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Effect of HRT on the Nitrate Removal From a Synthetic Groundwater in A Bench Scale Denitrifying MBBR

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Abstract— **Groundwater is the main source of drinking water in the world. In some countries, especially those located in droughty area, groundwater can be the only water resource. Despite its strategic relevance, the quality of groundwater has progressively been getting worse over the last years mainly owing to the increasing level of nitrate up to reach values beyond a critical threshold. The presence of nitrate in groundwater is basically due to the extensive use of chemical fertilizers in intensive agriculture as well as a consequence of the discharge on soil of domestic and livestock organic wastes. This paper presents the results of the start-up and operation of a bench scale 1.8L Moving Bed Biofilm Reactor (MBBR) filled with kaldnes K1 to remove biologically nitrate from a synthetic groundwater with 60 mg NO_3^--N·L^{-1} and 3 COD/ NO_3^--N mass ratio. Acetate was used as carbon source. Different values of hydraulic retention time (HRT), ranging from 24 to 8 h, were successfully tested, proving the effectiveness and robustness of MBBR to treat groundwater even in severe operational conditions**

Keywords— **Nitrate, Groundwater, MBBR, HRT, Denitrification**

I. INTRODUCTION

Nitrate–nitrogen (NO_3^--N) concentration in surface water as well as groundwater has increased in many places in the world in recent years [1] Anthropogenic sources of nitrogen into the environment are mainly due to the use of chemical fertilizers in agriculture, the discharge of the effluents from septic tanks, the disposal on soil of livestock waste. Rural areas characterized by massive agricultural and farming activities are therefore the most susceptible to experience a groundwater contamination by NO_3^--N.

Significant level of NO_3^- in water can have adverse effects on the environment as well as on human health. Actually, a high NO_3^--N amount in surface water is the major contributing factor for the occurrence of the eutrophication phenomenon in lakes and seas. Moreover the consumption of water with a high NO_3^--N concentration may cause health diseases, such as methemoglobinemia in infants: NO_3^- is converted by NO_3^- reducing bacteria living in the intestine to NO_2^-, which reacting with the hemoglobin in blood forms methaemoglobin, and, as a consequence, oxygen is no longer carried to cells tissues, thus causing even the death of the exposed consumer. Furthermore, nitrate in water can be the precursor of the production of nitrosamines in human stomach [2–3]. Such compounds are known to be carcinogenic.

The contamination of groundwater by NO_3^- is a cause for concern as this strategic resource can be compromised and not more suitable for drinking water purpose, unless it is treated. Conventional treatments, on the other hand, can be unaffordable for poor economic countries that mostly coincide with those affected by water scarcity. The conventional treatments to remove NO_3^- from raw water, actually, operate using physical-chemical processes and include ion exchange, reverse osmosis and electro-dialysis. All these methods require high capital as well management costs, the latter mostly due to energy demand and waste disposal [4] The use of biological denitrification to convert nitrates to harmless chemical compounds (i.e. nitrogen gas) according to the equation [5] represents a valuable and economically convenient technical alternative to remediate groundwater contaminated by nitrate [6].

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Different biological systems can be used to perform the biological removal of nitrate from raw water, such as activated sludge, biofilters, bacterial beds and lagoon. Among them, the Moving Bed Biofilm Reactors (MBBRs) are the most promising. Actually, MBBRs exhibit the advantages of both, attached and suspended growth systems. They are based on the use of carriers where the biomass attaches and grows [7] and are operated similarly to the activated sludge reactors as carriers are in constant movement in the biological tank [8].

The performance of $MBBR_S$ depends on the shape and amount of carriers used to fill the reactor: commonly the volumetric percentage of tank occupied with carriers varies from 50 and 70%. Carriers are characterized by an extremely high specific surface area and this aspect enables the chance of having a higher biomass concentration in a smaller reactor volume than in conventional suspended growth system even taking into account that the whole surface area of carriers is

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not useful for growing biomass, but at least a 70%, as reported in the literature [9], thus reducing generally the costs of treatment.

