J Ind Microbiol Biotechnol (2005) 32: 195–203
DOI 10.1007/s10295-005-0229-y

ORIGINAL PAPER

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Comparison between biological and chemical treatment of wastewater containing nitrogen and phosphorus

Received: 2 February 2004 / Accepted: 24 March 2005 / Published online: 4 May 2005
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Abstract The present work compared chemical and biological treatment methods to achieve the most efficient treatment for the reduction or elimination of phosphorus and nitrogen from mixed industrial–domestic wastewaters. Batch chemical precipitation by ferric chloride and aluminum sulfate (alum) and a continuous biological suspended growth system were investigated as well as the optimum operating conditions. Concerning chemical treatment, Alum generally achieved a higher removal efficiency percentage for the investigated pollutants compared with $FeCl_3$ at their optimum pH and dose, especially with chemical oxygen demand (COD). $FeCl_3$ treatment achieved success only with phosphorus removal, while none of the COD, 5-day biochemical oxygen demand (BOD_5), total nitrogen (TN) and $N–NH_3$ achieved acceptable treatment and remained above the maximum permissible limits (MPL). Thus, for such wastewaters, alum is more efficient than $FeCl_3$. Biological treatment exhibited higher efficiencies, particularly towards nitrogen. TN removal increased by increasing the flow rate to 30–60 l/day. $N–NH_3$ removal was effective at the slowest flow rate and decreased with increasing flow rate, while an opposite trend was recorded for $N–NO_3$. At all flow rates, phosphorus levels were below the accepted MPL for discharging into natural systems. Moreover, there was a general trend for the proposed biological treatment to achieve a high removal efficiency for BOD_5 and COD, bringing them to acceptable levels to be released into watercourses safely, especially at the slowest flow rates. Thus, integration between the proposed chemical and biological treatment is highly recommended, producing high-quality effluents acceptable by the environmental law.

Keywords Activated sludge · Chemical · Nitrogen · Phosphorus · Treatment

Introduction

Excess nitrogen and phosphorus enhance the growth of harmful algae and the excretion of potent toxins by specific groups [10]. Their ultimate decomposition by aerobic bacteria and fungi consumes large amounts of dissolved oxygen (DO), leading to oxygen depletion and eutrophication. Nitrogen is becoming increasingly important in wastewater management because it can have many adverse effects on the environment and public health. Ammonia is extremely toxic to fish and many other aquatic organisms [7]. Although nitrate itself is not toxic, its conversion to nitrite is a concern to public health, especially in water consumed by infants [12]. Lake Mariut, Alexandria, Egypt, is one of the most polluted lakes in the world. It receives agricultural, industrial and municipal wastewater rich in nitrogen and phosphorus. Therefore, environmental engineers consider the removal of phosphorus and nitrogen from point sources, such as sewage treatment plants, a cost-effective and appropriate method for controlling the level and extent to which eutrophication occurs [8, 11, 15, 17, 21]. Biological treatment is an efficient technology for the removal of nitrogen, phosphorus and organic matter. Coagulation is the main physicochemical process used in phosphorus and organic matter removal [10, 23]. In some cases, a combination of these treatment methodologies is used.

As water resources from the Nile are limited and the population and economy are growing, the irrigation

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sector will increasingly be forced to use non-conventional water resources. These include the renewable groundwater aquifer in the Nile valley and Delta and the reuse of treated agricultural drain and sewage water. Accordingly, the role of lakes and reservoirs will become more important from the viewpoints of storage of fresh water resources. Therefore, their protection from pollution resulted from dumping untreated wastewater is a must.

The present work aimed to compare chemical and biological technologies to determine the most efficient reduction or elimination of phosphorus and nitrogen in the primary treated effluent of the west wastewater treatment plant (WWTP), Alexandria, Egypt, to minimize the environmental impact on the receiving ecosystem of Lake Mariut.

Materials and methods

Characterization of water quality

The primary treated water samples collected from the effluent of the WWTP were subjected to measurement of some physico-chemical parameters before and after treatment for phosphorus and nitrogen removal. The investigated parameters included pH, turbidity, 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total phosphate (TP) and phosphate $P–PO_4$, nitrite nitrogen ($N–NO_2$), ammonia nitrogen ($N–NH_3$), nitrate nitrogen ($N–NO_3$), organic nitrogen (O–N), total nitrogen (TN) and total Kjeldahl nitrogen (TKN). The TKN represents the digested nitrogen forms using the Kjeldahl method, while TN represents all forms of nitrogen, including nitrate and nitrite. All the investigated parameters were determined according to the standard procedures described in the standard methods for the examination of water and wastewater [4].

