

Water Research 38 (2004) 3031-3042



www.elsevier.com/locate/watres

Removal of carbon and nutrients from domestic wastewater using a low investment, integrated treatment concept

Sunny Aiyuk^a, Joyce Amoako^a, Lutgarde Raskin^b, Adrianus van Haandel^c, Willy Verstraete^{a,*}

^a Laboratory of Microbial Ecology and Technology (LabMET), Faculty of Agricultural and Applied Biological Sciences, Ghent University, Coupure Links 653, GentB B-9000 Ghent, Belgium

^b Newmark Civil Engineering Laboratory, Department of Civil and Environmental Engineering, University of Illinois at Urbana-Champaign, IL 61801, USA

^c Research Program for Basic Sanitation (PROSAB), Sanitary Engineering Group, Department of Civil Engineering, Federal University of Campina Grande, Paraiba, Brazil

Received 11 February 2003; received in revised form 20 November 2003; accepted 15 April 2004

Abstract

An integrated chemical–physical–biological treatment concept for the low-cost treatment of domestic wastewater is proposed. Domestic wastewater was subjected to a chemically enhanced primary treatment (CEPT), followed by treatment in an upflow anaerobic sludge blanket (UASB) reactor. In addition, a regenerable zeolite was used to remove NH_4^+ , either after CEPT pretreatment or after biological treatment in the UASB reactor. The CEPT pretreatment consisted of the addition of a coagulant (FeCl₃) and an anionic organic flocculant and removed on average 73% of the total chemical oxygen demand (COD_t), 85% of the total suspended solids, and 80% of PO₄³⁻ present in the wastewater. The UASB system, which consequently received a low COD_t input of approximately 140 mg/L, was operated using a volumetric loading rate of 0.4 g COD_t/L. d (hydraulic retention time [HRT] = 10 h) and 0.7 g COD_t/L. d (HRT = 5 h). For these conditions, the system removed about 55% of the COD_t in its influent, thus producing an effluent with a low COD_t of approximately 50 mg/L. The zeolite, when applied in batch mode before the UASB reactor, removed approximately 45% of the NH₄⁺, whereas its application as a post-treatment cartridge resulted in almost 100% NH₄⁺ removal. The simple design and relatively low operating costs, due to low costs of added chemicals and low energy input (estimated at \in 0.07–0.1 per m³ wastewater treated), combined with excellent treatment performance, means that this system can be used as a novel domestic wastewater treatment system for developing countries. Therefore, the system is called a Low Investment Sewage Treatment (LIST) system.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Domestic wastewater; Anaerobic treatment; CEPT pretreatment; Zeolite; UASB; LIST

1. Introduction

There is a tremendous need to develop reliable technologies for the treatment of domestic wastewater

in developing countries. Such treatment systems must fulfill many requirements, such as simple design, use of non-sophisticated equipment, high treatment efficiency, and low operating and capital costs [1,2]. In addition, consonant with population growth and increase in urbanization, the cost and availability of land is becoming a limiting factor, and "footprint size" is increasingly becoming important in the choice of a treatment system.

^{*}Corresponding author. Tel.: +32-92-6459-76; fax: +32-92-6462-48.

E-mail address: willy.verstraete@rug.ac.be (W. Verstraete).

Nomenclature		P _{tot} rpm	total phosphorus revolutions per minute		
BOD	biochemical oxygen demand	SMA	specific methanogenic activity		
BOD_5	BOD after incubation of 5 days	SD	standard deviation		
$B_{ m v}$	volumetric loading rate	SS	suspended solids		
CEPT	chemically enhanced primary treatment/sedi-	SV ₃₀	sludge volume after 30 min of settling		
	mentation	SV_{60}	sludge volume after 1 h of settling		
COD	chemical oxygen demand	TAN	total ammoniacal nitrogen (i.e., NH ₄ ⁺ -		
COD _s	soluble COD		$N + NH_3$)		
CODt	total COD	TKN	total Kjeldahl nitrogen		
EGSB	expanded granular sludge bed	TSS	total suspended solids		
HRT	hydraulic retention (residence) time	UASB	upflow anaerobic sludge blanket (bed)		
LIST	low cost, Integrated Sewage Treatment	VFA	volatile fatty acid		
Р	power requirement (W) per unit volume (m ³)	VSS	volatile suspended solids		

