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EVALUATION OF THE TREATABILITY OF MUNICIPAL WASTE LANDFILL LEACHATE IN A SBR AND BY COAGULATION-FLOCCULATION ON A BENCH SCALE

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Abstract - This article describes bench scale sequential, biological and coagulation-flocculation treatment of mature leachate for the removal of nitrogen and biodegradable and recalcitrant carbonaceous material. The biological stage was conducted on two SBRs, one of which inoculated with nitrifying sludge, another without an inoculum, for 152 and 133 days, respectively. The coagulation-flocculation stage used four coagulants at different doses and pH adjustments. The treatment conducted on the inoculated SBR when a pH control was used produced mean removals of BOD_5, COD and TKN of 69.6%, 38.5% and 51.6%, respectively, and practically complete denitrification. Coagulation-flocculation applied to the effluent of the inoculated biological reactor showed a superior effectiveness of the ferric coagulants, when the pH was adjusted to close to 6.0, producing removals of turbidity, COD and true color close to 95%, 78% and 92%, respectively.

Keywords: Leachate; Sequential batch reactor; Nitrification; Coagulation; Flocculation.

INTRODUCTION

Despite more than forty years of research efforts, the treatment of leachates is still a complex requirement for municipal solid waste landfill operators. During this period, several research studies were performed to experiment with different technological arrangements for effluent treatment to condition it to the standards for emission into surface water bodies. However, few publications have reported successful apparatus for this task and, when successful, generally come up against the issue of high costs associated with the treatments. It is now considered that the effective treatment of leachates is a combination of biological processes allocated to the simultaneous removal of biodegradable carbonaceous material and nitrogen, and physicochemical processes used to remove recalcitrant COD (Li *et al*., 2009).

Sequential batch reactors (SBR) are a variation of the activated sludge process in which various stages of treatment, such as aerobic process, anoxic metabolism and settling occur sequentially in a single versatile tank. The technology which originated in research done at the beginning of the 20th Century has been studied more attentively since the 1970s. Its application to leachates aims at constituting different environments for different metabolisms, especially directed at the oxidation of ammonia and its later conversion to molecular nitrogen. In general, the operation of SBRs can be described as the composition of

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*To whom correspondence should be addressed five phases (USEPA, 1993): (a) filling, with or without mixing and aeration; (b) reaction, usually with mixing and aeration; (c) sedimentation, with a sludge and supernatant separation phase in which the SBR operated as a secondary settler; (d) emptying; (e) resting, with or without mixing and aeration.

The treatment of leachates using SBRs is based on the generation of an initial aerobic phase in which, after heterotrophic organisms consume part of the biodegradable COD, the autotrophic fraction will have the opportunity of oxidizing ammoniacal nitrogen, converting it into nitrites and nitrates. Then an anoxic phase is established in which heterotrophic organisms will use the oxidized forms of nitrogen as electron acceptors in the oxidation of the remaining biodegradable carbonaceous material, converting them into molecular nitrogen gas. According to Aziz *et al.* (2013) SBRs have the flexibility needed for these successive stages to take place satisfactorily. The successive nitrogen transformation processes are called, respectively, nitrification and denitrification. Nitrification stoichiometry is presented by Metcalf and Eddy (2003):

1st Phase: Conversion of ammonia to nitrite (nitritation)

$$\begin{aligned}&55NH_4^+ + 76O_2 + 109HCO_3^- \rightarrow \\ &C_5H_7O_2N + 54NO_2^- + 57H_2O + 104H_2CO_3\end{aligned} \tag{1}$$

2nd Phase: Conversion of nitrite to nitrate (nitratation)

$$\begin{aligned}&400NO_2^- + \ NH_4^+ + 4H_2CO_3 + HCO_3^- \\ &+195O_2 \rightarrow C_5H_7O_2N + 3H_2O + 400NO_3^-\end{aligned} \tag{2}$$

Frick and Richard (1985) exemplify the stoichiometry to reduce nitrate to molecular nitrogen (denitrification), using acetic acid as a carbonaceous source:

$$\begin{aligned}&5CH_3COOH + 8NO_3^- \rightarrow \\ &4N_2 + 10CO_2 + 6H_2O + 8OH^-\end{aligned} \tag{3}$$

Several articles describe experiments aimed at removing nitrogen contained in leachate. Table 1 shows some of these results. The coagulation-flocculation process can be considered to be the destabilization and agglomeration of suspended and colloidal particles present in the liquid by adding a chemical agent (coagulant). The flocs formed must be separated from the supernatant by physical processes. The great majority of colloidal particles dispersed in water present a negative charge, thus these particles repel each other mutually before they can collide (Alley, 2007). The signal and magnitude of the primary charge of colloids are often affected by the pH and by the ionic content of the aqueous phase (Weber, 1972). Because of their masses and electrical charges, their natural sedimentation times are extremely high, and no particle aggregation occurs. When an electrolyte with an opposite charge to that of the colloids is employed, a process with distinct phases occurs: (a) hydrolysis of the coagulants and destabilization of the particles present in the suspension; (b) precipitation and formation of chemical compounds that polymerize, becoming large three-dimensional chains with active extremities; (c) adsorption of the polymer chains on the colloid surface by linkage to their empty sites, leaving the extremities extended into water; (d) mutual adsorption between colloids: the extremities mentioned may adhere to other colloids that have empty sites, forming

Table 1: Results reported in aerobic treatment aiming at removing leachate TKN.

