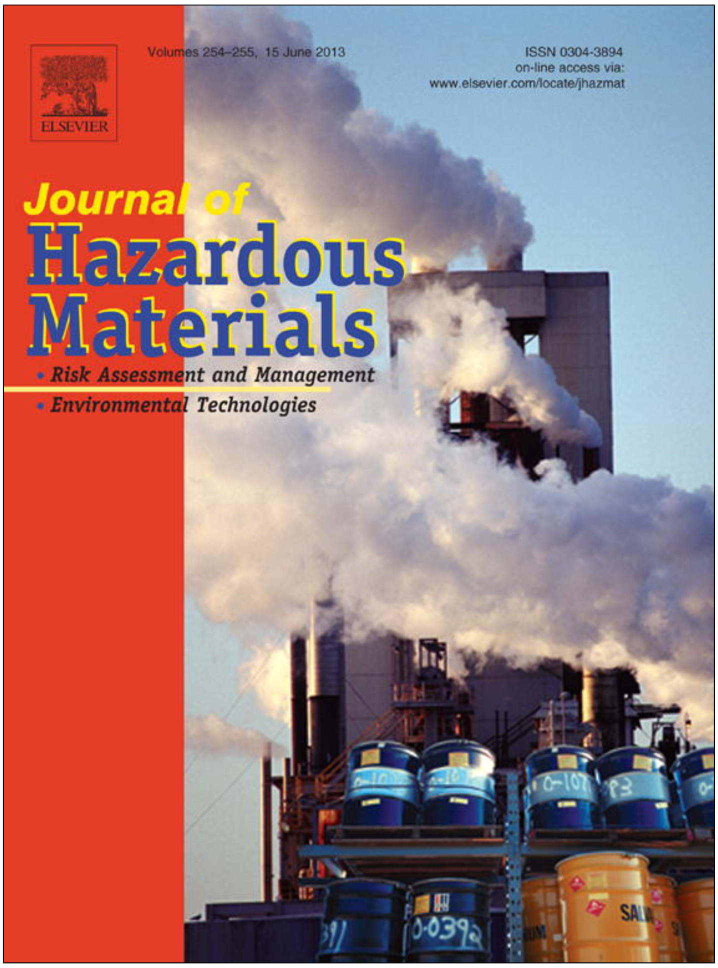
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Removal of carbon, nitrogen and phosphorus from the separated liquid phase of hog manure by the multi-zone BioCAST technology

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HIGHLIGHTS

- Biological treatment of hog waste using multi-environment bioreactors is discussed.
- COD and TP removal increased with the increase of COD/TN and COD/TP ratios.
- TN removal did not show any dependence on COD/TP or TN/TP ratios.
- Low biomass yields of 2.6–12.6%, based on the consumed COD, were obtained.
- High free ammonia concentration inhibited the oxidation of ammonia, but not nitrite.

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ABSTRACT

The removal of chemical oxygen demand (COD), total nitrogen (TN) and total phosphorus (TP) at concentrations of 960 ± 38 to 2400 ± 96 mg/L, 143 ± 9 to 235 ± 15 mg/L and 25 ± 2 to 57 ± 4 mg/L, respectively, from the separated liquid phase of hog manure by the multi-zone BioCAST technology is discussed. Despite the inhibitory effect of hog waste toward microbial activities, removal efficiencies up to 89.2% for COD, 69.2% for TN and 47.6% for TP were obtained during 185 d of continuous operation. The free ammonia inhibition was postulated to be responsible for the steady reduction of COD and TP removal with the increase of TN/TP ratio from 3.6 to 5.8. On the contrary, the increase of COD/TN ratio from 4.8 to 14.1 improved the removal of all contaminants. Nitrogen removal did not show any dependence on the COD/TP ratio, despite the steady increase of COD and TP removal with this ratio in the range of 19.3–50.6. The removal efficiencies of organic and inorganic contaminants increased progressively owing to the adaptation of microbial biomass, resulting from the presence of suspended biomass in the mixed liquor that circulated continuously between the three zones of aerobic, microaerophilic and anoxic, as well as the attached biomass immobilized inside the aerobic zone.

1. Introduction

The effective treatment of agricultural wastewaters, especially those originating from animal husbandry such as liquid hog waste, has posed a serious challenge to the wastewater treatment industry. These wastewaters have very high organic loads as well as high concentrations of suspended solids, nitrogen and phosphorus, and pathogens.

Land application of raw or partially separated hog waste as a biofertilizer often results in the emissions of greenhouse gas, ammonia and odor, and potential nutrient contamination of surface and groundwater due to excess concentrations of nitrogen and phosphorus that exceed the soil-crop assimilation capacity. The treatment of liquid hog waste is particularly important in Canada and Quebec since hundreds of lakes and rivers have been contaminated with blue-green algae as a result of excessive discharge of nitrogen and phosphorus. The discharge of untreated or undertreated wastewaters of agriculture industry with high nutrient contents has been largely blamed for the increased concentration of nitrogen and phosphorus in surface waters. In Quebec, the volume of generated hog waste has drastically increased due to increased pig production that has almost tripled during the last twenty years.

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High-strength animal wastes including hog waste are often treated by a combination of physicochemical and biological processes for the separation of solids from liquid and the removal of organic and inorganic contaminants. The treatment systems that use biological processes commonly include an anaerobic system to remove organic carbonaceous compounds, followed by a polishing aerobic treatment [1] or by nutrient removal processes, usually nitrification and denitrification for nitrogen removal, and enhanced biological phosphorus removal (EBPR) or chemical processes for the removal of phosphorus.