Anaerobic technologies should be considered for domestic wastewater treatment as an alternative to more conventional aerobic technologies in most developing countries for a variety of reasons. Anaerobic technologies already have been applied successfully for the treatment of a number of waste streams, including lowstrength wastewaters such as domestic wastewater, particularly under tropical conditions [3-5]. Anaerobic treatment can be carried out with technically simple setups, at any scale, and at almost any place. It produces a small amount of excess, well stabilized sludge, and energy can be recovered in the form of biogas. The process can be carried out in both centralized and decentralized modes, and the latter application can lead to significant savings in investment costs of sewerage systems [6,7]. However, while anaerobic processes have gained popularity over the past decade, skepticism related to their application for domestic wastewater treatment remains widespread [6,8–10].

Within the spectrum of anaerobic treatment technologies, the upflow anaerobic sludge blanket (UASB) reactor offers great promise, especially in a developing country context [11,12]. It is a robust high-rate reactor system, generally without moving parts, limiting both capital and operating costs [13,14]. The reactor retains a high amount of biomass in the form of dense granules or aggregates of microorganisms. Furthermore, good contact between biomass and wastewater is ensured due to mixing as a result of recirculation and biogas production. However, when the volumetric loading rate is below 1-2 g chemical oxygen demand (COD)/L. d, biogas production is limited [15]. The expanded granular sludge bed (EGSB) reactor, a modified version of the UASB reactor, has a much higher upflow velocity, which would enable greater mixing when loading rates are low, but would cause washout of fine biomass particles that typically form after prolonged treatment at low loading rates [16].

While domestic wastewater has a low organic content with a typical COD concentration in the range of 250-1000 mg/L [17], it contains a relatively large fraction of suspended organic material. When treating such wastewaters with high levels of suspended organic matter in UASB reactors, hydrolysis can be a limiting factor [15]. This drawback can be eliminated by pre-settling the wastewater to remove most of the suspended solids (SS). Such settling can be aided by chemical addition, as natural settling is often inefficient and slow [18]. Moreover, since inorganic compounds such as NH_4^+ and PO_4^{3-} are only removed to a limited extent during anaerobic treatment, additional treatment is required when nutrient removal is necessary. Therefore, integration of SS and nutrient removal in an anaerobic treatment process should be a powerful alternative to anaerobic treatment only, for domestic wastewater treatment.

The objectives of this study were to perform a technical evaluation and a preliminary cost assessment of a treatment concept, which would make it possible to reuse and recycle domestic wastewater, especially for developing countries with warm climates. The proposed strategy consists of a coagulation/flocculation presedimentation step to remove SS and PO_4^{3-} , followed by treatment of the supernatant in a UASB reactor to remove soluble organics. In addition, NH_4^+ is removed by a zeolite ion exchange system, preferably placed after the UASB system. This ion exchange system is regenerated by biological nitrification. The overall treatment concept is referred to as a Low Investment Sewage Treatment (LIST) system.

2. Materials and methods

2.1. Domestic wastewater

Domestic wastewater was collected every two weeks, between 10:00 and 12:00 h in the morning, for a period

of 450 days (between July 2001 and October 2002), from the Ossemeersen wastewater treatment plant, city of Ghent (Belgium). The wastewater was pumped just below the water surface using a submersible pump (Nocchi VIPVORT 130/5, Lugnano (Pisa), Italy) immediately after the screens and grit chamber, and was stored at 4° C in tightly closed, 40-L containers.

2.2. Selection of coagulant and flocculant

Before a coagulant and flocculant were selected, a series of jar tests was carried out to determine which coagulant and coagulant/flocculant combination was most suitable for pretreatment of the wastewater used in this study. One percent FeCl₃ and Al₂(SO₄)₃ solutions were prepared in distilled water using FeCl₃.6H₂O (Merck, Ghent, Belgium) and Al₂(SO₄)₃, respectively. The coagulants were evaluated at doses of 50, 100, and 250 mg/L. Subsequently, 0.1% solutions of a variety of flocculants were prepared in distilled water by leaving the solutions overnight on a shaker in order to be homogenized. The flocculants were dosed at 5 or 10 mg/L in combination with 50 mg/L of each coagulant: The following flocculants were evaluated: (#1) Allied colloids M 156 (anionic), (#2) Allied Colloids Zetag 89 (cationic), (#3) Synthofloc 8022 H-PWG (anionic), (#4) Betz-Benelux 1120 P (anioic), (#5) Allied Colloids E 10 (anionic), (#6) Caldic Calflock P-1558 (cationic), (#7) Praestol 644 BC (cationic), (#8) Caldic Calfloc P-2900 (anionic), (#9) Praestol 857 BS (cationic), (#10) Praestol 2515 (anionic), (#11) Betz-Benelux 1558 E (cationic), (#12) Caldic Calfloc P-1552 (cationic), and (#13) Praestol 2500 (neutral). Allied Colloids flocculants were obtained from Allied Colloids (Bradford, England); Synthofloc flocculants from Synthofloc (Duisburg, Germany); Betz-Benelux flocculants from Betz-Benelux (Herentals, Belgium); Caldic Calfloc flocculants from Caldic (Hemiksen, Belgium); and Praestol flocculants from Stockhausen (Krefeld, Germany).