Author	Conditions	Results
Tengrui *et al.* (2007)	Old leachate with 1100 mgNH_4-N.L^{-1}, applied at 0.51 kgN.m^{-3}.d^{-1} in an aerated biofilter maintained at 30-33 ºC, with pH maintained at 7.4-8.6, HRT: 9h.	TKN removal of 99%
Spagni and Libelli (2009)	Old leachate, with 1319-1530 mgTKN.L^{-1} and 2623-2055 mgCOD.L^{-1} applied in a laboratory-scale SBR	Nitrification and nitrogen removal were usually higher than 98% and 95%, respectively, whereas COD removal was approximately 20–30%; 0.117-0.3 mgN.mgMLVSS^{-1}.d^{-1}
He *et al.* (2007)	Leachate with 2900 mgNH_4-N.L^{-1} and 220 mgCOD. L^{-1} applied in a 150 L SBR	0.0690-0.2843 gTKN.gMLVSS^{-1}.d^{-1}
Liang and Liu (2006)	Leachate with 1800-1300 mgTKN.L^{-1} and 1500-16,000 mgCOD.L^{-1} applied at a rate of 0.2-1.0 kgN.m^{-3}.d^{-1} in a aerobic biological reactor	TKN removal of 60%–74%

spongy masses of suspended particles linked by polymer chains; (e) sweeping action: when they sediment, the clots entrain in their path new particles that are incorporated into the microflocs that are forming.

According to Letterman (1999) humic substances have a negative electrical charge, present as compounds with low to medium molecular weight. It is therefore predictable that the fractions with higher molecular weight, which present colloidal behavior, be removed by coagulation-flocculation.

Historical attempts of leachate treatment using coagulants commonly employed for sewage and water, such as aluminum sulfate, have not produced satisfactory results. However, experiments using polyvalent cationic coagulants have given good results, as reported in Table 2.

METHODS

The leachate used in the experiment was from the Central de Resíduos do Recreio (The Recreio Waste Plant), in Minas do Leão, Brazil, a landfill that has operated for over ten years and produces mature leachate. The characteristics determined for the leachate used in the experiment are shown in Table 3.

Table 2: Reported experiences of leachate treatment using coagulation-flocculation.

Author	Leachate tested	Coagulant / Dosage	pH adjustment	COD removal
Wang *et al.* (2002)	raw	$FeCl_3$; 0.34 $gFe^{+3}.L^{-1}$	7.6	24%
Lin and Chang (2000)	old	0.2 $gPACL^{-1}$	5.0	70%
Guo *et al.* (2010)	pre-treated	$FeCl_3$; 0.28 $gFe^{+3}.L^{-1}$	5.0	36%
Castrillón *et al.* (2010)	raw	4.0 $gPAC.L^{-1}$	6.5	34%
Castrillón *et al.* (2010)	raw	$FeCl_3$; 0.59 $gFe^{+3}.L^{-1}$	5.0	73%
Rui *et al.* (2012)	old	$FeCl_3$; 1.03 $gFe^{+3}.L^{-1}$	7.0	37%
Samadi *et al.* (2010)	raw	$Fe_2(SO_4)_3$; 0.42 $gFe^{+3}.L^{-1}$	12.0	71%
Pi *et al.* (2009)	air stripping effluent	$FeCl_3$; 0.21 $gFe^{+3}.L^{-1}$	9.0	37%
Tatsi *et al.* (2003)	partially stabilized by recirculation	$FeCl_3$; 0.69 $gFe^{+3}.L^{-1}$	10.0	80%

Table 3: Characteristics of the raw leachate used in the experiments.

Parameters	Unit	Maximum	Minimum	Mean	s
pH	-	8.47	8.00	8.30	0.12
Conductivity	$mS.cm^{-1}$	28.7	19.4	26.2	4.5
Chemical Oxygen Demand	$mgO_2.L^{-1}$	7272	3039	4786	857
Biochemical Oxygen Demand, 5d, 20 ºC	$mgO_2.L^{-1}$	2200	1250	1617	312
BOD_5/COD	-	0.48	0.24	0.30	0.08
Unfiltered turbidity	FAU	1400	925	1093	159
Filtered turbidity	FAU	1053	625	782	119
True color	$mgPt\text{-}Co.L^{-1}$	18,564	1200	10,353	2589
Ammoniacal nitrogen	$mgN.L^{-1}$	1792	1030	1441	207
Total Kjeldahl nitrogen	$mgN.L^{-1}$	1961	1344	1607	164
Nitrate	$mgN.L^{-1}$	9.54	ND	3.90	2.31
Nitrite	$mgN.L^{-1}$	3.10	ND	0.60	0.81
Alkalinity	$mgCaCO_3.L^{-1}$	14,400	5630	7970	2220
Total solids	$mg.L^{-1}$	17,670	14,935	15,911	1516
Total volatile solids	$mg.L^{-1}$	4092	3207	3740	469
Total fixed solids	$mg.L^{-1}$	13,578	11,015	12,171	1300
Total suspended solids	$mg.L^{-1}$	2060	1080	1653	511
Volatile suspended solids	$mg.L^{-1}$	1020	460	773	286
Fixed suspended solids	$mg.L^{-1}$	1040	620	880	227

s: standard deviation; ND: not detected

Two identical cylindrical 6 L SBRs made of acrylic were used, with an inner diameter of 30 cm and inner height of 15.5 cm. The reactor called SBR1 operated with sludge generated and enriched by the aeration of the leachate itself, while reactor SBR2 was inoculated with sludge with a nitrifying characteristic from a sewage treatment plant, slowly acclimated to the leachate. In order to ensure that the effluent was mixed with the biomass, the SBRs were equipped with rotary systems comprising axes with propellers coupled to motors. The air supply for each reactor came from a porous stone diffuser, of the type used in domestic aquariums, fixed at the bottom of the reactors and connected to pumps with a manual adjustment of air flow. Raw leachate feed and effluent removal were performed through peristaltic pumps connected to the reactors by hoses. Agitation, aeration, influent feeding and effluent removal were performed manually through taps installed in the reactors. Reactors SBR1 and SBR2 were operated, respectively, for 152 and 133 days.