The effectiveness of MBBRs is the result of attachment, growth and detachment of biofilm, and all these processes are influenced by the environmental and operating conditions: shape of carriers, thickness of biofilm, mixing intensity, pH, nutrients content, water ionic strength, temperature, nitrate loading rate (NLR), hydraulic retention time (HRT), etc...

HRT is one of the most critical designing and operating parameters, as a too short HRT will result in low removal rates, whereas an excessively long HRT will make the system not economically feasible. The optimal operating conditions for a MBBR is reached when the system operates with the shortest possible HRT associated with the most efficient removal rate [10]

The aim of this study, actually, has been to start-up and test the performance of a bench scale MBBR system to remove nitrate varying the HRT. Synthetic water miming a real groundwater affected by a significant level of nitrate was used as raw water, whereas acetate was used as external carbon source for feeding the denitrifying heterotrophic bacteria.

II. MATERIALS AND METHODS

A. MBBR configuration

In Figure 1 is reported a scheme of the bench scale MBBR system used in the experiment. The MBBR consisted of a plastic cylinder vessel (total volume of 2 L) with a working volume of 1.8 L. The top of MBBR is closed to ensure anoxic conditions.

The bioreactor was filled with kaldnes K1 as carriers up to have a filling percentage of 50 %. Carries are made of high density polyethylene (HDPE) (Figure 2a.).

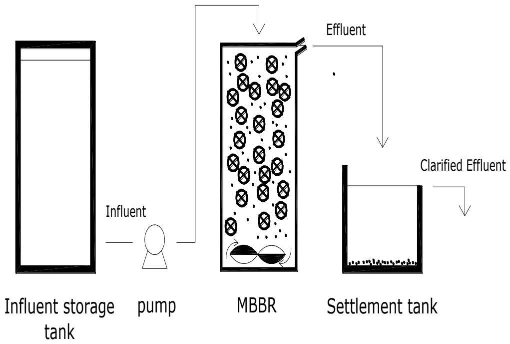

Fig. 1 MBBR system

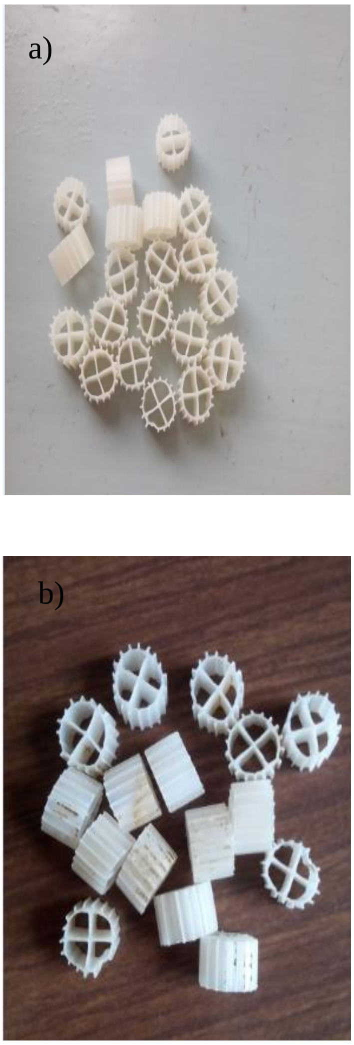

Fig. 2 Kaldnes K1 at the beginning (a) and at the end (b) of the MBBR start-up

A magnetic stirrer system was placed on the bottom of the reactor to perform the mixing of the bulk, thus avoiding the settlement of carriers and promoting the contact between biomass and substrates.

B. Bioreactor operation procedure

The MBBR was inoculated with activated sludge taken from a municipal wastewater treatment plant located in Nola, Italy. The initial sludge concentration in the reactor was 13.43 g/L as total solids (TS). The MBBR was fed in continuous mode with synthetic water doped with 30 mg/l NO_3^--N. The HRT was initially set to 24 hours. A peristaltic pump (WATSON MARLOW 520 Du) was used to transfer the influent from a 10 L storage tank to the biological reactor. The start-up of the MBBR took 5 weeks. During this time, a layer of biofilm grew on the surface of kaldnes (Figure 2b). At the end of start-up time the MBBR was operated for 10 days with the same HRT and a NO_3^--N concentration twice compared to that one used previously. The HRT was progressively reduced according to the sequence reported in table 1