Various bioreactor designs, aiming at increased solid retention time, have been used for the anaerobic digestion of pig manures, including anaerobic baffled reactors [2,3] upflow anaerobic filters [4] and suspended particle-attached growth reactors [5]. Aerobic treatment systems for swine wastes aim at reduced odor emissions and ammonia volatilization. Figueroa et al. [6] used aerobic granulated sludge grown in a sequential batch reactor for organic matter and nitrogen removal from swine slurry at loading rates of 4.4 kg COD/m^3 d and 0.83 kg N/m^3 d, respectively, and achieved organic matter removal efficiencies up to 87% and nitrogen removal efficiencies up to 70%. The use of organic biofilters has been implemented in the development of BIOSOR technology [7] which forms an important component of a hybrid process for the treatment of highly concentrated effluents of animal farms. The use of upflow biological aerated biofilter for the treatment of pig manure at pilot-scale was reported by Westerman et al. [8]. Karakashev et al. [9] used a new process scheme called PIGMAN that includes a combination of thermophilic anaerobic digestion with sequential separation by decanter centrifuge, post-digestion in UASB reactor, partial oxidation, oxygen-limited autotrophic nitrification–denitrification (OLAND) process, and phosphorus removal by precipitation as struvite (PRS). Vanotti et al. [10] demonstrated the operation of a full-scale treatment system for the removal of nitrogen, phosphorus, heavy metals, pathogens, ammonia and odor from liquid swine waste. This system used a multiplicity of processes including solid–liquid separation using polymer flocculation, biological nitrogen removal by nitrification/denitrification, phosphorus removal by calcium phosphate precipitation, and disinfection. The multiple biological and physical–chemical processes and unit operations used in these treatment systems are needed for the removal of different organic and inorganic contaminants from hog waste that exist at high concentrations in liquid and solid phases. The developed technologies often have elaborate designs, large footprints, and high maintenance and control requirements. In addition, they usually generate large amounts of biological solids (sludge) that require further handling and treatment.

An in-barn separation technique has been developed and investigated by Godbout et al. [11] to separate solids from liquid in hog waste, and to concentrate phosphorus in the solid phase. Several treatment techniques are currently under investigation for the solid wastes. Moreover, the liquid phase has to be treated since it does not conform to environmental standards for surface discharge. This paper presents the results of continuous treatment of separated liquid phase of hog manure by the integrated, multi-zone BioCAST system that uses two interlinked reactors containing a multiplicity of zones with different environmental conditions. Hog waste treatment in the examined system followed the treatment of synthetic wastewater which had lasted for 310 d. The results of synthetic wastewater treatment by the BioCAST system were reported before [12–14]. Those studies showed the capacity of this treatment technology for the continuous removal of organic and inorganic contaminants with loading rates of 0.95–1.86 kg COD/m^3 d, 0.02–0.08 kg TN/m^3 d and 0.014–0.02 kg TP/m^3 d. Removal efficiencies up to 98.9%, 98.3% and 94.1% were obtained for COD, total nitrogen (TN) and total phosphorus (TP), respectively. The examined treatment system generated reduced amounts of sludge, producing an average biomass yield of 6.4% based on the consumed COD.

2. Materials and methods

2.1. Wastewater composition and operating conditions

The hog waste used in this study was the separated liquid phase of hog manure from an in-barn separation technique, supplied by the Institut de recherche et de développement en agroenvironnement (IRDA), in Québec, Canada. The COD, total nitrogen (TN), total phosphorus (TP) concentrations in the hog waste were in the range of 71,000 ± 2800 to 120,000 ± 4400 mg COD/L, 7800 ± 480 to 17,800 ± 1000 mg TN/L, and 720 ± 52 to 1380 ± 110 TP/L. This wastewater was diluted with tap water, resulting in concentrations in the range of 960 ± 38 to 2400 ± 96 mg COD/L, 143 ± 9 to 235 ± 15 mg TN/L, 25 ± 2 to 57 ± 4 mg TP/L, and 350 ± 22 to 1800 ± 125 mg TSS/L. The influent COD:BOD ratio ranged from 1.9:1 to 1.1:1, implying the presence of a higher percentage of organic biodegradable matter than the oxidizable inorganic substances in the wastewater, which suggests the potential biodegradability of this wastewater.

The hydraulic retention time (HRT) in the first and second reactors were maintained in the range of 1.43–1.75 d and 0.17–0.21 d, respectively. A feast and famine regime of feeding (20 min feast:40 min famine) was used during the treatment operation in order to improve the activity of microorganisms and to enhance the removal of contaminants, as suggested by Tay et al. [15]. It has been shown that during the short feast period, the microorganisms store carbon source in their intracellular space to be further used during the famine period when the external carbon source is not available for their survival [16]. During the famine period, the microorganisms become extensively hydrophobic which facilitates microbial aggregation in the mixed liquor [15].

The integrated wastewater treatment system operated for 185 d during the treatment of hog waste, immediately following 310 d of synthetic wastewater treatment. The results are reported from three weeks after the onset of hog waste treatment when the COD removal efficiency reached 75%.