For acclimation to leachate and sludge enrichment, both reactors operated in 24-hour cycles, divided into 22.25 h of agitation and aeration, 1.5 h of sedimentation and 0.25 h of effluent removal. In fact, the SBRs operated as a semi-batch system, with intermittent leachate feedings occurred throughout each cycle every 2.5 to 3.0 hours.

When the mixed liquors reached 3000 mgMLVSS.L^{-1}, the anoxic phase was added to the cycles, switching off the aeration and mixture maintenance. Thus, the reactors operated on a new total cycle comprising 12.25 h of aeration with mixing, 10.25 h of mixing without aeration, 1.25 h of sedimentation and 0.25 h of effluent removal. The system was fed in eight equal aliquots throughout the reaction period, so that the hydraulic retention time was kept at 2 d, therefore within the 1.0-3.2 d range recommended by Kurniawan *et al.* (2010). At the beginning of the anoxic phase, acetate was added as an external source of carbon, observing the stoichiometry of 6.071 milligrams of sodium acetate trihydrate per milligram of nitrogen to be denitrified. The relative lack of phosphorus was supplied by adding potassium monohydrogen phosphate, so as to keep, at the beginning of each cycle, the BOD_5:N:P ratio close to 100:5:1. The cellular retention time was kept at 25 d by daily removal of a 4% fraction of the mixed liquor.

The SBR temperature was kept at 21-25 ºC throughout the experiment. Since during the operation period an increase in the pH was observed up to the level of 9.0-9.2 in the aerobic phase, an unexpected phenomenon, in an established number of operational cycles concentrated sulphuric acid was added manually to adjust the pH to close to 7.2, as a strategy to avoid inhibiting the nitrifying organisms. There was no effective control of dissolved oxygen concentrations in the reactors, but they were regularly monitored, and in the aerobic phases the concentrations were observed to be between 2.0-4.5 $mgO_2.L^{-1}$.

The parameters monitored during the biological phase were temperature, pH, dissolved oxygen, conductivity, color, turbidity, BOD_5, COD, nitrogen series (organic, ammoniacal, nitrate and nitrite), alkalinity and solids series. All determinations used methodologies standardized by APHA/AWWA/WEF (1999).

The coagulation-flocculation tests were carried out on jar-test equipment with adjustable angular velocity mixers, with the simultaneous use to six cups with a capacity of 2 L. Different coagulants were tested, as follows:

- Aluminum polychloride (PAC); concentration of active material: 16.5-17.5% of Al_2O_3 (in mass);
- Ferric chloride; concentration of active matter: 38% $FeCl_3$ (in mass, minimum);
- Ferric sulphate (*oxidized ferrous sulphate*); concentration of active material: 17% of Fe^{+3} (in mass);
- Tannin: commercial name: Tanfloc SG.

The coagulation-flocculation tests occurred in successive stages; in each of them an attempt was made to check the removal efficiencies as dosages were modified and pH adjusted. In this sense, for each coagulant the operation was performed in four stages: (1) determination of the optimum dosage, (2) determination of the optimum adjustment of pH, (3) determination, by fine adjustment, of the optimum dosage, (4) determination, by fine adjustment, of the optimum pH. A last stage (5), operated with repetitions, and complementary determinations were performed.

The ranges of dosages and pH adjustments initially tested, as well as the times and gradients of mixtures adopted, were fixed based on coagulation-flocculation experiments previously carried out by the authors, using raw leachates. Table 4 summarizes the values of the test variables used.

The parameters monitored during the physicochemical phase were pH, true color, turbidity and COD, besides other occasional determinations. All determinations used methodologies standardized by APHA/AWWA/WEF (1999). A filtration process was adopted before the determination of color and turbidity to determine true color, pursuing the idea, when on a real scale, to equip the system with a percolating filter to remove suspended solids from the raw

Table 4: Values of the test variables used in the coagulation-flocculation tests.

Variable / Coagulant	PAC	Ferric Chloride	Ferric Sulphate	Tannin
Effluent Initial Characteristics	Turbidity: 675-683 FAU; COD: 2672-2987 $mgO_2.L^{-1}$; Color: 9400-11,575 $mgPt\text{-}Co.L^{-1}$	Turbidity: 725-1044 FAU; COD: 2761-3168 $mgO_2.L^{-1}$; Color: 11,100-12,100 $mgPt\text{-}Co.\ L^{-1}$	Turbidity: 667-800 FAU; COD: 2870-3244 $mgO_2.L^{-1}$; Color: 9400-11,575 $mgPt\text{-}Co.L^{-1}$	Turbidity: 675-750 FAU; COD: 2844-3168 $mgO_2.L^{-1}$; Color: 9400-11,475 $mgPt\text{-}Co.\ L^{-1}$
Fast mixing time (min)*	0.5, 1, 2, 3 , 4, 6			
Fast mixing gradient (s^{-1})*	180, 350, 425, 600, 950, 1200			
Slow mixing time (min)*	5, 10, 15, 20, 30, 45			
Slow mixing gradient (s^{-1})*	10, 20, 40, 60, 80, 100			
Initial pH (first tests)**	5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.1, 8.5, 9.0, 9.5, 10.0	5.0, 5.5, 6.0, 6.6, 7.0, 7.5, 8.0, 8.5, 8.9, 9.0, 9.5, 10.0	5.0, 5.5, 6.0, 6.6, 7.0, 7.5, 8.0, 8.5, 8.6, 9.0, 9.5, 10.0	5.0, 5.5, 6.0, 7.0, 7.2, 7.5, 8.0, 8.5, 8.9, 9.0, 9.5, 10.0
Dosages (first tests)**	0.50, 1.00, 1.50, 2.00, 3.00, 4.00 g $Al_2O_3.L^{-1}$	0.17, 0.34, 0.69, 1.03, 1.38, 1.72 g $Fe^{+3}.L^{-1}$	0.20, 0.50, 0.80, 1.00, 1.50, 2.00 g $Fe^{+3}.L^{-1}$	1.00, 2.00, 3.00, 4.00, 6.00, 8.00 $g.L^{-1}$
Initial pH (final tests)**	6.4, 6.7, 7.0, 7.3, 7.5, 7.8	5.7, 5.9, 6.1, 6.3, 6.5, 6.7	5.4, 5.6, 5.8, 6.0, 6.2, 6.4	5.3, 5.5, 5.7, 5.9, 6.1, 6.3
Dosages (final tests)**	0.90, 1.10, 1.30, 1.50, 1.70, 1.90 g $Al_2O_3.L^{-1}$	0.55, 0.62, 0.69, 0.76, 0.83, 0.90 g $Fe^{+3}.L^{-1}$	0.80, 0.90, 1.00, 1.10, 1.20, 1.30 g $Fe^{+3}.L^{-1}$	6.00, 7.00, 8.00, 9.00, 10.00, 12.00 $g.L^{-1}$