Jar tests were performed with a Geppert apparatus, type NRS 6 (Geppert Ruhrtechnik, Dreieich, Germany). A simple expression was used to equate mixing intensity with power input per unit volume [19]. A raw domestic wastewater sample (600 mL) was dosed with a coagulant, rapidly mixed for 1 min at 100 revolutions per minute (rpm) (power requirement $[P] = 2500 \text{ W/m}^3$), after which a flocculant was dosed, followed by a slow mixing of 10 min at 40 rpm [20,21] ($P = 1000 \text{ W/m}^3$). At the end of the test, the content of a jar was transferred into a volumetric cylinder and the development of sludge bed and supernatant were monitored during 30 min (SV_{30}) . After the 30 min period, the sludge bed and supernatant were characterized by performing total suspended solids (TSS), volatile suspended solids (VSS), total COD (COD_t) and soluble COD (COD_s) analyses. Furthermore, the pH was measured and a sample to which neither coagulant nor flocculant was added was evaluated as a control.

2.3. Experimental setups

2.3.1. Chemically enhanced primary treatment (CEPT)

Every other day, FeCl₃ coagulant (50 mg/L) was added to 15 L (phase 1) or 25 L (phases 2 and 3) of raw wastewater in a 30-L mixing tank, rapidly mixed at 100 rpm for 1 min ($P \sim 2500 \text{ W/m}^3$). Subsequently, 10 mg/L of the anionic Allied colloids E 10 flocculant was added and slowly mixed at 40 rpm for 10 min ($P \sim 1000 \text{ W/m}^3$). The impeller size/tank size ratios were similar in the jar tests and CEPT runs. After a settling period of 1 h, the supernatant was decanted into a supernatant container of 24 L, sampled, and characterized, and the volume of the settled sludge was measured. The settled sludge was poured into an Imhoff cone and the volume (SV₆₀) read off after 1 h.

2.3.2. Zeolite application

During phases 1 and 2, a natural zeolite (clinoptilolite) (Caldicare Zeoflocc, Hemiksem, Belgium) was dosed at 10 g/L (batch) to the supernatant obtained after CEPT pretreatment in order to remove NH_4^+ . After addition of the zeolite, the wastewater was stirred at 300 rpm for 2 h and the zeolite was allowed to settle for 3 min. The zeolite was reused three to four times and then collected for regeneration by nitrification. On days 150 and 300, commercially available nitrifying sludge with a biomass concentration of 2.5 g VSS/L (ABIL [Ammonium Binding Inoculum Liquid] Avecom, Ghent, Belgium) was diluted by adding 1 part of sludge to 4 parts of tap water. The diluted sludge (0.5 L) was activated by adding 0.5 g NH₄Cl and shaking overnight at 120 rpm on a shaker table at room temperature (Giogyrotory, New Jersey, USA). The following day, the sludge was added to 9.5 L of tap water in a 20-L container, and 1 kg of charged zeolite was added to the mixture, or proportions thereabout. This suspension was kept at room temperature, stirred slowly, and aerated by a small aeration pump (Rena Air 400, Annecy, France) fitted with an air stone to supply fine air bubbles. NH_4^+ and NO_3^- concentrations and pH levels were monitored over two days. When the NH_4^+ level dropped below the detection limit, the regeneration was considered complete, the suspension was allowed to settle for 3 min, the supernatant was decanted, and the zeolite was dried and reused.

During phase 3, removal of NH_4^+ was accomplished by allowing the UASB effluent to percolate through a column charged with 1.2 kg of zeolite with a granule size of 1–2 mm. The column had the following characteristics: surface area at each end = 0.004 m²; flow rate = 0.4 L/h (0.3 bed volumes/h); depth = 0.37 m; volu $me = 0.0015 m^3$. At the end of phase 3, it had not yet been necessary to regenerate the zeolite column.

