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EFFECT OF RECYCLE RATIO AND HYDRAULIC RETENTION TIME ON DENITRIFICATION-NITRIFICATION PROCESS

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Abstract: In this study, the elimination of nitrogen compounds from is based on nitrifiication and denitrification. Ammonium released from the mineralization of nitrogen-containing organic compounds is oxidized first to nitrite/nitrate in nitrification process. During denitrification, nitrate is reduced to dinitrogen. The parameters effect this process are pH, temperature, electron donor/accepter ratio, hydraulic retention time nitrate-recycling rate etc. In this study, sequential batch denitrification-nitrification reactor was operated for testing different nitrate recycling ratio (100-700%). The batch reactor was fed with Kahramanmaraş urban wastewater during 80d at constant temperature of 25±0.5°C. The reactor performance was determined by color, ammonium (NH_4^+), nitrate (NO^-_3), nitrite (NO^-_2), inorganic carbon (IC), total organic carbon (TOC) parameters. According to our results, 100% recycling time was found optimum. Nitrate and ammonium removals were over 99%.

Keywords: Urban wastewater; denitrification; Nitrification; recycle rate

INTRODUCTION

In the past few decades, the existence of nutrients in wastewater has received considerable attention due to its potential eutrophic problems and other hazardous effects on the receiving bodies (Camargo and Alonso, 2006). The major effect of releasing wastewater rich in organic compounds and inorganic chemicals such as phosphates and nitrates on receiving body is mainly eutrophication There are different technologies for nitrogen removal such as ion exchange (Sancho et. al. 2017), adsorption (Chatterjee et al., 2009), membrane separation (Richards et al., 2010; Alikhani & Moghbeli, 2014), electrodialysis (Öznülüer et al., 2013) and biological denitrification-nitrification. Biological methods are more cost effective compared with physical–chemical techniques (Fan et al., 2009). Therefore, biological nitrification-denitrification is the most prevalently used process for nitrogen removal from wastewater (Park et. al. 2017). In a conventional approach, nitrogen elimination is done through sequential nitrification and denitrification.

Biological nitrogen removal from wastewater may be performed by adopting various process configurations. One of them is the sequential batch reactor (SBR). The SBR, unlike all continuous systems, operates as a time-orientated activated sludge system. The denitrification process, which is the first step, can be classified as heterotrophic denitrification or autotrophic denitrification. An organic carbon source is used as an electron donor to convert nitrite and nitrate to free nitrogen gas under anoxic conditions by heterotrophic bacteria. This process is very efficient in wastewater when a sufficient carbon source is available (Chung et. al. 2014). Autotrophic denitrification, in which denitrifying bacteria rely on inorganic electron donors and use inorganics (carbon dioxide or bicarbonate) as carbon sources. The heterotrophic denitrification process is the most greatly used denitrification process because of its high denitrifying rate (Xu et. al. 2015). The process of denitrification is the heterotrophic oxidation of nitrate, first to nitrite then to gaseous nitrogen compounds in anoxic conditions, however the process of nitrification is the autotrophic oxidation and this process is including two steps. In the first step, ammonium is converted to nitrite and then nitrite is converted to nitrate in the second step under aerobic conditions (Jianlong et. al. 2008).

Temperature, pH, dissolved oxygen concentration and solids retention time (SRT) are important parameters in nitrification and denitrification kinetics, so it needs to be checked frequently with equipments. In previous studies showed that the denitrification efficiency of nitrogen removal from black water reached to about 73% with a low dissolved oxgen (DO) range of 0.15–0.35 mg/L (Hocaoglu et. al. 2011). It is also very important to select an appropriate temperature in the denitrification proses were carried out with various centigrade degrees (0–40 °C) and optimum temperature for denitrification was observed at 25–27°C (Canion et. al. 2014). Additionally, Pan *et. al.* (2012) found the best nitrogen removal efficiency in the pH optimal range of 7.5–8.0. Besides these, liquid recycle ratio is a significant operating parameter that controls the amount of nitrate to be denitrified in the anoxic zone, because the circulation of liquid that contains nitrate and nitrite was necessary in conventional biological nitrification–denitrification process combined anoxic and aerobic units. Researchers found that when recycle ratio increased, denitrification efficiency would be strengthened (Tan et. al. 2008). In addition to these parameters, the rate of recirculation also affects the efficiency of nitrification-denitrification. It is necessary to select a suitable recycle ratio to obtain the optimum condition for both processes, because the effects of recycle ratio on denitrification and nitrification are quite different.