Primary treatment at the WWTP

Wastewater samples were collected from the final effluent of the WWTP of the Alexandria General Organization for Sanitary Drainage, Egypt, after primary treatment. The WWTP receives domestic–industrial wastewater, which is collected through different pumping stations and transferred to the WWTP through a tunnel. At the WWTP, Alexandria wastewater is screened using one or more of the six bar screen channels. The screened wastewater flows to the aerated grit chambers where the majority of the heavier inorganic materials are allowed to fall into the grit hoppers at the bottom of the chambers. After that, wastewater is distributed to one or more of eight rectangular sedimentation tanks. The sedimentation tanks allow the settling of heavier organic materials to the bottom, while lighter materials float to the surface and clarified effluent flows over weirs to the plant effluent channel, which directly discharges into Lake Mariut.

Batch chemical treatment

Samples were chemically treated by coagulation in batch experiments, using alum and ferric chloride. Batch treatment was carried out using the jar test procedure described by Cohen [5]. To determine the optimum pH for each coagulant, pH values ranging from 5 to 8 at a fixed coagulant dose were examined. To study the effect of coagulant concentration, different coagulant doses ranging from 50 mg/l to 400 mg/l were examined at the pre-determined optimum pH. During the treatment, each sample was stirred rapidly (250 rpm) while the coagulant was added slowly for 3 min. The speed was reduced in a stepwise manner, at an interval of 100 rpm every 60 s until the flocculation stage was reached. The speed was then maintained at 20–30 rpm for a further 10 min for optimum floc formation. The characteristics of the chemically treated effluents were determined after 30 min settlement. Samples for analysis were taken by a suction device allowing the withdrawal of accurate amounts from jars for complete analysis [1, 2, 22].

Continuous biological treatment

An aerobic reactor using activated sludge was used for biological treatment of the contaminated samples on a continuous basis. Activated sludge was allowed to settle and acclimatize, reaching a steady state within 1 week, after which treatment was carried out and samples were collected from the system at each flow rate. Biological treatment by activated sludge in the present study took place at eight different rates ranging between 5 l/day and 60 l/day, with a hydraulic retention time ranging from 48 h to 4 h. At each flow rate, six runs were carried out containing different loads of pollutants. At each run, the percent removal efficiency (RE) of the different pollutants was calculated after treatment and the average percent REs of these parameters for each flow rate were calculated.

Biological treatment unit

In the present study, a compact activated sludge biological unit was used, similar to that used by Abou ElEla et al. [1, 2]. The conventional settler was substituted with a high-rate settler. The unit consisted of an aerated packed column and inclined plate settler. The aerated packed column is a biological reactor without recycle. The high-rate settler usually reduces liquid retention time in the settling device by reducing the distance necessary for the flocculated particles to reach the boom [2]. Different hydraulic loads were examined to define the optimum operating conditions for the removal of both nitrogen and phosphorus. In the design of the treatment reactor, rounded corners were avoided to eliminate any difficulty in the manufacturing process. Also, the aeration and sedimentation tanks were combined in one unit, which represents a compact system. A peristaltic pump was used to control the inflow of a known volume of wastewater. The unit consisted of the following [2]:

a. Aeration tank: dimensions 10×25×40 cm, volume = 10 l
b. Sedimentation tank with high-rate settler: volume = 12 l.

Characteristics of the activated sludge

Sludge volume, sludge weight, volatile matter content, DO level in the reactor and sludge volume index (SVI) were all determined using standard procedures [4]. Sludge volume and weight were determined using a measuring cylinder in which sludge was placed and allowed to settle for 30 min, after which the sludge volume and weight were measured.

Results and discussion

Characterization of the raw wastewater

Raw samples were collected over six different weeks according to the experimental scheme to achieve average effluent strengths. Table 1 represents characterization of the raw samples at each sampling time in addition to their averages during the study period. Averages recorded for pH, COD, BOD_5, TN, N–NH_3 N–NO_3 N–NO_2, O–N and P–PO_4 during the study period were 7.52, 357.6, 170.15, 27.48, 24.85, 0.11, 0.02, 2.62 and 6.12 mg/l, respectively. These results showed that the levels of nutrients (nitrogen, phosphorus) and organic matter (BOD_5, COD) far exceeded the levels stated by Egyptian Environmental Law no. 4/1994 for discharging wastewater into natural water systems. In that law, the maximum permitted levels (MPL) of BOD_5, COD, P, N–NH_3 and N–NO_3 should not exceed 60, 100, 5.0, 3.0 and 40.0 mg/l, respectively, while in the raw samples their averages recorded much higher levels except for nitrates. The estimated increased levels recorded were 2.84-, 3.58-, 1.2- and 8.25-fold higher than the MPL for the first four, respectively. These results indicated very dangerous levels of such contaminants for any receiving water. Such pollutants adversely affect DO levels by consuming it during their aerobic decomposition; and the extremely high level of ammonia is highly toxic to the aquatic life and consumes large amounts of DO to reach stability during the nitrification process. Phosphorus and TN levels in the raw effluents represent a hazardous source of pollution in Lake Mariut since they are continuously discharged at these high levels, leading to advanced eutrophication and deterioration of the Lake Mariut ecosystem. Thus, removal of such contaminants from the raw effluents is of high priority to protect such a system.