2.2. Design and operation of the treatment system

The design and operation of BioCAST treatment system have been reported before [12–14]. This system uses two interlinked bioreactors, each containing a multiplicity of zones with different environmental conditions (Fig. 1A). Reactor I contains aerobic, microaerophilic (also known as microaerobic) and anoxic zones for biological treatment, as well as a clarification zone for solid–liquid separation. Reactor II contains an anaerobic zone at the bottom, a solid–liquid separation zone in the middle, and a filtration unit at the top. The aerobic zone, located in the center of the first reactor contains both fixed-film and suspended microorganisms, thus increasing the biomass retention capacity of the system, producing a high solid retention time (SRT) that has been shown to increase the specific rate of contaminant removal. The aerobic and the adjacent microaerophilic zones have been designed based on the concept of air-lift reactors. The mixed liquor flows upward in the aerobic zone (riser) and downward in the microaerophilic zone (downcomer) on a continuous basis. Air is introduced through three custom-built air diffusers located at the bottom of aerobic zone. Aeration supplies oxygen for the aerobic microorganisms in this zone, and provides mixing of liquid, while causing the circulation of mixed liquor between the three adjacent zones of aerobic, microaerophilic and anoxic. The continuous circulation of liquid

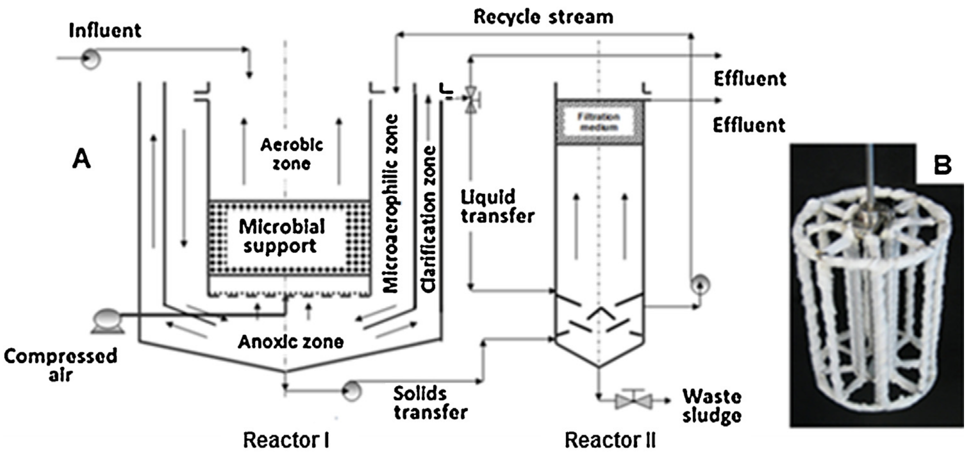

Fig. 1. (A) Schematic diagram of the multi-zone BioCAST technology. (B) Structure of the microbial support.

exposes the contaminants to three environmental conditions every few minutes. Eight openings with adjustable sizes of ¼ in. to 1 in., located at the top of aerobic zone, provide additional control for the circulating liquid flow rate and dissolved oxygen concentration in the aerobic and microaerophilic zones. The fixed-film biomass grows on a custom-built support medium that consists of two stainless steel concentric cylindrical structures, uniformly wrapped in geotextile (Fig. 1B) and located in the middle of aerobic zone. The geotextile had a filamentous structure, facilitating biomass attachment and formation of biofilm. A polyethylene continuous non-woven geotextile (Texel Inc., Quebec, Canada) with the density of 950 kg/m^3, specific surface area of 1500 m^2/m^3, and porosity of 0.88 was used.

The second reactor is designed for sludge digestion and solid–liquid separation. The effluent from the first reactor is directed to the second reactor for additional clarification, while the generated sludge is transferred from the anoxic zone in the first reactor to the anaerobic zone, located at the bottom of the second reactor, for digestion. The digestion of waste sludge in the anaerobic zone provides volatile fatty acids (VFAs) that are needed for the phosphorus removal and denitrification processes. A recycle stream between the anaerobic zone of the second reactor and aerobic zone of the first reactor returns a mixture of solids and liquid that contain phosphorus accumulating organisms (PAOs), needed for phosphorus removal, as well as the generated VFA which can be used as a source of easily biodegradable carbon for the denitrification and phosphorus removal processes. The reactors were fabricated by the company AC Plastics in Quebec, Canada. The volumes of aerobic, microaerophilic and anoxic zones were 17, 61 and 22 L, respectively, while the volume of clarification zone was 85 L. The second reactor had a total volume of 12 L. The reactors had a height of 1.13 m. The filtration unit in the second reactor was left empty during this study due to the continued turbidity of effluent as a result of the generation of extracellular polymeric substance, as reported before [12,13].

2.3. Monitoring and control of physical–chemical parameters

The dissolved oxygen (DO) concentration, liquid pH and oxidation–reduction potential (ORP) were continuously monitored and/or controlled in various zones of the treatment system using the corresponding electrodes and probes. The DO concentration was controlled at 3–5 mg/L in the aerobic zone and 0–2 mg/L in the microaerophilic zone. The ORP assumed the following values: >+100 mV, 0–100 mV, <−300 mV, and <−300 mV in the aerobic, microaerophilic, anoxic, and anaerobic zones, respectively. ORP values in the range of +50 to +325 mV, −50 to +50 mV and −200 to −50 mV have been reported for aerobic, anoxic and anaerobic conditions, respectively [17]. A lower ORP value of −225 mV was reported for the anoxic condition by McIntosh and Oleszkiewicz [18], while ORP values of <−300 mV were also reported for the anaerobic condition [18,19]. The microaerophilic (microaerobic) condition is commonly defined by low dissolved oxygen concentrations under 2 mg/L [20]. The ORP values observed in the anaerobic and anoxic zones of the examined treatment system during hog waste treatment were lower than the values observed during the treatment of synthetic wastewater by this system, as reported before [12,13]. The liquid pH was adjusted in the influent hog waste, producing pH values in the range of 7.5–8.3 in the mixed liquor, 6.8–8.0 in the anoxic zone, and 7.0–8.0 in the anaerobic zone. The pH values in different zones were continuously monitored by probes and electrodes and were controlled within the required range by acid/base addition using 1 N HCl/NaOH solutions, if needed. The treatment operations were conducted at room temperature (20 ± 1 °C).