The aim of this study was to investigate the effect of different nitrate recycles rates and hydraulic retention times on nitrogen removal in the sequential batch denitrification-nitrification reactor.

MATERIAL AND METHODS

Microbial culture and wastewater

The SBR system were inoculated with sludge taken from a full-scale municipal wastewater treatment plant (Gaziantep Wastewater Treatment Plant, Gaziantep, Turkey), and acclimatized for 30 days. A sludge age of 20 days was maintained by withdrawing the necessary volume of biomass/liquid mixture daily. The mixed liquor suspended solid (MLSS) concentration was kept 3000 mg/L during operation. In this study, urban wastewater was taken from influent of wastewater treatment in Kahramanmaras, Turkey and average characterization of wastewater is shown in **Table 1.**

Reactor and Experimental Matrix

Laboratory scale sequencing two sequencing batch reactors (SBRs) with a working volume of 1 L were used for the removal of nitrogen from urban wastewater (**Fig. 1**). Aeration was provided to nitrification reactor by air pump run on a timer connected to plastic tubes through gas-diffusing inlets evenly placed at the bottom of the reactors. The temperature of SBR was at 25±1 ºC. pH was monitored with a pH electrode (Mettler Toledo,

Table 1. Characterization of Urban Wastewater

Pollutions	Value
TOC	120 mg/L
IC	100 mg/L
NH_4^+	20 mg/L
NO_3	2 mg/L
pH	8
Color	270 Pt-Co

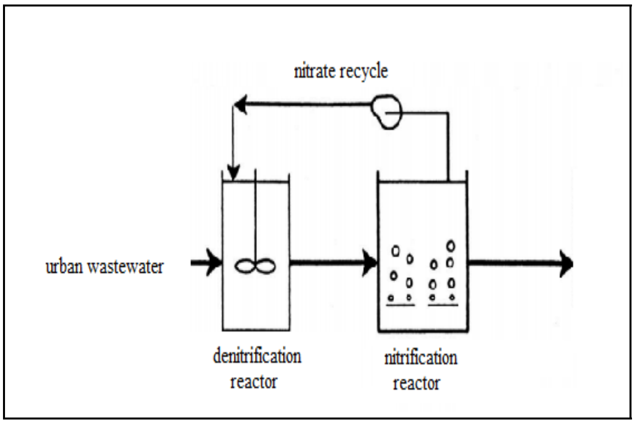

Figure 1. Schematic view of SBRs

Table 2. Denitrification reactor operating conditions

Parts	Hydraulic retention time(HRT) (h)	Nitrate recycle ratio (R) (% of the influent flow)	Sludge retention time (SRT) (d)
I	12	without recycle	15
II	24	100	15
III	24	300	15
IV	24	700	15

USA). During the cycle measurements, pH, amonium, nitrate, IC, color were monitored. The reactor performance was evaluated for around 80 days in three different parts (**Table 2**).

Summary of reactor operating conditions is shown in **Table 2**. In the first part of study (start-up), the system was operated without nitrate recycling at HRT of 24h for both reactors. Later, HRT was decreased to 12h in nitrification reactor and 100% nitrate recycling was applied (Part II). Later, nitrate recycling was increased to 300 and 700% in Period III, and Period IV, respectively. Nitrification reactor was fed with denitrification reactor effluent. At start-up period, MLSS concentration in nitrification reactor was 2000mg/L, but was kept 3000mg/L for the rest of study.