Primary treatment of effluent at the WWTP

The plant has been designed to handle flows averaging 185,000 m^3/day. Under optimum operating conditions, the facility removes a minimum of 85% of the influent total suspended solids, 27% of the total solids, 68% of the BOD_5 and 72% of the COD. However, after the primary treatment, the levels of most pollutants still exceed the MPL stated by Egyptian Environmental Law no. 4/94. Therefore, elimination or minimization of the pollution strength in that effluent is a must to protect the ecosystem of Lake Mariut.

Optimizing the pH for batch chemical treatment using alum

Figure 1a shows the residual concentrations of the investigated pollutants, after using a fixed alum dose of 150 mg/l at different pHs in the range of 5–8 with an interval of 0.5 pH units. The results indicated that, at this dose, the optimum for turbidity, TN and TP removal was pH 6, while for the highest removal of COD it was pH 7. Coagulation with alum achieved maximum percent removal efficiencies of 65.5, 91.1, 5.9 and 86.7% for COD, turbidity, TN and TP, respectively. Therefore,

Table 1 Characterization of the primary treated effluent of the WWTP

Parameter	Weeks						Maximum	Minimum	Average
	1	2	3	4	5	6			
PH	7.28	7.39	7.48	7.67	7.64	7.66	7.67	7.28	7.52
COD (mg/l)	346.9	359.9	334.4	328.2	371.8	404.2	404.2	328.2	357.61
BOD (mg/l)	158.3	161.6	141.5	164.2	176.9	218.3	218.3	141.5	170.15
TN (mg/l)	31.01	34.31	24.42	24.11	22.50	28.55	34.31	22.50	27.48
NH_3 (mg/l)	28.71	32.13	22.40	22.22	21.02	22.03	32.13	21.02	24.75
NO_3 (mg/l)	0.06	0.13	0.04	0.09	0.19	0.15	0.19	0.04	0.11
NO_2 (mg/l)	0.01	0.03	0.03	0.01	0.03	0.03	0.03	0.01	0.02
O–N (mg/l)	2.23	2.06	1.97	1.80	1.29	6.37	6.37	1.29	2.62
PO_4 (mg/l)	5.79	6.15	5.01	7.47	5.41	6.89	7.47	5.01	6.12

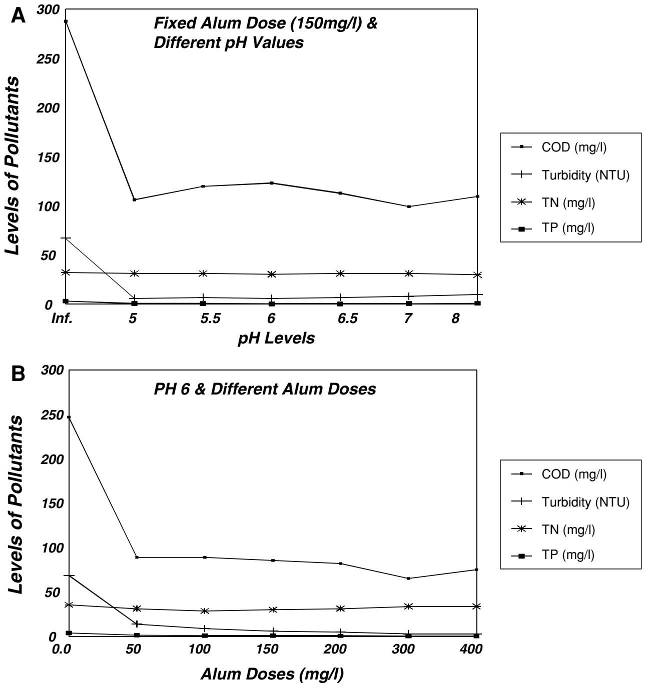

Fig. 1 Residual concentrations of the investigated pollutants, after using a fixed alum dose of 150 mg/l at different pH (**a**) or different alum doses at fixed pH (**b**)

alum had a high efficiency for turbidity, TP and COD removal, while the highest removal efficiency achieved for TN was only 5.9%, which was considered insufficient. According to the environmental law (4/94), alum treatment at this dose brought TP, COD and turbidity to levels acceptable for discharge into surface water without hazardous impact, while it was not acceptable in the case of TN.

