regeneration for fertilizer production.
4. There is no other pollutant.

This treatment has some disadvantages:

1. Unsatisfactory anion resin condition.
2. Unsatisfactory vacuum evaporation condition.

In order to improve the wastewater treatment plant detailed analyses were made of all parameters, which influence the ion exchange process. These parameters are:

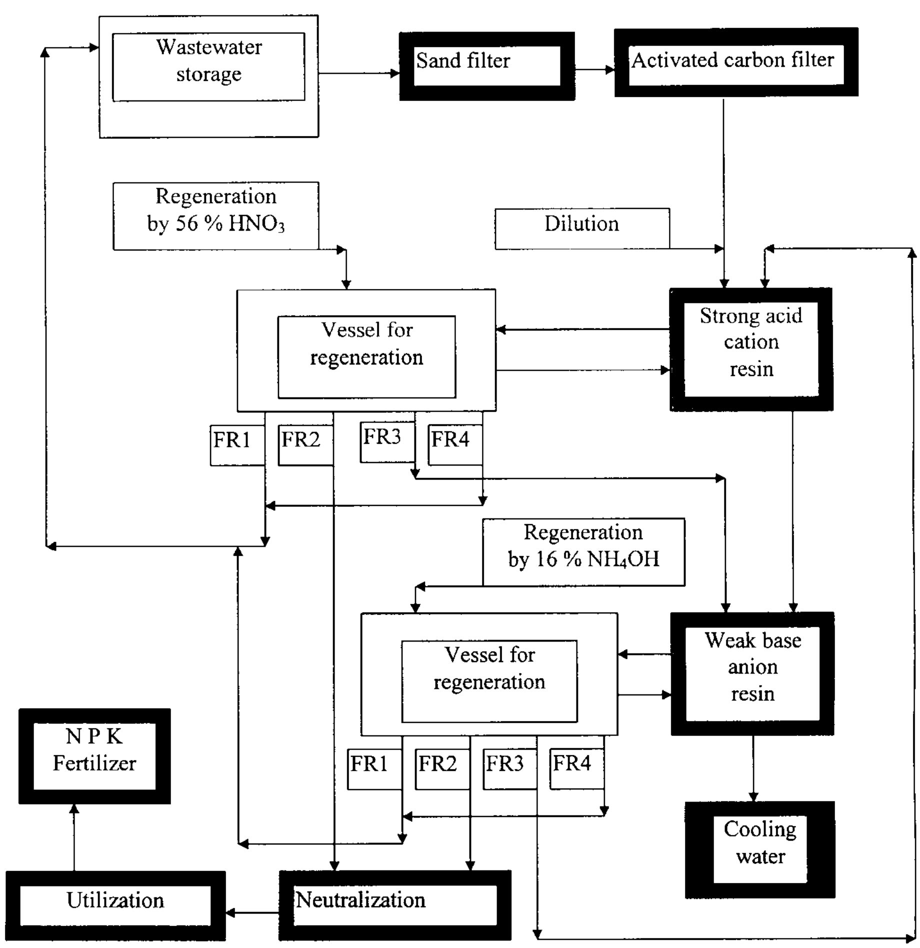

Fig. 1. Schematic review of the wastewater treatment plant by ion exchange in Petrokemija Kutina.

1. Saturation conditions:
   - High concentration of nitrogen.
   - Dilution process.

2. Regeneration conditions:
   - Chemicals: 56% HNO_3 and 16% NH_4OH.
   - External regeneration.

3. Overloading of ion resins:
   - Influence of HNO_3 on anion resin.

4. Wastewater chemical composition: Ca^{2+}, Mg^{2+}, P_2O_5, SiO_2, F^-, NO^{2-} and SO_4^{2-}
5. Ion resins quality.

This paper presents the possibility of wastewater dilution with treated wastewater. The influence of nitric acid on the ion exchange capacity of anion resin was investigated under laboratory conditions.