2.3.3. UASB reactor operation

The pretreated wastewater was pumped semi-continuously from the supernatant container into the UASB reactor. The supernatant container was not mixed to avoid introduction of air. The gas-tight, glass UASB reactor (Schott-Duran, Mainz, Germany) was operated at $33\pm1^{\circ}$ C. It was seeded with 250 mL of granular anaerobic sludge obtained from a potato processing wastewater treatment plant (Primeur, Waregem, Belgium) with a specific methanogenic activity (SMA) of 0.40 g CH₄. COD/g VSS.d.

The UASB reactor had a height of 0.9 m, an internal diameter of 0.05 m, and an effective volume of 2.10+0.01 L. It carried a decantation sphere of 0.5 L volume at the top. Peristaltic Watson Marlow pumps (313 S, Falmouth-Cornwall, England), connected by means of thick and flexible connector tubes (internal diameter 14 mm), were used to introduce influent at the bottom and for recycling. The influent pump was operated every hour for 5 min and supplied 5.0 ± 0.5 L (phase 1) or 10.0 ± 0.5 L (phases 2 and 3) of influent every day. The recycle pump worked continuously, so that an upflow velocity of 1.0+0.1 m/h was attained. The effluent was collected through a U-shaped plastic tube (internal diameter 14mm). A gas discharge tube (internal diameter 10 mm) left the bulbous headspace of the reactor and conveyed biogas to a graduated and clamped column filled with acidified water colored with methyl orange for visibility.

The volumetric loading rate (B_v) was 0.4 g COD/L. d during phase 1 and 0.7 g COD/L. d during phases 2 and 3, corresponding to hydraulic retention times (HRTs) of 10±0.2 h and 5±0.2 h, respectively. During phase 2, a small amount (10 mg/L of feed) of a mix of vitamins and minerals (Avecom, Ghent, Belgium) was added to the influent or directly to the reactor content, whereas this mix was not added during phases 1 and 3.

The COD removal efficiency of the UASB reactor was calculated every other day. At the end of a two-day period, the influent remaining in the supernatant container, which was slightly more concentrated than the influent used during the beginning of the cycle due to settling of SS remaining after pretreatment, was well mixed, sampled, and the COD_t was analyzed. Using this measurement, combined with the total COD_t present in the supernatant container at the beginning of the cycle, the amount of COD_t received by the UASB reactor over a two-day time period could be calculated. Using this value combined with the total amount of COD_t that left the reactor during a two-day time period allowed calculation of the COD_t removal efficiency. This approach of calculating the COD_t removal efficiency was selected rather than stirring the supernatant

container to homogenize the UASB influent because the latter procedure can introduce air.

2.4. Analytical techniques

The pH was measured with a digital pH-meter (Knick-Elcolab n.v., Kruibeke, Belgium). Alkalinity was determined by acid titration from the initial pH of the samples to pH 4.5 [22]. Methane (CH₄) and carbon dioxide (CO_2) in the biogas of the UASB reactor were analyzed with an Intersmat IGC 120 MB gas chromatograph (Intersmat, Lyon, France) connected to a Hewlett-Packard 3390 A integrator. Volatile fatty acids (VFA) in the effluent of the UASB reactor were extracted by diethylether as described by Holdeman et al.[23] and measured with a gas chromatograph (Carlo Erba Fractovap 4160, Milano, Italy) equipped with a flame-ionization detector (FID) and a Delsi-Nermag integrator (ENICA-31). The gas chromatograph was equipped with a capillary free fatty acid phase column (25 m by 0.53 mm; 1.2 µm film thickness). The carrier gas was nitrogen at a flow rate of 20 ml/min. Temperatures were 130°C (column) and 195°C (injection port and FID).

For total Kjeldahl nitrogen (TKN) determination, a sample was digested according to the Kjeldahl procedure. NH₃ was distilled off by a Kjeltec apparatus (Tecator 2200 Kjeltec Auto Distillation, S-263 21, Hogamas, Sweden), captured by a boric acid solution, and the concentration was determined by titration with sulfuric acid [22]. For total ammoniacal nitrogen (TAN) (i.e., NH₄⁺-N + NH₃-N), the TKN procedure was used, but the digestion step was omitted. During zeolite regeneration, NH₄⁺-N and NO₃⁻-N were monitored with analytical test strips (Merck, Darmstadt, Germany). Total phosphorus (P_{tot}) was determined by ashing at 450°C, dissolution in nitric acid, and colorimetric analysis at a wavelength of 700 nm [22]. For PO₄³⁻-P analysis, the digestion step was omitted.