Optimizing alum dose

Figure 1b shows residual concentrations of the investigated parameters at the fixed optimum pH 6 with different alum concentrations (50–400 mg/l), which resulted in different removal efficiencies. The maximum achieved percent REs were 73.6, 95.6, 19.1 and 94.4% for COD, turbidity, TN and TP, respectively. These results showed higher REs for all the investigated parameters, compared with those obtained at 150 mg/l alum and pH 6, as shown in the previous treatment. Results also indicated that, although the maximum RE for removing COD and turbidity was obtained at 300 mg/l alum, TN at 100 mg/l alum and TP at 400 mg/l alum, a concentration of 200 mg/l resulted in high REs for COD (66.7%), turbidity (92.7%) and TP (81.3%), all of which are acceptable under law 4/94. However, the highest removal efficiency of TN achieved by this treatment (19.1%) at 100 mg/l alum was not sufficient, since the level of TN still exceeded the MPL.

Chemical treatment using alum at the optimum pH and concentration

Table 2 represents residual concentrations and the average percent RE of all parameters before and after treatment using the optimum pH and alum concentration. This treatment was repeated four times with wastewater collected at different times; and thus the initial levels of the investigated parameters were slightly different. The removal efficiency ranges of the investigated parameters in the four treatment batches were as follows: COD 35.9–62.5%, BOD_5 55.47–66.35%, TN 3.65–16.91%, N–NH_3 2.4–17.0%, N–NO_3 3.3–66.7%, N–NO_2 50–100%, O–N 4.94–18.26% and P–PO_4 77.55–97.4%. Figures resulting from alum treatment indicated that reasonable removal for biodegradable organic matter (BOD_5) and phosphorus was obtained, which enabled them for safe discharge, while this was not true for COD and N–NH_3.

Optimizing the pH for chemical treatment using $FeCl_3$

Figure 2a represents residual concentrations of the different investigated pollutants at a pH range of 5–8 and a fixed dose of $FeCl_3$ (150 mg/l). Results indicated that, at this dose, the highest achieved percent REs were between pH 5.5 and pH 6.0. Generally, treatment at pH 6 brought the levels of COD, turbidity and TP into

Table 2 Batch chemical treatment of the WWTP effluent using the optimum alum dose (200 mg/l) at the optimum pH 6. *Inf.* Influent, *Effl.* effluent

Parameter	Inf.1	Effl.1	Inf. 2	Effl. 2	Inf. 3	Effl. 3	Inf. 4	Effl. 4	Average RE (%)
pH	7.9	6.7	7.8	6.7	8.1	6.4	8.4	6.5	
COD (mg/l)	277.4	133.6	274.0	102.7	219.2	140.4	236.3	123.3	49.5
BOD (mg/l)	111.15	49.5	117.14	39.21	111.44	42.55	98.11	39.74	60.83
TN (mg/l)	31.03	28.87	29.28	24.33	32.58	31.39	35.32	31.6	9.51
N–NH_3 (mg/l)	27.3	25.5	27.7	23.0	24.2	23.6	23.5	21.9	8.2
N–NO_3 (mg/l)	0.21	0.07	0.16	0.1	0.26	0.09	0.3	0.29	43.22
N–NO_2 (mg/l)	0.02	0	0.02	0	0.02	0	0.02	0.01	87.7
O–N (mg/l)	3.5	3.3	1.4	1.23	8.1	7.7	11.5	9.4	10.26
P–PO_4 (mg/l)	2.73	0.61	3.07	0.33	4.3	0.11	3.85	0.39	88.47

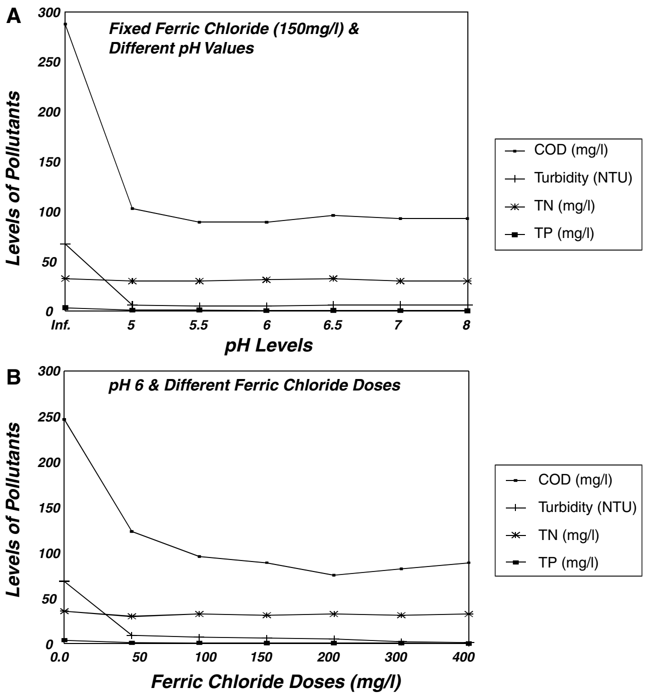

Fig. 2 Residual concentrations of the different investigated pollutants at a pH range of 5–8 and a fixed dose of $FeCl_3$ (**a**) and at different $FeCl_3$ doses in the range of 50–400 mg/l at pH 6 (**b**)