*preliminary tests
**definitive tests using quick mixing for 2 minutes at 250 s^{-1}, slow mixing for 20 minutes at 60 s^{-1} and 2-hour sedimentation time

leachate and adopt a very efficient process downstream from coagulation-flocculation for solid-liquid separation.

RESULTS

During the periods of operation, the MLVSS concentrations in mixed liquors were monitored three times a week. The SBR1 and SBR2 reactors were operated, respectively, after a 30-day phase of acclimation and enrichment with volatile suspended solids concentrations of 1220-3667 and 2319-4882 $MLVSS.L^{-1}$.

The SBR1 reactor showed inconsistent nitrification, despite practically total denitrification, producing an average of nitrogen removals over the cycles of approximately 17%, with a minimum of 1.5% and maximum of 30.9% (when operating with a pH control). On the other hand, the SBR2 reactor operated with much more consistent nitrification, especially when manual control of pH was established, which occurred between days 98 and 122. In this sense, as the work developed, special attention was given to the operation of reactor SBR2, whose effluent was chosen for application in the physicochemical stage (coagulation-flocculation) because of its operational stability. Figures 1 and 2 show affluent and effluent TKN and the performance of the reactors SBR1 and SBR2 throughout the cycles of operation in terms of TKN removal. During the period of stable operation of the SBR2 reactor, with effective pH control, the TKN removals were observed between 47.8% and 56.1%, with a mean of 52%. During the 31-135 cycles, in which the reactor maintained an anoxic phase in each cycle, the efficiency of denitrification presented a mean of 98.9%, never below 95.9%. The mean removal of total nitrogen (all forms) in the SBR2 reactor, over the period with pH control, was 51.6%, with a maximum at 55.7%. The variation of the oxidation rate of nitrogen in the reactors over the cycles is shown in Figure 3.

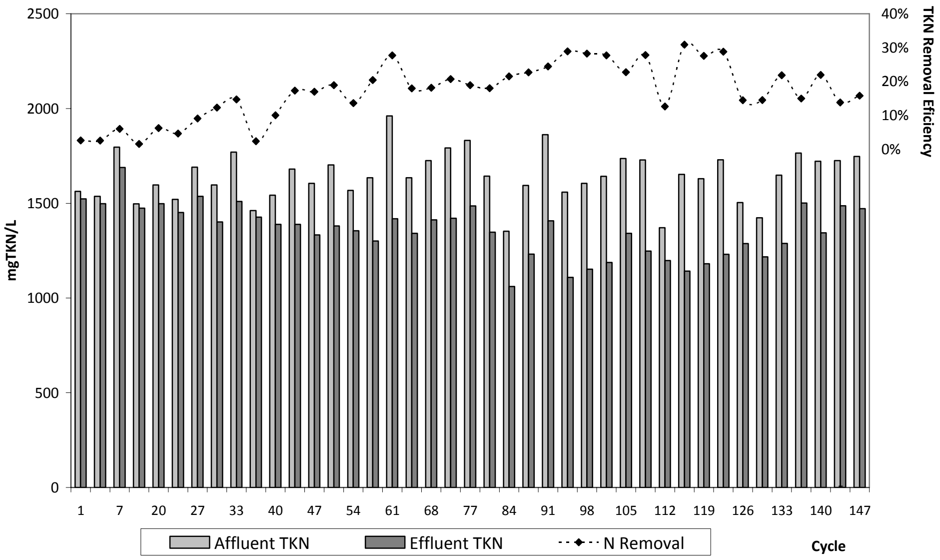

Figure 1: Nitrification efficiency in SBR1 during the monitored cycles.

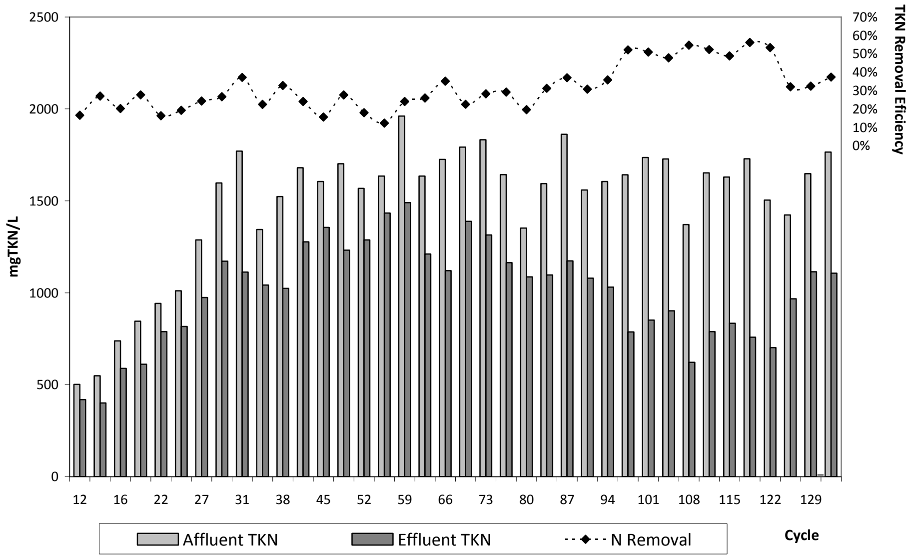

Figure 2: Nitrification efficiency in SBR2 during the monitored cycles.