Analytic Methods

Supernatant were firstly filtered through sterile syringe 0.45µm filter (Sartorius AG, Gottingen, Germany), before the ammonium, nitrate, nitrite and IC measurements. Inorganic carbon (IC) was measured using TOC-TN analyzer (Shimadzu, TOC-VCPN and TNM-1, Kyoto, Japan). An ion chromatography (Dionex ICS-3000) was used to measure the concentrations of ions (ammonium, nitrate, nitrite) (Dionex, Sunnyvale, CA, USA) with Ion Pac AG19 guard and AS19-CS19analytical columns. Eluent containing 8mM sodium carbonate (Na_2CO_3) and 1.5mM sodium hydroxide (NaOH) was prepared for nitrite and nitrate measurements. 20mM methanesulfonic acid (CH_3SO_3H) was prepared for ammonium measurements. Eluents were used for anion and cation analyses with a flow rate of 1 ml/min. Biomass concentration was measured as absorbance at 600 nm followed by reference to an experimentally derived standard curve (ABS600nm=0.621 MLSS + 213.93; R^2=0.989). pH was measured using a pH probe (340i, WTW, Oslo, Norway). Color (as Pt-Co) was analyzed using HACH DR/5000 spectrophotometer.

RESULTS AND DISCUSSION

NH_4^+(ammonium) removal performance

NH4 removal performance of both reactors is shown in **Fig. 2**. Influent ammonium concentration was about 20mg/L, however; as wastewater used for this study was real wastewater, fluctuation was observed and increased

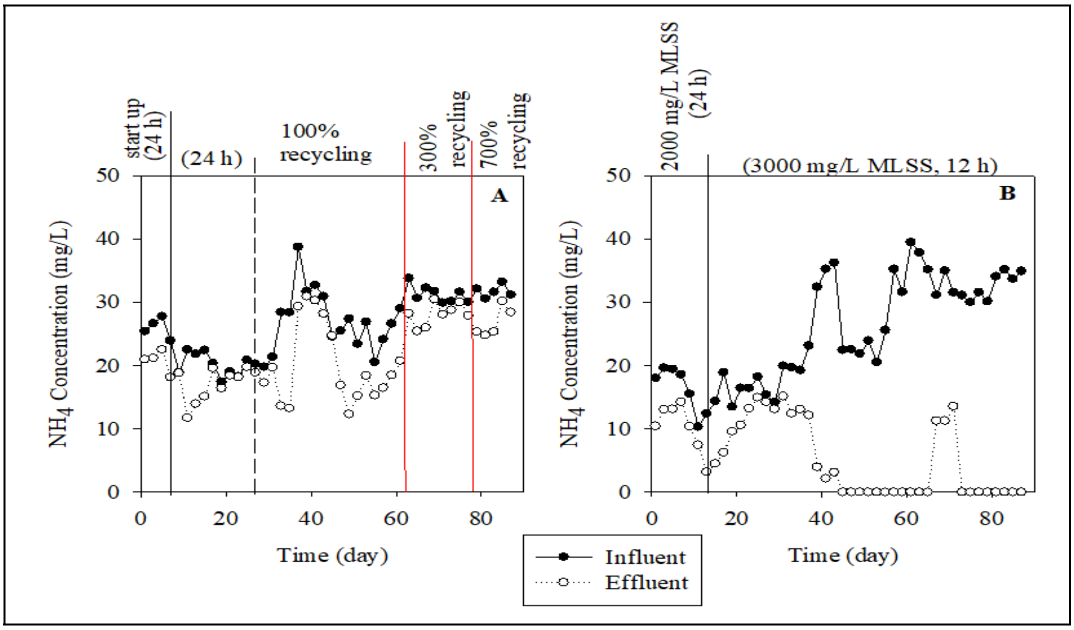

Figure 2. NH4+ removal profile (A: denitrification reactor, B: nitrification reactor)