compliance with the law (4/94) and they were under the MPL while, as with alum, the level of TN was not acceptable. Therefore, 150 mg/l $FeCl_3$ and pH 6 was considered optimum only for COD, turbidity and TP, which reached 89.0 mg/l, 5.0 turbidity units and 0.39 mg/l, respectively. However, coagulation using $FeCl_3$ was not a satisfactory treatment for the removal of TN, of which ammonia was the main component in the wastewater used in the present study.

Optimizing $FeCl_3$ dose

Residual concentrations of the investigated pollutants at the different $FeCl_3$ doses in the range of 50–400 mg/l at pH 6 are shown in Fig. 2b. Results indicated that 400 mg/l $FeCl_3$ achieved the highest removal of turbidity (98.5%) and TP (91.3%), while 200 mg/l $FeCl_3$ achieved the highest removal of COD (69.5%). However, 200 mg/l $FeCl_3$ can be considered as the optimum dose since it brought COD, turbidity and TP to levels acceptable by law 4/94, while TN levels were not environmentally accepted at any dose of $FeCl_3$ (as also shown with alum).

Chemical treatment using $FeCl_3$ at the optimum pH and concentration

The general averages (four runs) for the percent REs of the different pollution loads present in the raw effluents were calculated (Table 3). Coagulation using $FeCl_3$ at pH 6 and the optimum dose (200 mg/l) revealed that success was only achieved with phosphorus removal, while all the other investigated parameters were above the MPL, although high REs were obtained. In the case of P–$PO_{4,}$, the concentration range of the raw samples was 6.19–6.58 mg/l and this was reduced to a range of 1.28–1.9 mg/l, with 79.28% recorded as the highest RE. None of the COD, BOD_5, TN and N–NH_3 achieved acceptable treatment by $FeCl_3$. The highest achieved REs for those parameters were 50.32, 51.78, 14.20 and 13.66%, respectively, with general averages for the four batches of 38.98, 41.08, 5.55 and 5.62%, respectively. After treatment, the lowest achieved concentrations of COD, BOD_5, TN and N–NH_3 were 263.7, 90.05, 31.38 and 28.92 mg/l, respectively, all of which exceeded the MPL. With respect to nitrates and nitrites, their levels in the raw samples were very low and did not need treatment.

Comparison between alum and $FeCl_3$ efficiency in chemical treatment

In general, at their optimum dose and pH, alum achieved higher REs for the investigated pollutants than $FeCl_3$, especially with COD (Tables 2, 3). The average REs using alum were 49.5% (COD), 60.8% (BOD_5), 9.51% (TN), 8.2% (N–NH_3), 43.22% (N–NO_3), 87.5% (N–NO_2), 10.26% (O–N) and 88.47% (P–PO_4). In contrast, although high REs were obtained, $FeCl_3$ achieved success only with phosphorus removal (79.28%). The general RE averages for the four batches were 38.98, 41.08, 5.55 and 5.62% for COD, BOD_5, TN and N–NH_3, respectively, none of which achieved acceptable treatment. Thus, for such kinds of wastewater, alum is more

Table 3 Batch chemical treatment of the WWTP effluent using the optimum $FeCl_3$ dose (200 mg/l) at the optimum pH 6

Parameter	Inf.1	Effl.1	Inf. 2	Effl. 2	Inf. 3	Effl. 3	Inf. 4	Effl. 4	Average RE (%)
pH	7.35	6.38	7.50	6.67	7.28	6.78	7.20	6.50	
COD (mg/l)	486.30	345.89	530.82	263.70	455.48	304.79	486.23	273.97	38.98
BOD (mg/l)	187.11	90.23	158.24	94.50	168.56	123.44	165.21	90.05	41.08
TN (mg/l)	35.29	33.95	36.57	31.38	36.51	35.22	35.32	34.80	5.55
N–NH_3 (mg/l)	32.97	32.11	33.50	28.92	32.25	31.41	31.24	30.10	5.62
N–NO_3 (mg/l)	0.26	0.19	0.31	0.12	0.47	0.20	1.05	0.33	53.56
N–NO_2 (mg/l)	0.03	0.02	0.03	0.01	0.04	0.02	0.04	0.00	54.17
O–N (mg/l)	2.03	1.64	2.73	2.33	3.75	3.59	3.71	3.65	6.02
P–PO_4 (mg/l)	6.19	1.28	6.42	1.34	6.58	1.90	6.23	1.84	75.01