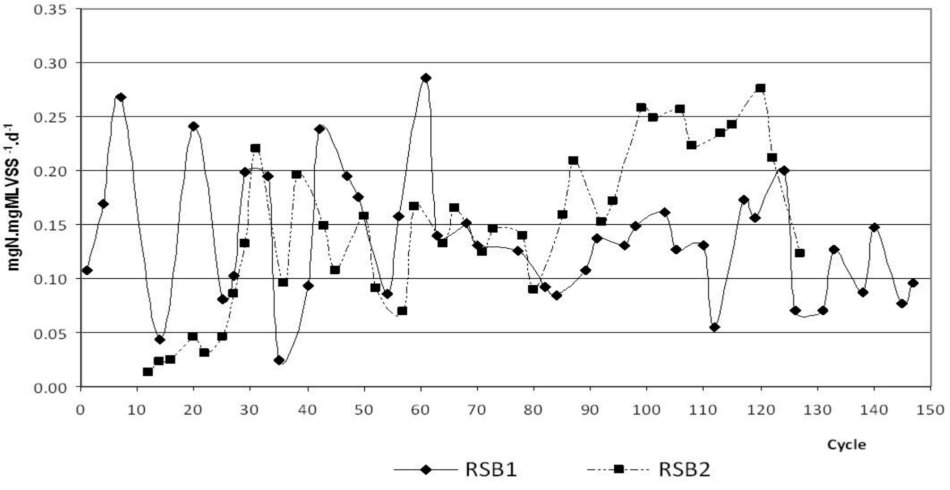

Figure 3: Nitrogen oxidation rate in sequential batch reactors during the cycles.

Results obtained from the monitoring of MLVSS, KTN removal efficiencies and removal rates (mgN.mgMLVSS^{-1}.d^{-1}) for the reactors were compared using analysis of variance (1) for the periods with and without pH control within the same reactor and (2) for equivalent periods with and without pH control of the reactors. The results of the ANOVA are shown in Table 5.

The pH control raised the medium concentrations of MLVSS in both reactors, but more prominently in SBR1, although the SBR2 reactor, inoculated with sludge, always presented higher concentrations of biomass present. The effect of pH control on TKN removal efficiency and removal rate (mgN.mgMLVSS^{-1}.d^{-1}) in SBR2 was more intense than in SBR1, although the removals and rates over the cycles without pH control were always superior in SBR2.

Although the removal rate presented relatively close means if the full periods of reactor operation were considered, in the cycles with pH control the SBR2 reactor presented a mean of 0.244 mgN. mgMLVSS^{-1}.d^{-1}, double the mean of 0.122 mgN. mgMLVSS^{-1}.d^{-1} found for SBR1. During the respective periods of pH control, mean concentrations of volatile suspended solids seen in the mixed liquors were slightly different in SBR1 and SBR2 (3010 and 3466 mgMLVSS.L^{-1}, respectively). The differences between the mean observed nitrification efficiencies, respectively 22.3% and 52% during the period, are ascribed mainly to the differences between the biological oxidation rates of nitrogen found in the reactors. Effluent alkalinity was monitored over the operation times, recording for the effluents of both reactors, as expected, consumptions during aeration periods and elevations in the anoxic phase. Logically, in the cycles in which acid was added to the reactors, there was an elevation of the alkalinity consumption.

Both reactors produced significant carbonaceous material removals during the operation periods with sludge age control. The SBR1 reactor, between cycles 20 and 146, presented a mean removal of BOD$_5$ and COD of 42.5% and 31.1%, respectively, while for reactor SBR2 these means were 61.8% and 27.7%. During the pH control phase, which coincided with high stability, the SBR2 reactor produced mean BOD$_5$ and COD removals of 69.6% and 38.5%, respectively. These results, together with ammoniacal nitrogen removals on the order of 50%, show the good potential for treating leachates with sequential batch reactors.

Reactor SBR2, which had a more stable operation, produced effluents with means of 3212 mgCOD.L^{-1} and 560 mgBDO$_5$.L^{-1}. During the stable phase, with pH control, the mean concentration of effluent total nitrogen (all forms) was 781 mgN.L^{-1}. The mean lowering of the BOD$_5$/COD ratio of the reactor effluents was 0.07.

The average removal rate for the SBR2 reactor during the pH control phase was verified to be 0.24 mgN.mgMLVSS^{-1}.d^{-1}, having reached a maximum of 0.28. These results come very close to those obtained by Spagni and Libelli (2009) and He *et al.* (2007), indicating that high removals of approximately 90% or more could probably be derived from the elevation of the HRT.

The tests using coagulation-flocculation employed effluent leachate from the SBR2 reactor, with a COD ranging between 2601 and 3244 mgO$_2$.L^{-1}. In a first stage, different dosages of the four coagulants used were tested. The pH of the leachates was initially adjusted to 6.0 for assays with inorganic coagulants, and the original pH of the effluent (7.2) was maintained for the tests with tannin. The cycles used a quick mixing for 2 minutes at 150 rpm (g ≈ 250 s^{-1}); slow mixing for 20 minutes at 60 rpm (g ≈ 60 s^{-1}) and a 2-hour sedimentation time: those were the best values found in preliminary tests. Table 6 summarizes the dosages used and the best results obtained in that stage.