METHODS

The research was carried out during industrial production and under laboratory conditions. The anion resin volume was 5700 dm^3. The time needed for resin saturation was 2–3 h. Under industrial conditions the specific flow rate of resins is 40 $dm^3/h/dm^3$, which means that 40 dm^3 of wastewater flow through 1 dm^3 of ion resin in 1 h. Under laboratory conditions the specific flow rate was the same. The resin volume was 50 cm^3. The column height was 40 mm and the diameter was 22 mm. The conductivity during resin saturation was controlled on line. Nitrate nitrogen in the effluent was determined by a spectroscopic method.

In the laboratory, the influence of 2% HNO_3 on the exchange capacity of LEWATIT S 4428 anion resin was investigated. The permeate concentration of nitrate nitrogen in the effluent of the wastewater treatment plant was 8 mg l^{-1} in 1995. The permeate capacity of the anion resin was therefore determined at that point. For saturation the wastewater from the industrial process was taken at the outlet of the cation exchanger.

All the analytical data were determined by the standard methods (APHA, 1985).

RESULTS AND DISCUSSION

The collected wastewater from nitric acid production, from CAN (calcium ammonium nitrate) and NPK fertilizer production in the period from October 1996 to September 1997 contained an increased quantity of ammonium nitrogen (325 mg l^{-1}) as well as nitrate nitrogen (201 mg l^{-1}). After the dilution process had been carried out, the average amount of ammonium nitrogen was 176 mg l^{-1}, while the amount of nitrate nitrogen was 93 mg l^{-1}. The treated wastewater contained 8.7 mg l^{-1} in the form of ammonium nitrogen and 7.0 mg l^{-1} in the form of nitrate nitrogen (Fig. 2).

From these results it can be concluded that an ion exchange process can be satisfactorily used for fertilizer wastewater treatment when the ammonium nitrogen content is under 180 mg l^{-1} while nitrate nitrogen is under 100 mg l^{-1}.

Together with nitrogen separation from wastewater by ion exchange process, the separation of other components is also provided.

Table 1 shows the chemical composition of wastewater after the dilution process and after treatment by ion exchange.

Four types of anion resin were used: under industrial conditions DUOLITE A 374, PUROLITE A 104/2561, AMBERLITE IRA 93 SP and LEWATIT S 4428. The data for working capacity

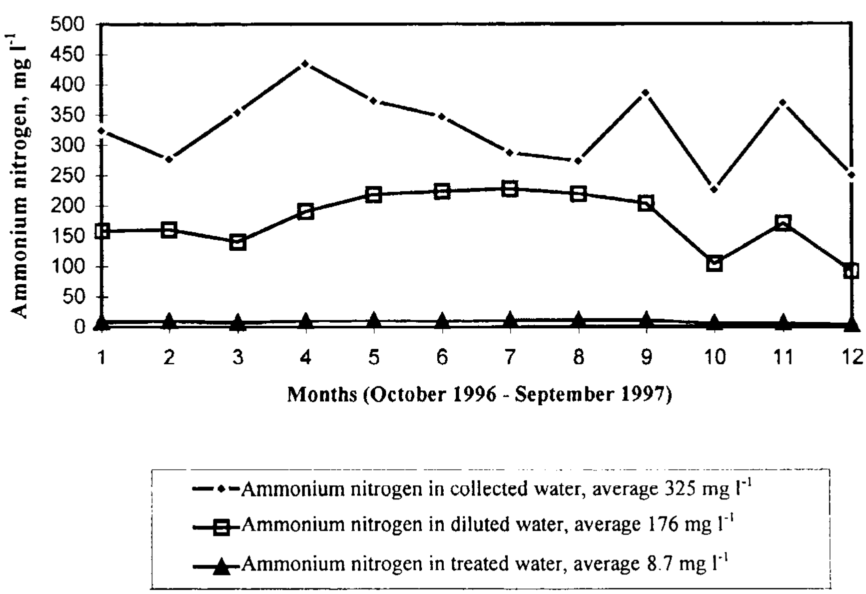

Fig. 2. Ammonium nitrogen removal in the wastewater treatment plant in the period from October 1996 to September 1997.