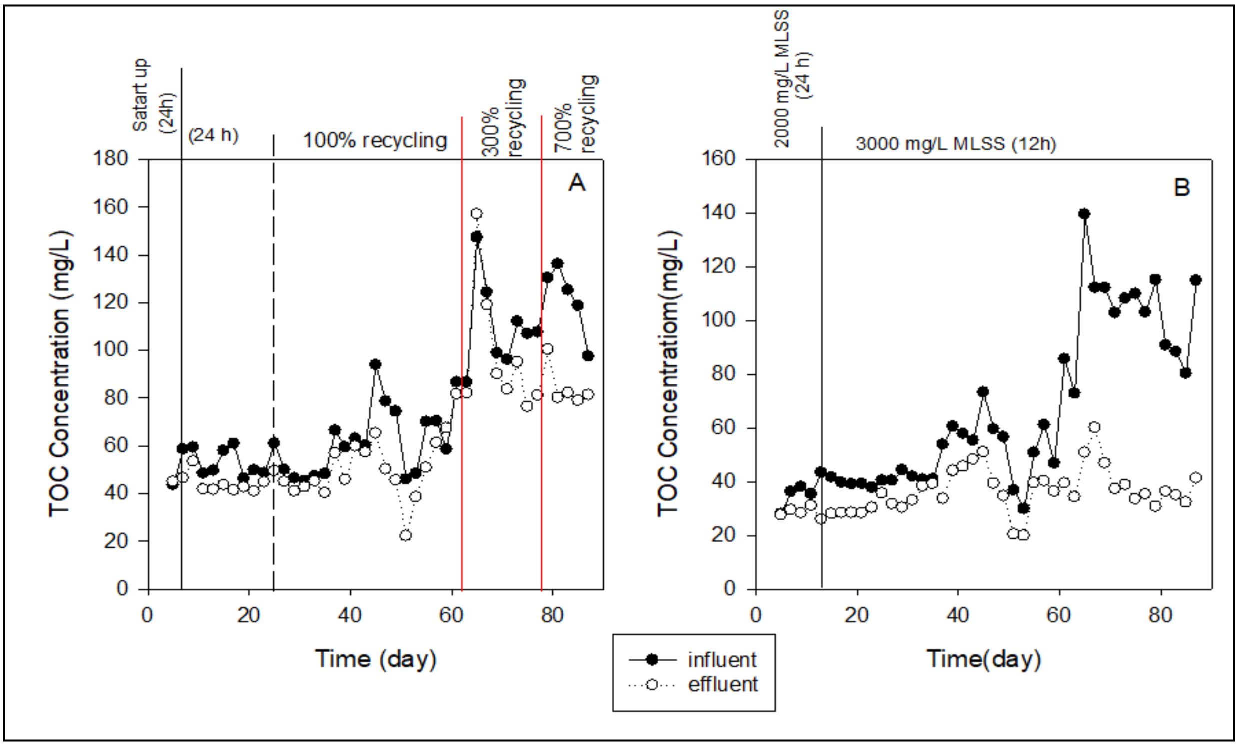

Figure 3. TOC removal profile (A: denitrification reactor, B: nitrification reactor)

to about 30mg/L. NH4removal in denitrification reactor was around 15-20%. As expected, ammonium removal in denitrification reactor was limited. This consumed ammonium was related to the bacterial nutrient demand. Ammonium was used for only as a source of nutrient for bacteria. Changing recycling ratio did not affect this phenomenon. In nitrification reactor, increasing bacteria concentration to 3000mg/L improved ammonium removal. After day 40, the removal efficiency was over 99%. Additionally, ammonium removal in nitrification reactor was increased significantly due to the dilution of return sludge (R= 100%) and nitrate recycling stream (increasing from 100% to 300-700%) and average effluent NH4 concentration was almost 0 mg/L.

TOC removal performance

The variations of TOC concentrations in the reactor system are presented in **Fig. 3**. In the first period, both reactors were operated at HRT of 24h. TOC removal efficiency was almost stable during study periods corresponding to 35%TOC removal. The reason for increasing influent TOC concentration after day 60 was due to the wastewater nature. Nitrate recycling was increased to 300 and 700% in Period III, and Period IV, respectively. This increase improved TOC removal in nitrification reactor corresponding 50% and 80%, respectively.