2.4. Analytical methods

Liquid and solid sampling from various zones was carried out at least twice per week and the reported values are the average of at least three measurements. Liquid samples were filtered through 0.45 μm syringe filters and the required dilutions were made for concentrated samples. The COD concentration was measured using closed reflux colorimetric method (EPA standard method 410.4). Total nitrogen (TN) and total phosphorus (TP) in the liquid samples were determined using colorimetric methods after digestion of the samples at 100 °C for 1 h. Total nitrogen (TN) concentration was determined according to the persulfate digestion method (HACH method 10071). Total phosphorus (TP) concentration was determined by the ascorbic acid method (EPA method 365.2). The concentration of NH_3-N was determined according to the Salicylate Method (EPA method 350.1). NO_2-N was measured by the diazotization method (EPA method 354.1), while NO_3-N was determined according to the reaction of nitrate ions with 2,6-dimethylphenol (EPA methods 353.2). Total Kjeldahl nitrogen (TKN) was calculated from the difference of TN and the sum of nitrate and nitrite.

The phosphorus content of sludge was measured spectrophotometrically using the vanadomolybdophosphate method [21]. The VFA concentration was determined using esterification method (HACH Method 10240), while the concentration of solids in the sludge was determined using gravimetric methods (Standard Methods 2540 B and D). The samples were oven-dried at

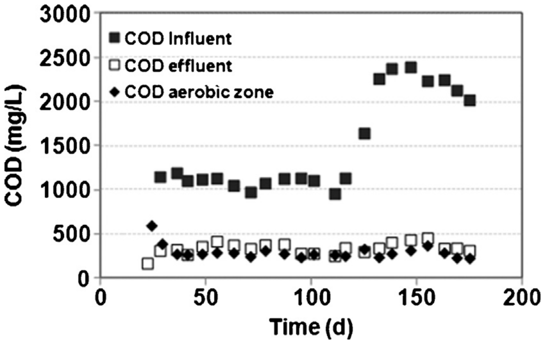

Fig. 2. COD concentrations in the influent, effluent and aerobic zone of the treatment system.

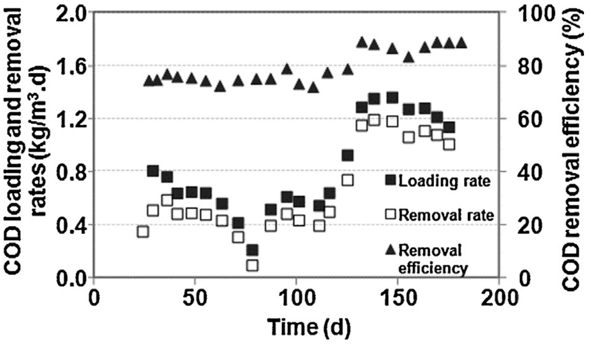

Fig. 3. Changes of the COD loading and removal rates and its removal efficiency during the course of treatment.

105 °C ± 2 °C for the measurement of TSS and were further ignited at 550 °C ± 2 °C to determine the VSS concentration of sludge. Microbial observations were performed using a Micromaster desktop microscope (Model S11035) equipped with a digital camera. The concentration of biofilm biomass was measured periodically by removing the microbial support from the aerobic zone for a few minutes to measure the biofilm thickness and to collect samples for biomass measurement and microscopic observations. The concentration of biofilm biomass was measured using gravimetric method described above for a mixed sample from different sections of the microbial support.

3. Results and discussion

3.1. Removal of carbon, nitrogen and phosphorus

The examined treatment system operated continuously during 185 d of hog waste treatment without any clogging of the support medium. This is contrary to the operation of biological aerated filters (BAF) where the support medium is periodically backwashed to avoid clogging, or to release the trapped suspended solids and control the biofilm growth.

The time-dependent changes in the concentrations of chemical oxygen demand (COD) in the influent and effluent streams and the aerobic zone during the entire course of hog waste treatment are shown in Fig. 2. The effluent COD concentration was close to its concentration in the aerobic zone, implying that the digestion of microbial biomass in the anaerobic zone had a minimal impact on the effluent COD concentration. This is important, knowing that although the removal of COD mainly occurs in the first reactor, the digestion of microbial biomass in the anaerobic zone of the second reactor produces VFA that can contribute to the increase of COD concentration in the effluent. However, the generated VFA is partly consumed by the bacteria (including the PAOs) in the anaerobic zone, and partly consumed by the heterotrophic bacteria in the first reactor, including denitrifiers during nitrogen removal process. Hence, the effluent COD concentration remained close to the COD concentration in the aerobic zone, as illustrated in Fig. 2. The effluent COD concentration varied between 168 ± 11 mg/L and 454 ± 23 mg/L despite the increase of influent COD concentration from 960 mg/L on day 110 to 2370 mg/L on day 138 in conjunction with the increase of COD loading rate (Fig. 3), demonstrating the adaptation of heterotrophic microorganisms that are mainly responsible for the removal of organic contaminants.