TABLE I

OPERATING CONDITIONS OF THE ANOXIC MBBR

Days of operation	COD/ NO_3^- -N	HRT (h)	NO_3^--N (mg/L)
0-10	3	24	60
11-19	3	18	60
20-28	3	12	60
29-36	3	8	60

C. Synthetic water composition

Synthetic water was prepared using demineralised water containing 150 mg/L of KH_2PO_4, 325 mg/L of $NaHCO_3$ and 1% (v/v) of a solution composed of $FeSO_4.7H_2O$ (0.20 mg/l), titriplex (0.565 mg/l), 0.1% (v/v) of a trace nutrient solution containing $ZnSO_4.7H_2O$ (0.1g/l), $MnCl_2.4H_2O$ (0.03g/l),H_3BO_3 (0.3 g/l), $CoCl_2.6H_2O$ (0.2g/l), $CuCl_2.2H_2O$ (0.01g/l), $NiCl_2.6H_2O$ (0.02g/l), and $NaMoO_4.2H_2O$ (0.03g/l).[11]

KNO_3 was added to the synthetic water as nitrogen source up to reach a concentration of 60 mg NO_3^--N/L. The source of external carbon source used in this work was acetate, preferred to methanol and ethanol that are less safety for human health [12-13]. Therefore 263.681 mg of sodium acetate (CH_3COONa) was added to the synthetic water up to reach COD/ NO_3^- -N ratio equal to 3

D. Analytical methods

Samples were collected from the influent and effluent once a day, filtered through 0.45 μm filter and analyzed according to Standard Methods [14]. In all samples collected from the MBBR, concentrations of nitrate and nitrite were measured using a 761 compact IC (Metrohm).

Total solids (TS) and chemical oxygen demand (COD) were measured respectively with the difference of mass after heating the samles at 105°C and with a Hach spectrophotometer (photoLab 6600 UV-VIS). T and pH values were measured with the relating probes.

III. RESULTS AND DISCUSSION

The effect of HRT on the anoxic MBBR performance is shown in Figures 2 and 3. The removal efficiency of NO_3^--N and COD showed a decrease every time the HRT was reduced.

The MBBR was able to recover in a short time steady state conditions and extremely high efficiency (i.e. NO_3^--N removal close to 100%) every time the HRT was changed. Results obtained in this work are in agreement with those reported by [15] that found a denitrification efficiency close to 99% when the HRT was set in the range 4.5 and 8 hours.

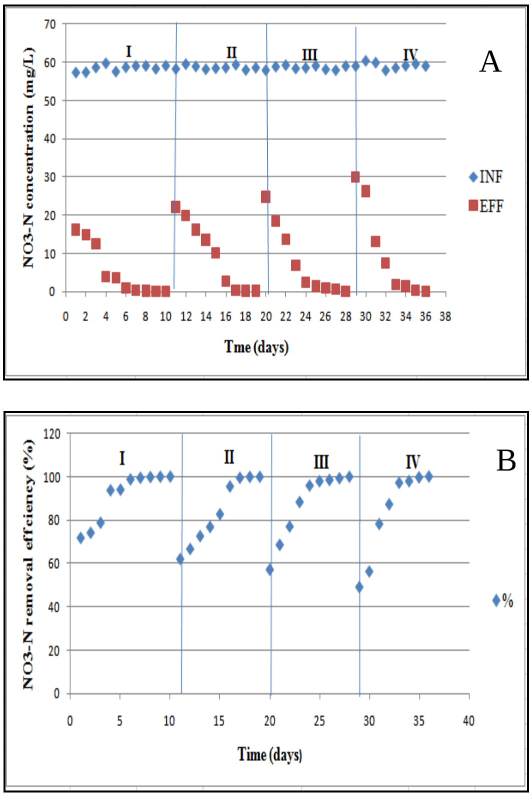

Fig. 3 Effect of NO_3^--N /L concentration in the effluent on the denitrication process: (A) numeric values; (B) percentage values. I, HRT =24h; II, HRT = 18h; III, HRT= 12; IV,HRT = 8h

In all HRT conditions the MBBR showed extremely good performance in removing nitrate. Moreover nitrates were completely reduced to nitrogen gas as no nitrite accumulation was found. A NO_3^--N removal percentage of 99.95 % was obtained with a HRT = 8.