It could be seen that nitrate removal efficiencies in this system were always kept as high as over 95% despite of the variation in influent nitrate concentration. Similar to our results, it was found that nitrate recycling ratios had neglectable effect on the removal efficiencies of chemical oxygen demand (COD) and ammonium (Chen et al., 2011). A higher nitrate recycling ratio resulted in a higher NO_3 load in the denitrification reactor. Therefore, along with the increasing of nitrate recycling ratio, a slightly high percentage of TOC removal was observed as a result of organic matter uptake and the aerobic oxidization as a result of DO recirculation (Andalib et al., 2011) from the nitrification reactor. When nitrate recycling ratio was increased to R = 300% to R = 700%, a higher TOC consumption was observed in the denitrification reactor, however effluent TOC concentration was increased. This indicated that the system was being operated under the high denitrification rate. Additionally, nitrate was exhausted hence electron accepter was limited for organic matter oxidation.

IC removal profile

Figure 4 shows schematically inorganic carbon production and consumption during operational conditions. Inorganic carbon production and consumption profile of periods was in accordance with the ammonium and nitrate conversion profile. Initial IC concentration was around 110 mg/L. The percent IC consumptions in nitrification reactor was almost stable until day 60, afterwards increased, corresponding to 36% and 42%, respectively. In denitrification reactor, IC was increased in effluent due to the alkalinity production, especially after day 60 in which nitrate recycling ratio was high.

Nitrate removal profile

The effects of various nitrate recycling ratios (R = 100%, R = 300%, and R = 700% on nitrate removal and production of the system were shown in **Fig. 5**. As known, nitrification is the two step biological conversion of ammonia to nitrite and then to nitrate under aerobic conditions. Mixed culture in the denitrification reactor could manage effective nitrate removal and effect of increasing recycling ratio to 300 and %700 during periods III and IV respectively, on anoxic nitrate removal efficiency was negligible, the effluent nitrate was increased too few. This was due to the DO recycling from nitrification reactor as DO is known to have adverse effect on denitrification. Almost complete denitrification was achieved and accumulation of nitrite was not observed. As expected, nitrate was produced due to the conversion of ammonium to nitrate in nitrification reactor. Increasing recycling ratio to 300

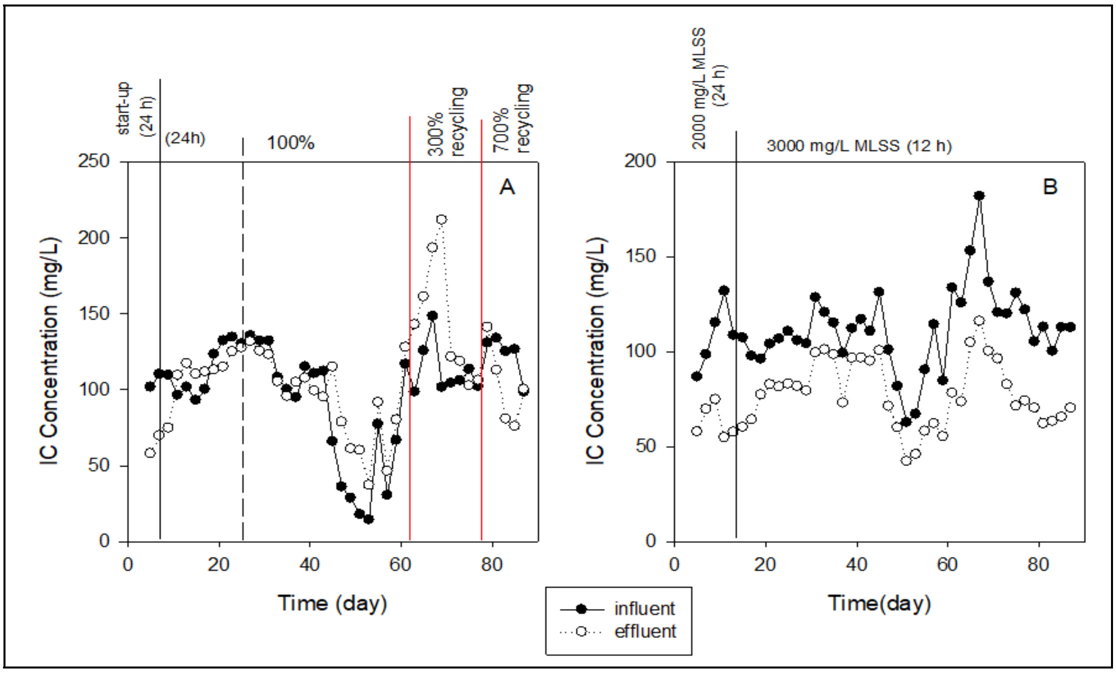

Figure 4. IC removal profile (A: denitrification reactor; B: nitrification reactor)