Table 1. Data for removing all components from wastewater in October 1997 under industrial conditions

Chemical composition	Plant inlet	Plant outlet
PH	8.7	5.1
N-(ammonium nitrogen) (mg l^{-1})	183	10.1
N-(nitrate nitrogen) (mg l^{-1})	100	7.2
N-(nitrite) (mg l^{-1})	1.3	0.3
$P_2 0_5$ inorganic(phosphate) (mg l^{-1})	1.4	0.5
F^- (fluoride) (mg l^{-1})	5.4	2.9
SiO_2 ionic (silica) (mg l^{-1})	7.6	6.4

of all the anion resins under industrial conditions are shown in Table 2.

After 3–4 months the DUOLITE A 374 resin had already an exchange capacity decrease of over 50%. The saturation condition and external regeneration had influence on physical properties as well as on the ion exchange capacity of the PUROLITE A 104/2561 and AMBERLIT IRA 93 SP resins. All of these resins were changed after 1 year. The best results were obtained with the LEWATIT S 4428 resin.

When analyzing the working conditions for wastewater processing, a particularly weak function of anion ion exchanger was detected. It was concluded that the nitric acid from the 3rd fraction, added for subsequent saturation, decreases the capacity of weak basic anion exchanger.

The influence of nitric acid on the exchange capacity of anion resin was studied on LEWATIT S 4428 resin in the laboratory. The influence of 2% HNO_3 on the ion exchange capacity of the anion resin was investigated after the period of 1, 3, 6, 12 and 24 days in the "batch" process.

The saturation was accomplished by decationized wastewater, from the wastewater treatment plant containing 90 mg l^{-1} of nitrate nitrogen. The nitrate permeate curves are given in Fig. 3. The experiment shows that the exchange capacity decreased from the initial 1.19 to the final 0.71 mol l^{-1}.

The investigation was continued with a dynamic activity of 2% HNO_3 on the anion resin in the column. The ion exchange capacity was controlled after 5, 10, 15 and 20 saturation cycles. It was accomplished by decationized wastewater from the real system, containing 140 mg l^{-1} nitrate nitrogen. The nitrate permeate curves are given in Fig. 4.

In this case the permeate capacity also decreased but from 1.37 to 0.92 mol l^{-1}. Thus, the harmful in-

Table 2. Data for determination of anion resins exchange capacity under industrial conditions

Saturation data	DUOLITE A 374	PUROLITE 104/2561	AMBERLIT IRA 93 SP	LEWATIT S 4428
Resin age (months)	6	10	3	3
N-NO_3– (inlet) (mg l^{-1})	146	98	115	92
N-NO_3–(outlet) (mg l^{-1})	6.9	7.9	18.1	3.1
Plant capacity (m^3h^{-1})	130	130	220	220
Saturation duration (h)	1.3	1.9	2.6	3.9
Resin volume (dm^3)	5700	5700	5700	5700
Working capacity (mol l^{-1})	0.3	0.28	0.69	0.96