The COD removal rate increased from an initial value of 0.35 ± 0.02 kg/m^3 d to 1.2 ± 0.05 kg/m^3 d, and closely followed its loading rate during the entire course of operation (Fig. 3). The close relationship between the COD loading rate, defined as the rate of COD entrance into the reactor per unit volume of reactor (kg COD/m^3 d) and COD removal rate, defined as the rate of COD removal per unit volume of reactor (kg COD/m^3 d), resulted in removal efficiencies in the range of 72.0–89.2% (Fig. 3) and linear relationships between the COD removal efficiency and COD removal rate and its loading rate, as presented in Fig. 4. The COD loading rate was estimated from the equation (S_0Q/V), while the COD removal rate was estimated from the equation ($(S_0 - S)Q/V$) where S_0 and S are the influent and effluent substrate concentrations, respectively, Q is the wastewater flow rate, and V is the reactor volume. COD removal efficiencies of 65%, 75% and 87% were reported during the treatment of swine wastewaters using an attached-growth anaerobic system with floating plastic ballast rings as a medium [22], upflow biological aerated filters [8], and aerobic granulated sludge grown in a sequential batch reactor [6], respectively. Higher removal efficiencies of organic material have been reported in hybrid processes. For example, 96% organic matter removal from pig manure was reported in the PIGMAN process [9], while the combination of a biofiltration system along with a decanter and anaerobic digestion in the BIOSOR process resulted in BOD removal greater than 97% [7], and the combination of anaerobic/oxic (A/O) and anoxic reactors for the treatment of a prescreened piggery wastewater produced 96% removal of organic materials [23].

The variations of TN and TP loading rates (kg/m^3 d) and their corresponding removal rates (kg/m^3 d) are presented in Fig. 5(a and b). The differences between the loading rates and removal rates of TN and TP during the early stages of treatment produced low removal efficiencies as observed in Fig. 6. The removal efficiencies of total nitrogen and ammonia nitrogen ranged from 11.9% to 69.2% and 9.6% to 75.7%, respectively, while the removal efficiencies of total phosphorus ranged from 19.6% to 47.6%.

Unlike the trend observed with the COD, the effluent concentrations of TN and TP were higher than their corresponding

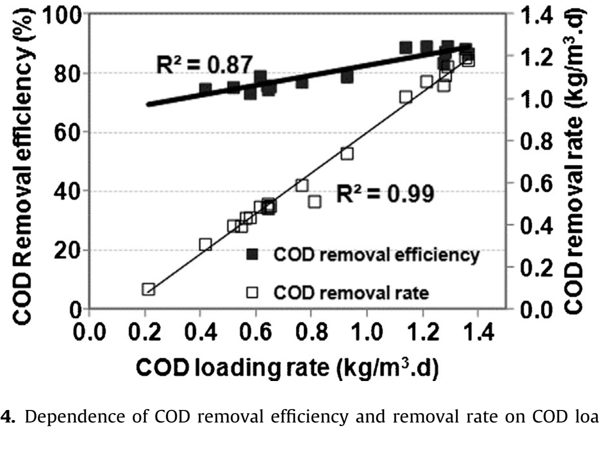

Fig. 4. Dependence of COD removal efficiency and removal rate on COD loading rate.

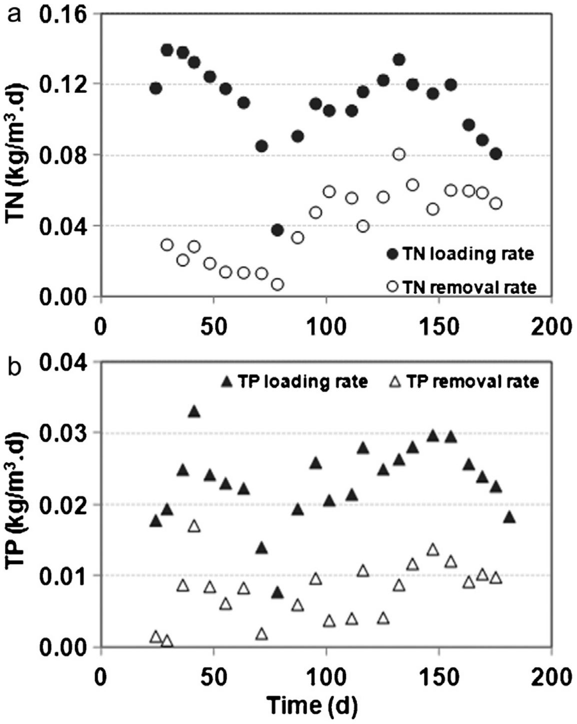

Fig. 5. Loading rates and removal rates of nitrogen and phosphorus.

concentrations in the aerobic zone, possibly due to biomass digestion in the anaerobic zone. Consequently, the reported removal efficiencies and removal rates are based on the concentrations in the aerobic zone, i.e. the filtered mixed liquor that show the biodegradation capacity of the treatment system. Obviously, the operation of the system needs to be optimized in order to produce low biomass yields that require high SRT and low sludge withdrawal on the one hand, and on the other hand, maintain the effluent quality that will be adversely affected by a high SRT and the digestion of microbial biomass in the anaerobic zone.