efficient as a first step in a combined treatment sequence, compared with Fecl_3. Smith et al. [24] obtained similar results on phosphorus removal from swine manure, using alum where 84% RE was obtained from an initial concentration of 5.5 mg/l in the normal manure, bringing the effluent to a final phosphorus concentration of 0.87 mg/l. In another study [13], FeCl_3 and alum were used (optimum dose range 90–100 mg/l) in a coagulation–flocculation treatment of wastewater for the removal of suspended solids (SS) and COD. REs of 55% and 95–100% were achieved for COD and SS, respectively. The optimum pH was determined as pH 6, which significantly affected SS removal, but the pH range of 6–8 did not affect COD removal.

Continuous biological treatment: activated sludge

The sludge analysis showed that the average volume of the sludge produced was 550 ml/l. The SVI ranged between 117 and 221 with an average value of 168. Volatile matter accounted for 60% of the total sludge and the average sludge weight was 3.6 mg/l. The DO level in the reactor ranged between 2.0 mg/l and 4.0 mg/l.

Biological treatment efficiency

Table 4 summarizes the effectiveness of the proposed biological treatment at the different operating conditions.

Nitrogen removal

The results clearly show that, with the increase in hydraulic load from 5 l/day to 20 l/day (retention time from 48 h to 12 h), the ammonia nitrogen removal reached nearly 100% due to the nitrification process. With the increase in flow rate from 30 l/day to 60 l/day (retention time from 8 h to 4 h), the percent ammonia removal decreased from 87.97% to 55.39%, with residual values of 5.52 mg/l and 10.60 mg/l, respectively. Thus, removing NH_3 from the present wastewater where it was the most common form was only effective up to a flow rate of 20 l/day and then slowed down with increasing flow rate, which was coupled with an increase in the organic load. An opposite trend was recorded for nitrate concentration where, at the slowest flow rate, high nitrate concentrations were recorded up to 20 l/day, after which a clear decrease was noticed, reaching the lowest recorded level at 60 l/day. This was mainly due to inhibition of the nitrification process at the fastest flow rates, leading to a reduction in nitrate formation from ammonia while, at the slowest flow rate, nitrification was effective so it reached the maximum recorded nitrate levels. Concerning TN removal, it was noticed that TN removal increased from 12.60% at the flow rate of 30 l/day to 40.76% at the flow rate of 60 l/day. The removal of TN may be due to the denitrification step associated with the decrease in nitrate concentration. Denitrification is almost the main reason for the increase in TN removal under the highest running flow rates,

Table 4 Average REs for different pollutants using an activated sludge reactor at different flow rates and retention times under aerobic conditions