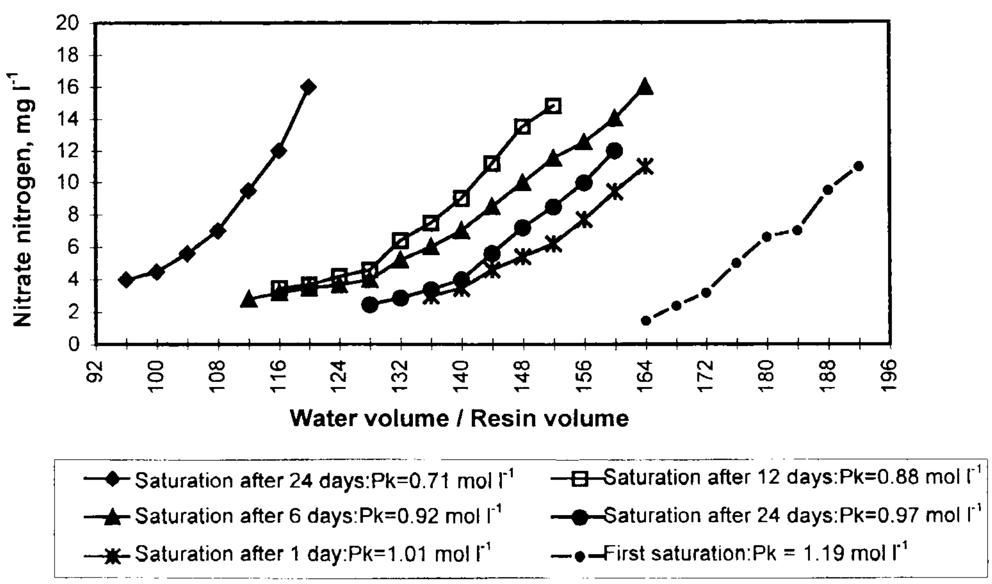

Fig. 3. Nitrate nitrogen permeate curves after 1, 3, 6, 12 and 24 days of 2% HNO_3 activity on the LEWATIT S 4428 resin.

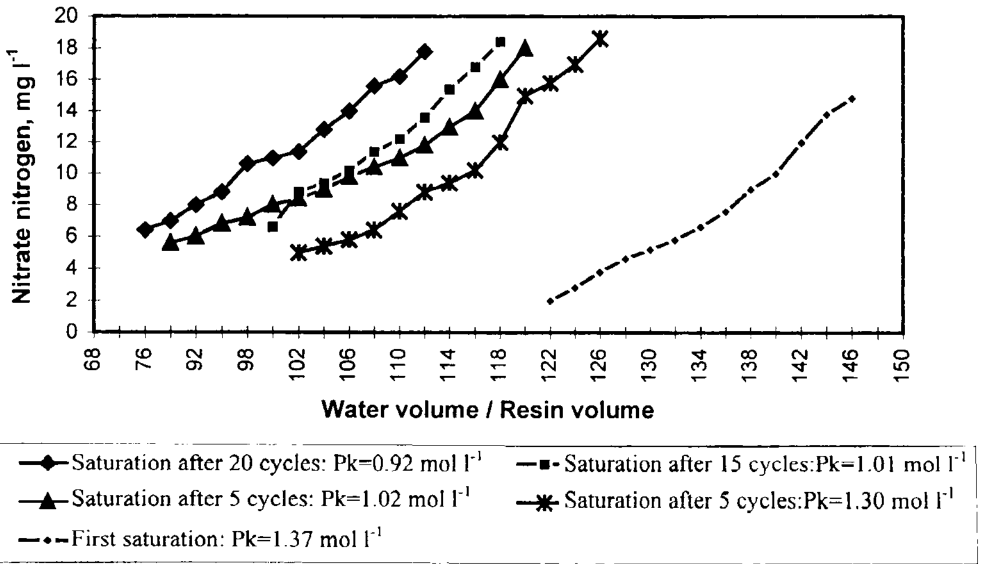

Fig. 4. Nitrate nitrogen permeate curves after 5, 10, 15 and 20 cycles of 2% HNO_3 activity on the LEWATIT S 4428 resin.

fluence of nitric acid on the ion exchange capacity of anion resin was confirmed.

In order to enhance the function of wastewater treatment plant, it would be advantageous to stop using the overloading of anion resin with the 3rd fraction from cation resin regeneration.

This would eliminate the harmful influence of nitric acid on the stability of anion resin and increase its lifetime.

At the beginning of the wastewater treatment plant operation, decarbonized water was used for dilution. The total hardness of decarbonized water was about 60 mg l^{-1} CaO. It can be concluded that besides NH_4^+ ions there were also other cations bound to cation resin. This influenced the decrease of NH_4^+ ions removal.

During the experiment in the laboratory the dilution was performed by treated wastewater from which all the cations were removed. For this activity the DUOLITE C 265 H cation resin was used. In the dilution with treated wastewater, the exchange capacity was 1.64 mol l^{-1} and in the dilution with decarbonized water it was 1.53 mol l^{-1} (Table 3 and Fig. 5).

The final recommendation is: the best choice for water dilution is treated wastewater. In this case the working capacity of cation resin will increase by 9.3%. This method has been used in Petrokemija for 2 years.