The design and operating conditions of the treatment system supported the nitrification and denitrification processes for nitrogen removal. The nitrification was supported by the level of dissolved oxygen concentration in the aerobic zone that was maintained above 3 mg/L at all times, consistent with DO level recommendations for non-limiting nitrification [24] and the immobilization of nitrifying bacteria on a support material as shown in our previous reports [14]. The increased efficiency of nitrification process has been shown to occur by increasing the retention time of nitrifying bacteria [25], commonly accomplished by their immobilization. The increase of nitrification rates in attached-growth swine waste treatment systems compared to suspended-growth treatment systems has been reported before [26]. The establishment of denitrification process for the removal of nitrite and nitrate depends on the availability of carbon source in the microaerophilic and anoxic zones [27]. The low concentration of biodegradable organic matter relative to the nitrogen and phosphorus contents of wastewater has been specified as a limiting factor in nutrient removal from swine waste [28]. Nutrient removal from swine waste has been increased in sequencing batch reactors (SBRs) by the addition of supplemental sources of organic matter such as glucose, methanol, acetate, and propionate [29–31]. Lee et al. [28] showed that the supplementation of swine wastewater with either acetate or fermented swine waste that contains VFA, enhanced biological nutrient removal in sequencing batch reactors. They reported a total nitrogen removal of 90% and a total phosphorus removal of 89% compared to a control reactor that received no supplementation and achieved total nitrogen and total phosphorus removals of 76% and 15%, respectively. In the present system, the digestion of biomass in the anaerobic zone provided an internal source of organic material for phosphorus removal and denitrification of the produced nitrite and nitrate without the need for the addition of any external carbon source. The use of an internally available carbon source for biological nitrogen and phosphorus removal without any external carbon source was also reported by Ra et al. [23].

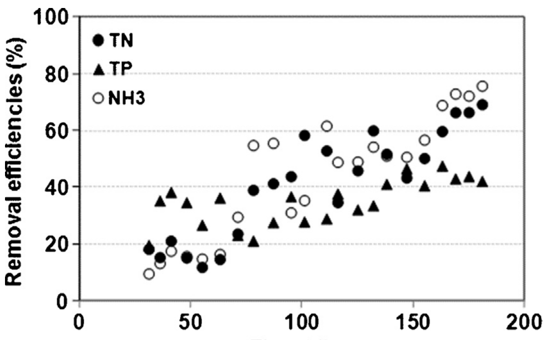

Fig. 6. Variations of the removal efficiencies of total nitrogen, total phosphorus and ammonia.

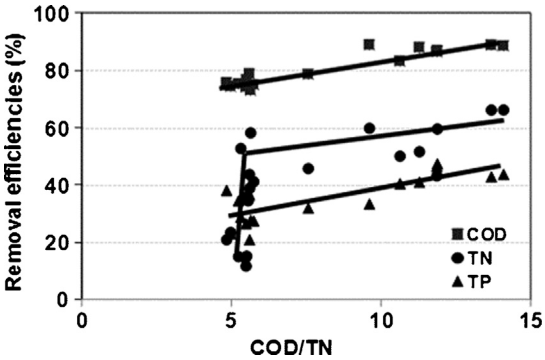

Fig. 7. Dependence of the COD, TN and TP removal efficiencies on the COD/TN ratio.

3.2. Impact of process parameters

The increase of COD/N ratio from 4.8 to 14.1 had a positive impact on the removal efficiencies of COD, TN and TP, as shown in Fig. 7. The removal efficiencies of COD and TP increased steadily at a constant rate with the increase of COD/TN ratio, and reached 88.8% and 43.9%, respectively, at the COD/TN ratio of 14.1. However, the TN removal efficiency showed a different trend and increased sharply at COD/TN ratio between 4.8 and 5.6, and then exhibited a slower rate of increase with further increase of this ratio to 14.1. The high percentage of easily biodegradable volatile fatty acids (VFA) in the influent that ranged from 34.2% to 63.3% of the overall influent COD combined with the VFA produced in the anaerobic zone by the digestion of biosolids, contributed to the increase of contaminant removal efficiencies with the increase of COD/TN ratio. The VFAs in the influent stream were produced by fermentation processes in the holding tank, because of the establishment of anaerobic conditions in this tank. Carrera et al. [32] and Zafarzadeh et al. [33] also found that COD removal rate increased when the COD/N increased, while Liu et al. [34] and Zhang et al. [35] showed the increase of TN removal efficiency with the increase of COD/TN ratio. The increase of nitrogen removal efficiency from 63% to 84% with the increase of COD/TN from 3.0 to 4.2 was reported to be related to the

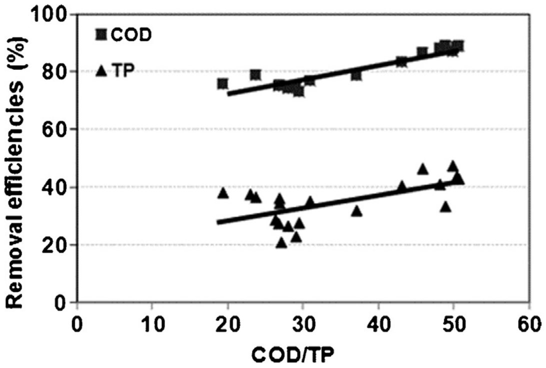

Fig. 8. Dependence of the COD and TP removal efficiencies on the COD/TP ratio.

introduction of influent to the anoxic zone, increasing the supply of COD and producing a pre-denitrification condition for nitrogen removal [35]. Danesh and Oleszkiewicz [36] showed that biological phosphorus removal in sequencing batch reactors improved significantly as a result of prefermentation of degritted raw wastewater that resulted in the production of VFA. They showed that the phosphorus concentration in the effluent of the system having a prefermentation step was typically less than 1 mg/L and most often less than 0.5 mg/L, while the phosphorus content in the effluent from the system which was fed directly with degritted raw wastewater was often in the range of 1.5–4.5 mg/L. The enhancement of biological phosphorus removal in wastewater treatment systems by the addition of short chain fatty acids, including sodium acetate, acetic acid and butyric acid has also been shown [37].