Table 5: ANOVA results for MLVSS concentration, KTN removal efficiencies and removal rates (mgN.mgMLVSS^{-1}.d^{-1}).

ANOVA Tests Within Reactors	SBR1 pH control x no pH control	SBR2 pH control x no pH control
MLVSS	DSS 2.5%	DNSS 5%
TKN removal	DNSS 5%	DSS 0.5%
mgN.mgMLVSS^{-1}.d^{-1}	DNSS 5%	DSS 0.05%
ANOVA Tests SBR1 xSBR2	**Cycles with no pH control**	**Cycles with pH control**
MLVSS	DSS 0.05%	DSS 1%
TKN removal	DSS 0.05%	DSS 0.05%
mgN.mgMLVSS^{-1}.d^{-1}	DSS 2.5%	DSS 0.05%

*DSS: difference statistically significant; DNSS: difference not statistically significant

Table 6: Results obtained during the phase of optimal dosage determination.

Coagulant	**PAC**	**Ferric Chloride**	**Ferric Sulphate**	**Tannin**
Dosages used	0.50, 1.00, 1.50, 2.00, 3.00, 4.00 g $Al_2O_3.L^{-1}$	0.17, 0.34, 0.69, 1.03, 1.38, 1.72 g $Fe^{+3}.L^{-1}$	0.20, 0.50, 0.80, 1.00, 1.50, 2.00 g $Fe^{+3}.L^{-1}$	1.00, 2.00, 3.00, 4.00, 6.00, 8.00 $g.L^{-1}$
Optimal dosage found	$1.50gAl_2O_3.\ L^{-1}$	$0.69gFe^{+3}.L^{-1}$	$1.00gFe^{+3}.L^{-1}$	$8.00g.L^{-1}$
Color removal (%)	92.33	90.54	96.99	81.83
Turbidity removal (%)	96.15	94.62	97.78	90.07
COD removal (%)	74.66	82.20	84.95	16.95
Final pH	3.8	3.41	4.45	6.17
Final Color (mgPt-Co.L^{-1})	721	1050	283	2017
Final turbidity (FAU)	26	39	15	72
Final COD (mgO_2.L^{-1})	678	564	432	2631

* results refer to the supernatant obtained from the best coagulant dosage used;
** turbidity was determined after filtration.

In the second stage, the coagulants were applied at the previously determined optimal dosage to samples of leachate with prior adjustments of pH between 5.0 and 10.0, in 0.5 unit increments, and to samples without pH adjustment, with a total of 12 different pH values tested for each coagulant used. Optimizations of the removal were observed at pH values of 7.0, 6.5, 6.0 and 6.0, respectively for PAC, ferric chloride, ferric sulphate and tannin. Table 7 summarizes the results obtained in this stage.

During the third stage, six dosages around those determined as optimal in the first stage were used for each coagulant, and the leachates underwent pH adjustments according to the best results of the previously described stage. Optimizations were observed in the removal (color, COD and turbidity) for the dosages of 1.30 $gAl_2O_3.L^{-1}$ (PAC), 0.83 $gFe^{+3}.L^{-1}$ (ferric chloride) and 0.90 $mgFe^{+3}.L^{-1}$ (ferric sulphate). In the specific case of tannin, as in the initial stage, the highest dosage gave the best results; in the present stage the dosages were extended to 12.00 $g.L^{-1}$, and a superior performance was obtained with this higher dosage.

During the fourth stage, the best dosages determined in the previous stage were adopted; and, for each coagulant, six pH adjustments close to those considered to be optimal in the second stage were tested. The adjustments that presented the best removal, and thus were considered ideal, were 7.5 for PAC, 6.3 for ferric chloride, 6.0 for ferric sulphate, and 5.5 for tannin. Some discrepancies between the efficiencies found between the third and fourth stages are due to impossibility of using factorial design in this series of experiments. The assays were repeated. Once this stage was over, the Brazilian market prices of the coagulants were evaluated and their performances were compared, as illustrated in Figure 4.

The results presented in Figure 4 should be interpreted with caution, since they come from experiments conducted on a bench scale, and may not be reproduced in a full scale system.

It was observed that the four coagulants used had a very similar performance as regards color and turbidity removal. However, for tannin, there was poorer COD removal, whereas ferric sulphate and ferric chloride had COD removals close to 80%, and were found to be the coagulants with the best overall performance.

The optimized tests using ferric chloride and ferric sulphate produced effluents with a COD between 432 and 564 $mgO_2.L^{-1}$, true color between 283 and 1050 and turbidity between 15 and 39 FAU. BOD_5 determinations for leachates treated with the ideal doses of PAC and ferric chloride produced the following results: 80 and 100 $mgO_2.L^{-1}$, respectively.

Table 7: Results obtained during the phase of optimal pH determination.

Coagulant	**PAC**	**Ferric Chloride**	**Ferric sulphate**	**Tannin**
Dosages used	$1.50g\ Al_2O_3.\ L^{-1}$	$0.69gFe^{+3}.L^{-1}$	$1.00gFe^{+3}.L^{-1}$	$8.00g.L^{-1}$
Optimal pH found	7.0	6.5	6.0	6.0
Color removal (%)	88.97	95.25	97.36	88.30
Turbidity removal (%)	94.88	97.89	93.25	93.19
COD removal (%)	52.75	78.56	84.90	19.62
Final pH	4.49	5.19	3.51	6.25
Final color (mgPt-Co.L^{-1})	1053	575	267	1100
Final turbidity (FAU)	35	22	45	46
Final COD (mgO_2.L^{-1})	1359	592	461	2286

* turbidity was determined after filtration.