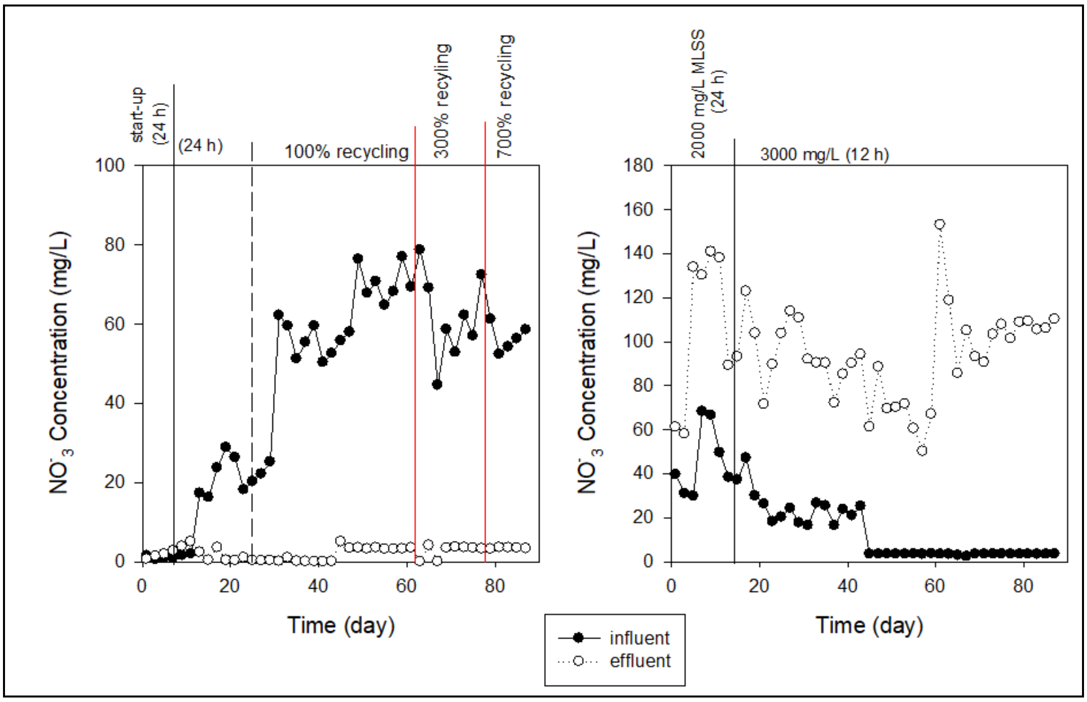

Figure 5. NO_3 removal profile (A: denitrification reactor, B: nitrification reactor)