A positive correlation was observed between the COD/TP ratio, that ranged from 19.3 to 50.6, and the removal efficiencies of COD and TP (Fig. 8), while there was no clear relationship between this ratio and the TN removal efficiency, indicating that the removal of nitrogen exhibits little dependence on the COD/TP ratio.

On the contratry, the removal efficiencies of COD and TP decreased steadily with the increase of TN/TP ratio from 3.6 to 5.8 (Fig. 9). The COD and TP removal efficeincies were 88.8% and 43.9%, respectively, at the TN/TP ratio of 3.6, and decreased to 74.6% and 23.1%, respectively, at the TN/TP ratio of 5.8. Despite a decreasing trend, the removal efficiency of TN did not exhibit a correlation with this ratio (data not shown).

The observed reduction of COD and TP removal with the increase of TN/TP ratio is in contrast to the trend observed during the treatment of synthetic wastewater [13] and is believed to be related to the inhibition of microbial activity concomitant with increased concentration of free ammonia during the operation period at high TN/TP.

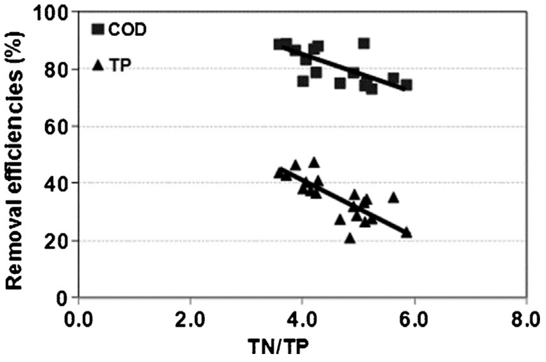

Fig. 9. Relationship between the removal efficiencies of COD and TP and TN/TP ratio.

3.3. Biomass production and yield

During the reported operation period, the biofilm biomass concentration was in the range of 38480 ± 2650 mg/L to 53100 ± 3290 mg/L, while the suspended biomass concentration in the mixed liquor ranged from 400 ± 22 mg/L to 1100 ± 50 mg/L. The high biomass concentration was accompanied by high solid retention times (SRT) in the range of 12–49 d. The maintenance of high biomass concentrations in both suspended and immobilized forms and high solid retention times (SRT), along with anaerobic degradation of organic matter in the oxygen-depleted microaerophilic and anoxic zones that inherently produce lower biomass yields, and anaerobic digestion of biosolids in the anaerobic zone produced low biomass yields with monthly values of 2.6–12.6% (based on the consumed COD) and an average value of 8.2%.

3.4. Wastewater toxicity

The lower removal efficiencies of contaminants, especially nitrogen and phosphorus, during the treatment of hog waste, compared to the results obtained during the treatment of synthetic wastewater [12–14] suggested that the examined hog waste exerted inhibitory effects on the activity of microorganisms. The observed inhibitory effect was verified by a toxicity bioassay (LC_{50} – 48 h) using *Daphnia magna*. This inhibition could have resulted from the presence of free ammonia or free nitrous acid at concentrations that proved to be inhibitory to the activity of microorganisms. The free ammonia concentration has been reported to inhibit ammonia oxidizing bacteria at concentrations above 10 mg/L and nitrite oxidizing bacteria at concentrations in the range of 0.1–1.0 mg/L, while all nitrifying bacteria are inhibited at free nitrous acid concentrations above 0.1–0.2 mg/L [38–40]. High ammonia concentration has been identified as one of the reasons that limit the proper treatment of piggery wastewaters. The inhibition of the anaerobic digestion of swine manure by ammonia was reported by Hansen et al. [41], while Zhang et al. [42] used air stripping as a pretreatment to remove ammonia for enhanced biomethanization of piggery wastewater. The free ammonia and free nitrous acid concentrations (mg/L) in the influent were estimated from the following equations as suggested before [38,39]:

$$NH_3 = 1.21 \times NH_4\text{-}N \times 10^{pH} / \exp\left(\frac{6344}{273 + T}\right) + 10^{pH} \quad (1)$$

$$HNO_2 = 3.36 \times NO_2\text{-}N / \exp\left(-\frac{2300}{273 + T}\right) \times 10^{pH} \quad (2)$$

All concentrations in Eqs. (1) and (2) are in mg/L.

Although the free nitrous acid concentration was found to be well below 0.2 mg/L throughout the course of operation, the free ammonia concentration was above 10 mg/L during the first 70 d of operation, contributing to the inhibition of ammonia oxidizing bacteria (Fig. 10).