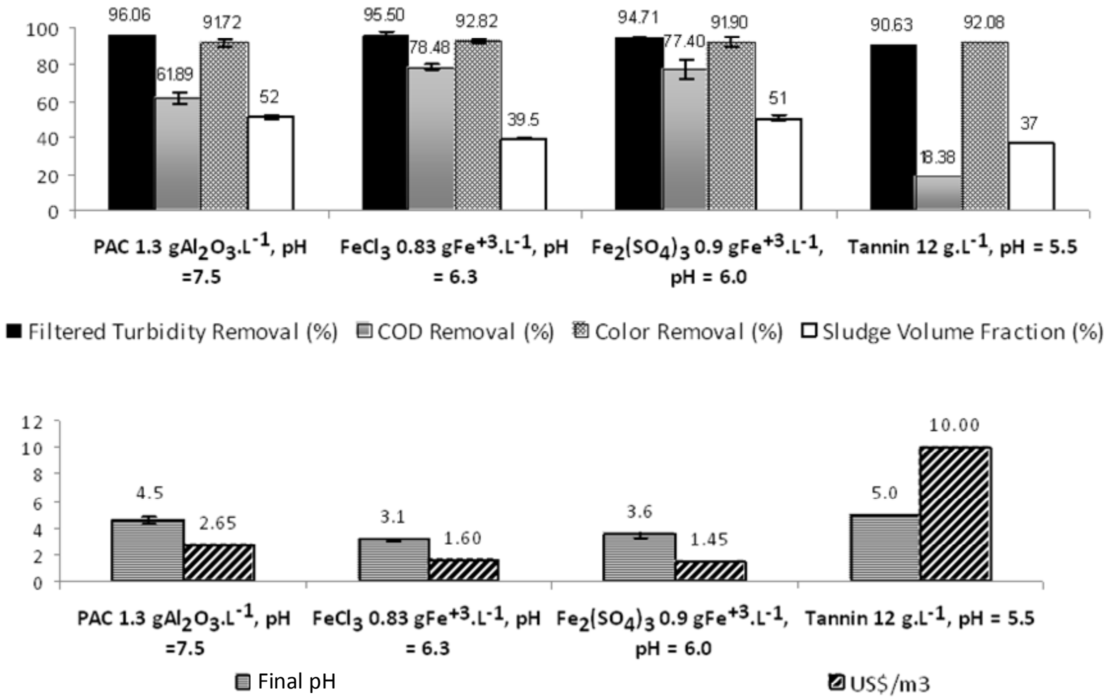

Figure 4: Summary of the results for coagulation – flocculation, using optimal pH dosages and adjustments for each coagulant, with repetition (except for tannin).

DISCUSSION

The elevation of the pH of the medium during the aerobic phase was the most important phenomenon observed during the SBR operation cycles. The nitrification requires alkalinity consumption, and, thus, conversely a drop in pH would be expected. Two causes can be suggested for this:

- Dissolved carbon dioxide desorption in the liquid medium, due to turbulence, which caused an imbalance of the CO_2/H_2CO_3 system that is sometimes responsible for the neutralization of part of the high alkalinity present in the leachate;
- Hydrolysis of the organic nitrogen, which consumes hydronium ions (H^+).

The use of wastewater sludge with a nitrifying characteristic slowly acclimated to the leachate proved to be effective, because SBR2 reactor inoculum produced a sludge with greater yield during the nitrification phase, whereas the SBR1 reactor, in which bacterial cells originally present in the raw leachate were the inoculum, presented much less consistent nitrification, which shows a quicker and more effective start-up when a well-selected inoculum is used.

As expected, the coagulation-flocculation of leachates which have been previously treated biologically consumed smaller doses of coagulants compared to the coagulation of raw leachates, which were the subject of preliminary studies that are not presented here. Although considered to be environmentally friendly, especially for producing biodegradable sludges, tannin required high consumption for slightly lower COD removals than those obtained using inorganic coagulants.

Despite the results cited by Samadi (2010) and Tatsi (2003), in this experiment the removal of turbidity, color and COD decreased when using pH adjustments above neutral. COD removals obtained with the use of ferric coagulants were similar to those obtained by the last mentioned author, who used a dose about 20% lower than those that provided the best results in our experiments.

A preliminary observation regards the cost of treatment per cubic meter required by the coagulants. According to the quotations obtained, the coagulants ferric sulphate and ferric chloride would cost, respectively, US$ 1.45 and US$ 1.60 for the ideal dosages per cubic meter of leachate to be treated. These are the coagulants with the best cost/benefit ratio among those tested, besides, as already emphasized, having produced the best results. For PAC and tannin, the best removals obtained would require, according to the prices quoted, US$ 2.65 and US$ 10.00 per cubic meter of leachate to be treated. However, there is no guarantee that these results will be repeated in a full scale system. As a disadvantage inherent to the two best coagulants, the iron contents present in the final effluent may require a process for their removal downstream from coagulation-flocculation.

CONCLUSION

The biological reactors presented partial removal of the biodegradable carbonaceous material and nitrogen present in the inflow. The reactor inoculated with nitrifying sludge, which operated more robustly and effectively during the nitrifying phase, produced removals of approximately half the concentration of all nitrogen present, which would require one more unit dedicated to nitrogen removal, such as an ammonia stripping tank, for instance, to meet the standard level reached for emission in terms of nitrogen concentration.

In the coagulation-flocculation tests carried out, the coagulants presented similar color and turbidity removals. Using ferric chloride, removals of approximately 92.8% and 95.5%, respectively, were obtained for true color and turbidity. The iron-based inorganic coagulants removed about 80% of the COD. The mean percentages of the sludge phase generated by these coagulants were 39.5-51%. The pH values of the leachate after coagulation-flocculation with ferric sulphate and ferric chloride were 3.6 and 3.1, respectively. This final pH range coincides with the range recommended to apply the Fenton Advanced Oxidation Process, which has been reported by researchers to be successful in removing refractory carbonaceous material from the leachates.