Parameter	Flow rate (l/day) and retention time (h)							
	5 l/day, 48 h		10 l/day, 24 h		15 l/day, 16 h		20 l/day, 12 h	
	Inf.	Effl.	Inf.	Effl.	Inf.	Effl.	Inf.	Effl.
pH	6.98–7.65	8.10–8.66	7.12–7.65	7.8–8.3	7.10–7.8	8.0–8.4	7.4–7.9	8.0–8.2
COD (mg/l)	265.3–435.4	13.6–61.2	278.9–513.6	44.9–75.0	302.7–394.6	50.0–65.0	224.5–459.2	20.4–105.4
BOD (mg/l)	100.1–180.2	5.4–30.3	127.2–183.1	17.9–30.0	123.0–165.1	20.1–26.0	112.3–229.7	8.2–42.2
TN (mg/l)	28.7–36.6	28.3–35.3	32.6–38.4	32.2–37.1	21.9–27.01	20.4–25.4	23.02–27.0	20.9–26.6
N–NH_3 (mg/l)	27.8–32.3	0.83–1.05	30.2–34.6	0.68–0.95	18.3–25.9	0.04–0.31	20.4–25.6	0.10–1.25
N–NO_3 (mg/l)	0.02–0.13	27.2–34.1	0.07–0.17	31.2–36.3	0.01–0.09	20.1–24.7	0.05–0.13	20.2–24.5
N–NO_2 (mg/l)	0.0–0.01	0.01–0.07	0.01–0.05	0.01–0.04	0.01–0.04	0.04–0.06	0.00–0.02	0.02–0.16
O–N (mg/l)	0.7–4.24	0.12–0.33	0.87–3.74	0.07–0.34	0.29–5.49	0.16–0.36	0.41–3.41	0.12–0.70
P–PO_4 (mg/l)	5.1–7.7	4.74–5.47	5.47–6.70	4.19–4.69	7.10–7.8	8.0–8.4	5.08–9.5	2.3–4.2
	30 l/day, 8 h		40 l/day, 6 h		50 l/day, 4.8 h		60 l/day, 4 h	
	Inf.	Effl.	Inf.	Effl.	Inf.	Effl.	Inf.	Effl.
pH	7.2–7.9	8.1–8.3	7.5–7.9	8.2–8.5	6.6–7.9	8.04–8.7	7.3–8.0	8.2–8.5
COD (mg/l)	316.3–503.4	44–112.2	316.3–540.8	78.2–142.9	248.3–384.4	34.01–98.6	383.6–571.9	106.2–154
BOD (mg/l)	136.7–251.8	17.6–44.9	193.0–278.1	32.3–57.1	135.03–175.0	11.9–35.5	125.0–180.1	31.8–51.8
TN (mg/l)	20.5–25.6	17.4–23.1	27.7–29.6	19.6–22.4	26.8–36.2	18.8–27.3	22.5–26.7	11.4–18.4
N–NH_3 (mg/l)	18.2–23.4	0.54–4.31	20.8–27.7	4.1–7.7	25.03–33.7	11.54–15.0	21.3–25.9	8.2–12.2
N–NO_3 (mg/l)	0.09–0.24	14.1–18.6	0.07–0.24	11.6–14.7	0.09–0.16	4.45–11.79	0.04–0.10	0.6–6.7
N–NO_2 (mg/l)	0.01–0.06	0.12–1.1	0.01–0.04	0.33–1.40	0.01–0.03	0.21–0.71	0.01–0.3	0.12–0.3
O–N (mg/l)	0.49–2.74	0.0–0.91	1.51–6.81	0.21–0.64	1.64–5.14	0.10–1.88	0.50–1.8	0.13–0.80
P–PO_4 (mg/l)	3.29–7.7	1.84–3.0	5.50–8.50	3.70–4.70	3.5–5.6	1.70–3.90	4.70–6.40	2.20–3.70

where DO levels decreased and organic load increased in the reactor leading to enhanced denitrification. Also, organic matter availability acts as electron source for the denitrification process.

The present results agree with those of Muller et al. [16], Green et al. [9] and Zhao et al. [27], where the nitrogen balance clearly indicated that the nitrogen loss due to simultaneous nitrification and denitrification in the aeration tank contributed to 10–50% of the influent TKN in the overall nitrogen removal. The results also confirm that ammonia oxidation by sewage sludge was found to be a function of the DO tension. In addition, it is most likely that a nitrifier is present in sewage sludge that concomitantly oxidizes ammonia and reduces nitrite to di-nitrogen at low DO tensions, which increases the removal at the hydraulic retention time. This way of denitrification may benefit the treatment of wastewater since organic substrates and ammonia are simultaneously oxidized during conventional treatment, which results in a shortage of the organic substrate needed for subsequent denitrification. Results of other studies postulated that, because of the competition between heterotrophic bacteria and nitrifiers, nitrification is not initiated until the soluble COD drops to less than 27 mg/l or the soluble BOD_5 drops to 20 mg/l [18, 19].

Phosphorus removal

Results in Table 4 shows that the percent RE of phosphorus increased with increasing flow rate from 5 l/day to 30 l/day as follows: 11.04, 27.48, 39.41, 53.98 and 50.64%, respectively. At the flow rate of 40 l/day, the percent RE decreased to 34.96% and then it rose again at flow rates of 50 l/day and 60 l/day: to 37.03 and 53.13%, respectively. The low level removal at the low flow rates may be due to the low levels of organic load, which leads to starvation of the microorganisms. The shortage in food supply consequently leads to an overall higher death rate, resulting in a decrease in the net amount of bio-phosphate bacteria present in the system. These results agreed with the study carried out by Brodjanovic et al. [3] that explained the deterioration of biological phosphorus removal at some WWTP sites due to the low levels of organic matter, which caused the death of bio-phosphate bacteria present in the system. The high nitrate levels during the lowest flow rates could also explain the lower phosphorus removal. Two explanations were stated for the inhibition of phosphate removal caused by the presence of nitrate in activated sludge: (a) competition for the same substrate between denitrifying bacteria and polyphosphate [poly(P)]-accumulating bacteria and (b) accumulation of poly(P) by poly(P) bacteria which are able to denitrify nitrogen [26]. Lo et al. [14] indicated that the addition of an anaerobic period in the activated sludge treatment system remarkably increased the phosphorus removal, reaching 99%. This was explained by other studies which indicated that the metabolism of phosphorus is based on the anaerobic consumption of volatile fatty acids and subsequent storage as poly-hydroxybutyrate (PHB), while energy and reduction equivalents are provided by the degradation of the internally stored poly-P and glycogen. During anoxic or aerobic conditions, the internally stored PHB is oxidized and used for growth, phosphate uptake, glycogen formation and maintenance [20, 25]. It was also postulated that, in the aerobic phase, phosphate-accumulating organisms oxidize the stored PHB to generate adenosine triphosphate, which is used for cell growth. Phosphate is also transported into the cell and stored as poly-P, resulting in phosphate removal from solution. If there is a low level of PHB in the cell, phosphate uptake decreases [6]. So one of the main reasons for the low percent removal of phosphate in the present study was the lack of an anaerobic process before the aeration tank. Therefore, another chemical treatment step must be added to bring the phosphorus concentration to a lower level than the MPL. However, at all the investigated flow rates, the levels of phosphorus were below the MPL and acceptable for discharging into natural systems.