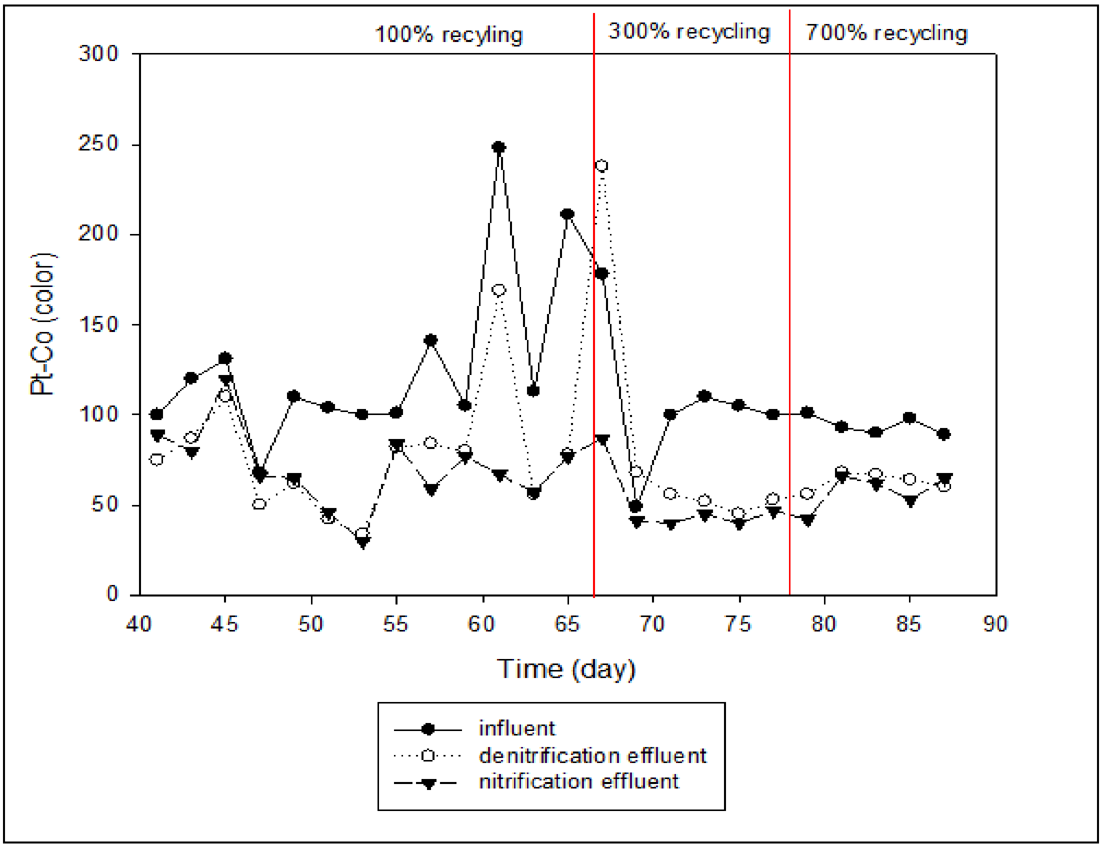

Figure 6. Color removal profile

and 700% during periods III and IV, improved nitrate production concentration (Ge et al., 2010). In an economic view, the energy consumption at nitrate recycling ratio of 300% and 700% was approximately three and seven times higher, respectively, than that of 100%. As a result, higher nitrate recycling ratio than 100% should be avoided in this system from an economical point of view.

Color removal profile

Colour in wastewater is an obvious indicator of water pollution. **Fig. 6.** shows schematically color removals during operational conditions. Fresh sewage is typically gray in color. However, as the travel time in the collection system increases, and more anaerobic conditions develop, the color of the wastewater changes sequentially from gray to dark gray and ultimately to black. In city of Kahramanmaraş, total flow rate of commercial/industrial discharges to sewage system is about 4,600m^3/d corresponding to approx.5%of total sewage flow rate. In addition, textile industry produce approx. 79% of dischargers. In Kahramanmaraş there are settled around 250 textile companies, in which 5 of these are among the 500 largest companies in Turkey. Untreated effluents from textile industries are usually highly colored and contain a considerable amount of contaminants and pollutants. For this reason, color removal is also tested in this study. The color removal was observed mostly in denitrification reactor. The role of nitrification reactor on color removal was negligible but 50% removals were observed in denitrification reactor.

CONCLUSION

In this study, the effects of various nitrate recycling ratios (R = 100%, R = 300%, and R = 700% on nitrification- denitrification system was determined. Obtained results were summarized below:

- Nitrate recycling rates greater than 100% of influent flow is seems to not beneficial because of insufficient substrate availability, dissolved oxygen recirculation that reduced nitrate removal.

- When deciding nitrate recycling ratios, actual conditions in the WWTPs and economic potential should be taken into consideration

- Anitrate-recycling ratio around 100-300% could provide aproper compromise between removal efficiency and costs.

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