The removal of carbonaceous material obtained in the biological and physicochemical sequence can be considered to be very significant, especially if the removals obtained in the stable operation phase of the biological reactors and the performances of the ferric coagulants are considered jointly. The effluent from the combined biological treatment in SBR with coagulation-flocculation using ferric coagulants in the optimized dosages with pH adjustment showed 416-897 mgCOD.L^{-1}, 873-1250 mgPt-Co.L^{-1} and 41-60 FAU.

NOMENCLATURE

APHA	American Public Health Association
AWWA	American Water Works Association
BOD$_5$	Biochemical Oxygen Demand in 5 days
COD	Chemical Oxygen Demand
FAU	Formazin Attenuation Unit
g:	gradient
HRT	Hydraulic Retention Time
MLVSS	Mixed Liquor Volatile Suspended Solids
MLVSS.L^{-1}	mixed liquor volatile suspended solids milligram per liter
PAC	polyaluminum chloride
SBR	Sequencial Batch Reactor
TSS	Total Suspended Solids
TKN	Total Kjeldahl Nitrogen
WEF	Water Environment Federation

REFERENCES

Alley, E. R., Water Quality Control Handbook. McGraw-Hill, p. 848 (2007).

APHA, AWWA, WEF, American Public Health Association, American Water Works Association, Water Environment Federation. Standard Methods for the Examination of Water and Wastewater. 21th Ed., Washington (1999).

Aziz, S. Q., Aziz, H. A., Mojiri, A., Bashir, M. J. K., Amr, S. S. A., Landfill leachate treatment using sequencing batch reactor (SBR) process: Limitation of operational parameters and performance. International Journal of Scientific Research in Knowledge, (IJSRK), 1(3), 34-43 (2013).

Castrillón, L., Nava, Y. F., Ulmanu, M., Anger, I., Marañón, E., Physico chemical and biological treatment of MSW landfill leachate. Waste Management, 30, 228-235 (2010).

Frick, B. R., Richard, Y., Ergebnisse und erfahrungen mit der biologischen denitrifikation in einem wasserwerk. Vom Wasser, 64, 145-154 (1985). (In German).

Guo, J.-S., Abbas, A. A., Chen, Y. P., Liu, Z. P., Fang, F., Chen, P., Treatment of landfill leachate using a combined stripping, fenton, SBR, and coagulation process. Journal of Hazardous Materials, 178, 699-705 (2010).

He, Y., Zhou, G., Zhao, Y., Nitrification with high nitrite accumulation for the treatmentof "old" landfill leachates. Environmental Engineering Science, 24(8), 1084-1094 (2007).

Kurniawan, T. A., Waihung, Lo., Chan, G., Sillanpaa, M. E. T., Biological processes for treatment of landfill leachate. Journal of Environmental Monitoring, 12, 2032-2047 (2010).

Letterman, R. D., Water Quality and Treatment. McGraw-Hill, p. 1231 (1999).

Li, H.-S., Zhou, S.-Q., Sun, Y.-B., Feng, P., Li, J.-D., Advanced treatment of landfill leachate by a new combination process in a full-scale plant. Journal of Hazardous Materials, 172, 408-415 (2009).

Liang, Z., Liu, J.-X., Control factors of partial nitritation for landfill leachate treatment. Journal of Environmental Sciences, 19, 523-529 (2007).

Lin, C. Y., Chang, F. Y., Chang, C. H., Co-digestion of leachate with septage using a UASB reactor. Bioresource Technology, 73, 175-178 (2000).

Pi, K. W., Li, Z., Wan, D. J., Gao, L. X., Pretreatment of municipal landfill leachate by a combined process. Process Safety and Environmental Protection, 87, 191-196 (2009).

Rui, L. M., Daud, Z., Latif, A. A. A., Coagulation-flocculation in leachate treatment by using ferric chloride and alum as coagulant. International Journal of Engineering Research and Applications, 2(4), 1929-1934 (2012).

Samadi, M. T., Saghi, M. H., Rahmani, A., Hasanvand, J., Rahimi, S., Shirzad Syboney, M., Hamadan landfill leachate treatment by coagulation-flocculation process. Iran. J. Environ. Health Sci. Eng., 7(3), 253-258 (2010).

Spagni, A., Marsili-Libelli, S., Nitrogen removal via nitrite in a sequencing batch reactor treating sanitary landfill leachate. Bioresource Technology, 100, 609-614 (2009).

Tatsi, A. A., Zouboulis, A. I., Matis, K. A., Samaras, P., Coagulation-flocculation pretreatment of sanitary landfill leachates. Chemosphere, 53, p. 737-744. (2003)

Tchobanoglous, G., Burton, L. F., Wastewater Engineering. Treatment, disposal, reuse. Metcalf & Eddy, Inc., 3rd Edition, Singapore, McGraw-Hill, p. 1334 (1991).

Tengrui, L., Al-Harbawi, A. F., Bo, L. M., Jun, Z., Long, X. Y., Characteristics of nitrogen removal from old landfill leachate by sequencing batch biofilm reactor. American Journal of Applied Sciences, 4(4), 211-214 (2007).

USEPA, United States Environmental Protection Agency, Cincinatti Manual. Nitrogen Control. Technology Transfer, p. 311 (1993).

Wang, Z.-P., Zhang, Z., Lin, Y.-J., Deng, N.-S., Tao, T., Zhuo, K., Landfill leachate treatment by a coagulation–photooxidation process. Journal of Hazardous Materials, B95, p. 153-159 (2002).

Weber, W. J. Jr., Physicochemical Processes for Water Quality Control. John Wiley & Sons, Inc. p. 640 (1972).