The existing inhibition was apparent from the high effluent ammonia concentrations during this period, indicating the inhibition of ammonia oxidation, leading to its accumulation (Fig. 11). The low concentrations of nitrite-N, <1 mg/L, despite inhibitory levels of free ammonia that stayed above 3.1 mg/L during the entire course of operation, suggests that either nitrite oxidizing bacteria were not inhibited at these levels of free ammonia, or other metabolic pathways contributed to the removal of nitrite, e.g. nitrite reduction in a process known as Anammox. We did not explore the nature of potential processes that might have contributed to nitrogen removal in the examined treatment system, and only suggest that the presence of this process may justify the very low nitrite concentrations observed. The nitrate-N concentrations were below

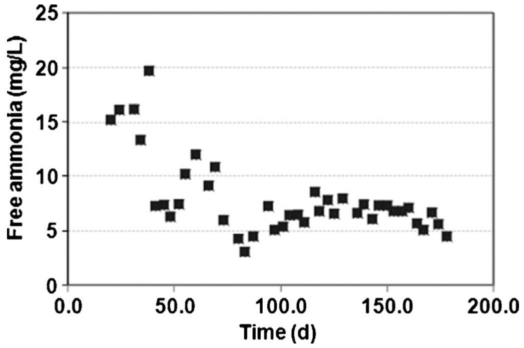

Fig. 10. Changes in the concentration of free ammonia in the influent during the course of operation.

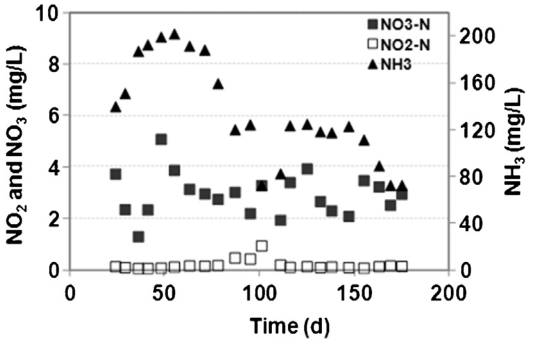

Fig. 11. Nitrite-N, nitrate-N and ammonia concentrations in the effluent of the examined treatment system.

6 mg/L throughout the course of operation (Fig. 11), but consistently higher than the values obtained in our previous treatment studies with synthetic wastewater [12,13] and suggest the inhibition of nitrate reducing bacteria. The progressive reduction of free ammonia concentration during the first 100 d of operation (Fig. 10) can explain the sharp increase of TN removal that occurred during the same period, and correspond to the change of COD/TN ratio in the narrow range of 4.8–5.6 (Fig. 7).

Despite the inhibitory characteristics of influent hog waste, the microbial community was not totally inhibited as shown by the high removal efficiency of COD, indicating that the heterotrophic microorganisms maintained their activity throughout the course of operation. This was due to the long solid retention time (SRT) in the treatment system that enhanced the adaptation of microorganisms. On the other hand, the autotrophic nitrifiers which are known to be more sensitive to the presence of toxic compounds than heterotrophs were inhibited, thus resulting in a low nitrification and lower removal of total nitrogen. The relationship between nitrogen and phosphorus removal, as shown before [12,13] prevented a complete removal of phosphorus, as exhibited in the low removal efficiencies of phosphorus obtained during the treatment.

The improved performance of the treatment system with the progress of operation, indicated by the increase in removal efficiencies of nitrogen and phosphorus (Fig. 6), resulted from the development and adaptation of different microbial cultures. Therefore, it is plausible that higher removal efficiencies of contaminants, especially nutrients, would be achieved if the treatment system had operated for a longer period.

4. Conclusions

The multi-zone BioCAST technology exhibited a high capacity for the treatment of the separated liquid phase of hog manure that contains high concentrations of organic carbonaceous compounds and inorganic nutrients. The applied dilution of hog waste was necessary to alleviate its inhibitory effect toward microbial activities and permit further biological treatment. On a commercial scale, this may be accomplished by using treated effluents of agricultural activities or rain water collected at the barn site. Operating with COD, TN and TP concentrations in the range of 960 ± 38 to 2400 ± 96 mg/L, 143 ± 9 to 235 ± 15 mg/L and 25 ± 2 to 57 ± 4 mg/L, respectively, the treatment system simultaneously removed organic compounds and inorganic nutrients with efficiencies in the range of 79.0–89.2% for COD, 11.9–69.2% for TN and 19.6–47.6% for TP. The removal of COD and TP increased steadily with the increase of COD/TN ratio from 4.8 to 14.1 and the increase of COD/TP ratio from 19.3 to 50.6, while decreasing with the increase of TN/TP from 3.6 to 5.8. The TN removal also increased with the increase of COD/TN ratio while it did not present any steady dependence on the COD/TP or TN/TP ratios. The inhibitory effect of the influent hog waste, caused by high levels of free ammonia that were estimated to be greater than 3.1 mg/L throughout the operation period, were postulated to be responsible for the negative impact of the TN/TP ratio on COD and TP removal. A low sludge (biosolids) yield with monthly values of 2.6% to 12.6% (based on the consumed COD) and an average value of 8.2% was obtained, owing to the reduced generation of microbial biomass during the operation of BioCAST system. The increased removal of all contaminants with time showed the improved adaptation of microbial culture, suggesting that higher removal efficiencies would be obtained during extended operation of the examined treatment system. Future research will investigate the optimization of operating conditions for increased removal of inorganic nutrients along with organic compounds while producing a reduced amount of biosolids.

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