Biochemical oxygen demand (BOD) was determined by the oxytop method [22]: samples to which an inoculum, buffer, nutrients, and a nitrification inhibitor were added were incubated for 5 days at 20°C in partially filled bottles fitted with electronic stoppers from which results were directly read. Final results were obtained by using a suitable dilution factor. Other parameters (% solids, TSS, VSS, COD_t , COD_s) were determined by their respective standard methods [22].

Analyses of COD_t were performed twice weekly, the pH was analyzed every other day, and the other parameters were analyzed once every two weeks.

The SMA of the inoculum was analyzed in triplicate as described by Valke and Verstraete [24]. The SMA test was carried out by the pressure-bottle technique, using acetate as the substrate in an anaerobic medium. Activity was determined as the maximum slope of the graph of methane formation (g CH₄-COD) per g of VSS against time [25].

Fecal colliforms were quantified using the spread plate technique [22], whereby a solid agar culture medium (MacConkay Agar CM7) was inoculated with 0.1 mL of sample in a dilution medium, and the plates were incubated at 43° C for 24 h.

3. Results and discussion

3.1. Wastewater characteristics

Average wastewater characteristics with standard deviations (SDs) for the 450-day operational period are shown in Table 1. The average COD_t of 522 mg/L, the COD/N/P ratio of approximately 65/5/1, and the SS levels (TSS of 200 mg/L and VSS of 125 mg/L) put this wastewater in the class of a medium-strength domestic wastewater according to Tchobanoglous and Burton [17].

Approximately 70% of the COD_t was present as suspended material. This value falls between values obtained for the same region in Belgium (up to 89% [26] and approximately 52%; [6]. Wastewater with such high levels of particulate COD requires pretreatment to remove suspended material if a UASB reactor is selected as the treatment process of choice [27]. The COD_s/VSS ratio was on average 1.3 and the TSS/COD_t ratio was 0.4. These values were similar to the corresponding ratios obtained by Kalogo and Verstraete [18] $(COD_s/VSS$ ratio of 1.4 and TSS/COD_t ratio of 0.5).

3.2. Selection of coagulant/flocculant

The evaluation of different coagulant doses (50, 100, and 250 mg/L) indicated that the 50 mg/L dose resulted in better sedimentation than the higher doses for both coagulants tested (FeCl₃ and Al₂(SO₄)₃). The higher doses resulted in slower sedimentation and higher sludge beds with very porous, uncompacted sludge.

Subsequently, the selected coagulant dose of 50 mg/L was evaluated for each coagulant in combination with 10 mg/L of each of 13 flocculants to narrow down the choice of flocculants. For FeCl₃, flocculants #5, #11, and #9 (in decreasing order of performance) gave the best results and produced clear supernatants and compact sludge beds. For Al₂(SO₄)₃, flocculants #11, #9, and #12 (in decreasing order of performance) also produced clear supernatants and compact sludge beds.

After the initial selection of flocculants based on visual inspection, more detailed analyses were performed during jar tests with each coagulant and the two best performing flocculants. In addition to flocculant doses of 10 mg/L, doses of 5 mg/L were evaluated. The analyses results of the samples taken from the jar tests are presented in Table 2. The pH in every jar test was 7.0 ± 0.3 . The control jar test (without coagulant and flocculant) resulted in little or no sedimentation after a 30-min settling time, indicating that implementation of primary sedimentation without chemical addition would be very wasteful.