Figure 3A shows the trend of COD concentration in the influent and effluent, whereas Figure 3B shows the percentage of COD removal as function of time.

Interestingly, the COD removal efficiency reached at steady state conditions slightly increased when the HRT decreased from 24 to 8 hours, up to reach the final maximum value of 88.77%. This result can be explained with the progressive growth and maturation of the biofilm on carriers surface. The residual concentration of COD can be decreased reducing the COD/ NO_3^--N ratio.

The good performance of the MBBR system is also exhibited by the trend of pH in the effluent and influent reported in Figure 4. An increase of pH in the effluent is a proof of the occurrence of the denitrification process that consumes acidity.

Literature indicates an optimum value of pH in the effluent ranging between7.6–8.6 [16].

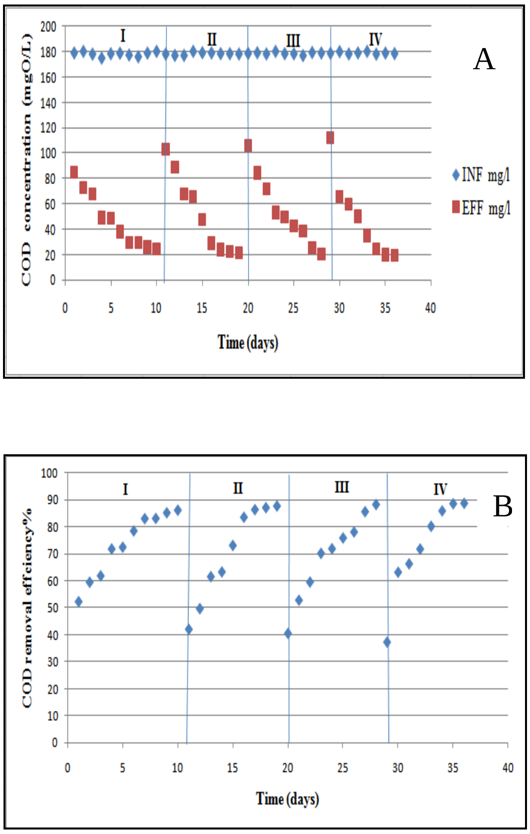

Fig. 4 COD removal efficiency: (a) numeric values; (b) percentage values. I, HRT =24h; II, HRT = 18h; III, HRT= 12; IV,HRT = 8h.

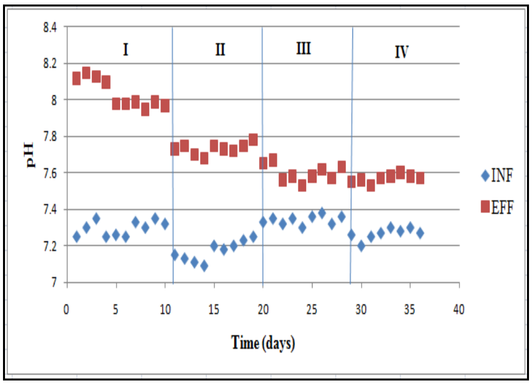

Fig. 4 pH trend in the influent and effluent of MBBR. I, HRT =24h; II, HRT = 18h; III, HRT= 12; IV,HRT = 8h.

V. CONCLUSIONS

The good results obtained from this work show the great potentiality of MBBR as convenient system to remove nitrate from groundwater. Actually, MBBR system showed a good resilience every time the operating conditions were changed and set to harder values

The best results with HRT equal to 8 hours in terms of NO_3^--N and COD removal efficiency were actually 99.95 and 88.77%, respectively. The residual amount of COD can be reduced by decreasing the COD/ NO_3^--N up to reach an optimal value or by providing the treatment system with an activated carbon filter.

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