BOD and COD removal

As a general trend, biological treatment had a high RE for BOD and COD and brought them to acceptable

Table 5 Comparison between chemical and biological treatments for the removal of the investigated pollutants. Results given are averages of six runs each. The $FeCl_3$ treatment used 200 mg/l at the optimum pH 6. The alum treatment used 200 mg/l at the optimum pH 6. The biological treatment was done at a flow rate of 40 l/day

Parameter	$FeCl_3$ treatment			Alum treatment			Biological treatment		
	Inf.	Eff.	RE (%)	Inf.	Eff.	RE (%)	Inf.	Eff.	RE (%)
pH	7.33	6.58	0.00	8.05	6.58		8.31	7.90	
COD (mg/l)	489.71	297.09	35.20	251.73	124.88	49.53	425.50	114.00	73.22
BOD (mg/l)	169.78	99.56	37.51	109.45	42.75	60.83	235.70	34.20	86.40
TN (mg/l)	35.92	33.84	2.66	31.03	29.05	9.51	27.90	26.60	4.60
$N–NH_3$ (mg/l)	32.49	30.64	2.94	25.68	19.73	8.15	25.80	3.10	88.00
$N–NO_3$ (mg/l)	0.52	0.21	48.27	0.23	0.14	45.12	0.03	22.00	
$N–NO_2$ (mg/l)	0.04	0.01	55.98	0.02	0.00	100.0	0.04	0.72	
O–N (mg/l)	3.06	2.80	3.12	6.13	5.41	10.26	2.07	0.87	49.30
PO_4 (mg/l)	6.36	1.59	73.59	3.49	0.36	88.48	5.50	3.02	43.70

levels to be discharged safely into watercourses, especially at the slowest flow rates. Both parameters showed the same trend of decreasing their percent REs with increasing flow rate from 5 l/day to 60 l/day, although their levels in most cases were still below the MPL, as clearly shown in Table 4. Results showed that the percent RE for BOD_5 decreased from an average of 91.76 % at 5 l/day (with a residual value of 13.22 mg/l) to record 71.30 % at 60 l/day (with a residual value of 42.45 mg/l). This means that even at the highest investigated flow rate (60 l/day) with the fastest retention time (4 h), BOD_5 levels were brought to less than the permissible levels (60 mg/l), which indicates a highly efficient kind of treatment. Concerning COD, the same trend was obtained where the percent RE achieved its highest value (91.12 %) at 5 l/day (with a residual value of 30.61 mg/l), reaching 72.73 % at 60 l/day (with a residual value of 126.71 mg/l). This kind of treatment achieved good and efficient removal of COD, considering the flow rate convenient for such removal. The high achieved BOD_5 and COD removal using the proposed reactor was attributed mainly to the high oxidizing capability of the activated sludge used.

The effect of organic loading on nitrification is very important because organic matter removal and nitrification are often carried out within one single reactor. Green et al. [9] reported that high organic loading in the wastewater always results in a lower nitrification percentage because of ammonia loss due to assimilation by heterotrophs and the inhibitory effect of the crowded heterotrophic cells on ammonia oxidation. Also, oxygen consumption during the oxidation of organic matter may reduce nitrification as a result of the reduction in the available oxygen.

In conclusion, as shown in Table 5, the proposed treatments (chemical, biological) exhibited a highly selective removal efficiency towards the target pollutants. Chemical treatment precipitated almost all the phosphate present in the wastewater, while biological treatment showed a high efficiency in the removal of all the nitrogen forms through aerobic digestion of the waste content and the use of ammonia in the nitrification process as a step before complete nitrogen removal. Therefore, the present study highly recommends an integrated approach, in which chemical and biological treatments are used in sequence to achieve a high-efficiency removal of both nitrogen and phosphorus.

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