The combination of FeCl₃ and 10 mg/L of flocculant #5 resulted in the most compact sludge bed (lowest SV₃₀), and the best quality supernatant (lowest TSS, VSS, and COD_t). The ratios of COD_s/VSS and COD_s/

Table 1

Average characteristics with standard deviations of raw domestic wastewater and of effluents of various treatment steps

Parameter (mg/ L) ^a	Raw wastewater	CEPT pretreated waste stream	UASB influent (phases 1 and 2)	UASB effluent	LIST effluent (phase 3)	LIST removal efficiency
TSS	200+15	30+3	33+5	35+4	24+9	88+6
VSS	125 ± 21	18 ± 8	17 ± 6	19 ± 10	13 ± 7	90 ± 5
CODt	522 ± 300	140 ± 50	140 ± 50	53 ± 28	45 ± 6	91 ± 5
CODs	154 ± 112	115 ± 14	115 ± 14	45 ± 6	44 ± 5	71 ± 6
BOD ₅	208 ± 213	70 ± 11	70 ± 11	25 ± 6	32 ± 17	85 ± 15
TKN	39 ± 9	30 ± 6	16 ± 6	17 ± 2	0.5 ± 0.1	99 ± 0.4
TAN	24 ± 11	23 ± 3	12 ± 8	13 ± 10	0.3 ± 0.2	99 ± 1
P _{tot}	8 ± 3	0.7 ± 0.2	0.7 ± 0.6	0.5 ± 0.2	0.5 ± 0.1	94 ± 1.2
PO ₄ -P	4 ± 2	0.8 ± 0.3	0.8 ± 0.3	1.0 ± 0.1	1.0 ± 0.2	75 ± 5
РН	7.4 ± 0.1	7.1 ± 0.2	7.0 ± 0.2	7.3 ± 0.4	7.2 ± 0.1	NA^b
Alkalinity	300 ± 37	240 ± 21	240 ± 21	247 ± 15	200 ± 12	NA ^b
Fecal	$10^7 \pm 10^2$	ND ^c	ND ^c	ND ^c	$8^{d}10^{5} \pm 10^{2}$	92 ± 2
Coliforms ^d						

^aExcept for pH (no units) and alkalinity (mg/L as CaCO₃).

^bNot applicable.

^cNot determined.

^d Determined as cfu/L.

Table 2					
Results of jar tests	performed to s	select the best	coagulant an	d flocculant co	ombination

Coagulant flocculant	SV ₃₀ (m	L/L) TSS (mg	g/L) VSS (mg	g/L) COD _t (m	ng/L) COD _s (m	g/L) COD _{s/}	VSS COD _{s/} COD _t
50 mg/L FeCl ₃							
$5 \text{ mg/L flocculant } \#5^{a}$	39	27	20	206	128	6.4	0.62
10 mg/L flocculant #5	28	16	13	138	88	6.8	0.64
$5 \text{ mg/L flocculant } #11^{\circ}$	43	33	27	278	167	6.2	0.60
10 mg/L flocculant #11	35	23	17	180	107	6.3	0.59
$50 mg/L Al_2(SO_4)_3$							
5 mg/L flocculant #9 ^b	52	28	19	252	108	5.7	0.43
10 mg/L flocculant #9	36	26	19	194	116	6.1	0.60
5 mg/L flocculant #11	44	25	20	201	119	6.0	0.59
10 mg/L flocculant #11	30	21	13	144	92	7.0	0.64
Control (no coagulant or flocculant) — ^d			115 ^e	522 ^e	154 ^e	1.3	0.30

^a #5 = Allied Colloids E 10.

^b #9 = Praestol 857 BS.

 c #11 = Betz-Benelux 1558 E.

^dNot quantifiable.

^eValues from Table 1.

 COD_t remained relatively high, indicating that this combination would result in a waste stream with a high level of readily biodegradable COD (relative to total organic content). The combination of Al₂(SO4)₃ and 10 mg/L flocculant #11 proved second best. Based on the above results, the combination of FeCl₃ (50 mg/L) and flocculant #5 (Allied Colloids E 10 (10 mg/L)) was selected for the CEPT pretreatment.

3.3. CEPT pretreatment

The COD_t of the raw domestic wastewater and the CEPT pretreated wastewater for the 450-day operational period are given in Fig. 1. The average COD_t concentration was $522 \pm 300 \text{ mg/L}$ for the raw waster and $140 \pm 50 \text{ mg/L}$ for the wastewater after CEPT pretreatment. Phases 1, 2, and 3 exhibited average COD_t removals of $72 \pm 5\%$, $78 \pm 6\%$, and $75 \pm 6\%$, respectively, with overall average COD_t removal of $76 \pm 7\%$. The CEPS pretreatment also eliminated most of the SS in the wastewater (on average 85%), resulting in an average effluent TSS concentration of $30 \pm 3 \text{ mg/L}$.