CONCLUSIONS

1. The treatment of wastewater from the fertilizer factory at Kutina by the ion exchange method yields satisfactory results when the wastewater

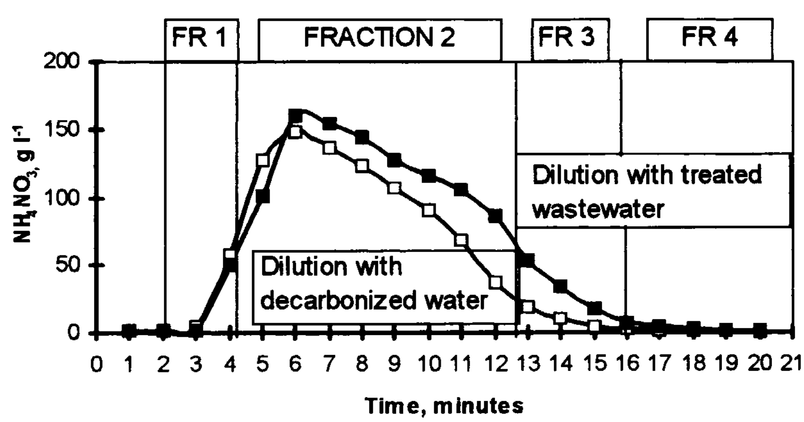

Fig. 5. Eluation curves determined after wastewater dilution with decarbonized water and with treated wastewater.

Table 3. The influence of dilution on the capacity of cation resin DUOLITE C 265 H under laboratory conditions

Saturation data	Dilution with decarbonized water	Dilution with treated wastewater
N-NO_{3-}(inlet) (mg l^{-1})	156	158
N-NO_{3-}(outlet) (mg l^{-1})	18	13
Water quantity (ml)	7760	7900
Resin volume (cm^3)	50	50
Working capacity (mol l^{-1})	1.53	1.64

contains less than 180 mg l^{-1} of N-NH_4^+ and less than 110 mg l^{-1} of N-NO_{3-}, respectively.

2. When wastewater contains more than 180 mg l^{-1} of N-NH_4^+ the wastewater dilution should be done prior to the ion exchange treatment. For this purpose the treated wastewater should be used.
3. The harmful effect of nitric acid on ion exchange capacity of anion resin was confirmed.
4. The wastewater treatment plant will be more efficient if the overloading of anion resin is stopped. This was confirmed by laboratory investigation.

REFERENCES

Andrews A. and Harward C. (1994) Islaham ion-exchange nitrate-removal plant. *J. IWEM* **8**, 120–127.

APHA (1985) *Standard Methods for Examination Water and Wastewater*, 16th edn. American Public Health Association, Washington, DC.

Arion N., Jagušt J. and Džendžo Ž. (1986) Fertilizer plant waste water treatment by ion exchange. *Nitrogen* **8–9**, 28–34.

Belhateche D. H. (1995) Choose appropriate wastewater treatment technologies. *Chemical Engineering Progress* **8**, 32–51.

Clifford D. and Xiaosha X. (1993) Ion exchange for nitrate removal. *Journal AWWA* **85**, 135–143.

Davies R. (1994) Troubleshoot ion-exchange equipment. *Chemical Engineering Progress* **1**, 63–71.

Davis M. (1994) Use advanced methods to treat wastewater. *Hydrocarbon Processing* **8**, 43–46.

Halling-Sørensten B. and Jørensten S. E. (1993) *The Removal of Nitrogen Components from Waste Waters*. Elsevier, Amsterdam.

Kataoka T. and Muto A. (1991) *Removal of Dilute Silicate by Ion Exchange. International Conference of Ion Exchange, Tokyo.*

Kroiss H. (1994) *Waste Water Treatment Plants with Nitrogen and Phosphorus removal. EWPCA International Conferences, Lisabon.*

Matsumoto R., McGinly P. M. and Jensen J. N. (1992) Wastewater treatment physicochemical processes. *Water Environment Research* **64**(4), 337–346.

Mijatović I. (1992) *Denitrification*. TEMPUS-EFAPTEM report, pp. 1–44. Narbonne, France.

Philipot J. M. and De Laminat G. (1988) Nitrate removal by ion exchange. *Water Supply* **6**(3), 45–50.