There were large variations in the COD_t concentration of the raw wastewater (200–1250 mg/L), in agreement with seasonal variations in domestic wastewater composition [2,18]. Yet, there was only a small spread around the mean value of the COD_t removal efficiency of the CEPT pretreatment as indicated by a low overall coefficient of variation (SD/mean) of 0.09, even though coagulant and flocculant concentrations were kept the same. Thus, the coagulation/flocculation treatment step showed considerable capacity to resist pulses of shock loading. As a consequence of this stable performance,



Fig. 1. COD_t concentrations of raw domestic wastewater (\blacklozenge), of CEPS-pretreated waste stream (\Box), and of UASB effluent (\blacktriangle) during the 450-day experimental period.

the usual detrimental effects of shock loading on downstream biological processes were circumvented.

The pretreated wastewater served as influent for the UASB, indicating that, based on the COD_t and TSS concentrations, the UASB was fed with a wastewater that was even more dilute than a weak domestic wastewater [17]. The COD_s/VSS and TSS/COD_t ratios of the CEPT pretreated wastewater had changed to average values of 6.8 and 0.2, respectively (from corresponding values of 1.3 and 0.4 in the raw wastewater). This means that, although the raw wastewater had higher organic matter content than the pretreated wastewater, the organic matter was relatively more available after pretreatment, which is beneficial for the low HRT used in the UASB reactor. In contrast to results obtained by Kalogo and Verstraete [18], the COD_s/VSS ratio of the pretreated wastewater did not

vary widely, as indicated by a low overall coefficient of variation of 0.12.

The COD was removed in the form of a compact sludge, and the SV_{60} ranged between 1.4 and 2.0% (v/v) of the treated wastewater with a mean of $1.5\pm0.3\%$ (v/v). The sludge had a dry matter content of 8.4% by weight. The sludge production was lower than that obtained by Kalogo and Verstraete [18] (average 2.8% (v/v)), who used a similar treatment, indicating an optimization of the CEPT stage.

The average amount of P_{tot} in the raw wastewater was 8 ± 3 mg/L and only 0.7 ± 0.2 mg/L of P_{tot} remained in the CEPT effluent (Table 1), corresponding to an average Ptot removal efficiency of 91%. Thus, most of the Ptot was eliminated from the wastewater with the sludge. The TKN in the raw wastewater was $39 \pm 9 \text{ mg/L}$ and 30+6 mg/L was present in the CEPT effluent (Table 1), which is equivalent to an average TKN removal efficiency of 23%. The COD/N/P ratio after CEPT pretreatment was therefore 400/86/2. Thus, the N and P concentrations relative to the COD content in the CEPT pretreated wastewater were higher than the minimum nutrient requirements necessary for anaerobic digestion (COD/N/P ratio of 400/5/1) [25], suggesting that subsequent treatment in a UASB reactor should not be nutrient limited.

In conclusion, the optimized CEPT pretreatment evaluated in this study performed similar to or better than analogous treatment steps reported in the literature. The sludge production was lower (by a factor 0.3) compared to the study of Kalogo and Verstraete [18] who used a CEPS (chemically enhanced primary sedimentation)—UASB system to treat domestic sewage. The primary settling applied by Seghezzo et al. [28] to domestic sewage prior to digestion in a UASB reactor was only 32% effective in removing TSS, compared to the 85% removal achieved in this study. The results obtained are similar to those of Harleman and Murcott [29], who reported that the CEPT stage provided a TSS removal of up to 80%.

3.4. Zeolite treatment

Zeolites can be effectively employed to eliminate TAN from wastewaters [30–32]. The large interstitial spaces in the framework lattices of zeolites allow for replacement of cations such as Na⁺, K⁺, Ba²⁺ by NH₄⁺ through ion exchange. First the effectiveness of a zeolite ion exchanger to remove NH₄⁺ after CEPT pretreatment and before the UASB was evaluated using a batch system with 10 g/L of zeolite, following optimal dose tests (results not given). TAN concentrations of the raw wastewater and after zeolite treatment, together with the zeolite removal efficiency, are presented in Fig. 2. The average zeolite removal efficiency was $44\pm14\%$ for phase 1 and $56\pm7\%$ for phase 2. The zeolite removal efficiency was lower for higher TAN concentrations, indicating that a fixed amount of zeolite had a fixed capacity for NH_4^+ uptake. The removal efficiency declined after a zeolite batch of 10 g/L had been used for an average of three times (Fig. 2).

The COD/N/P ratio of the waste stream after zeolite treatment was 400/46/2. Thus, the *N* and *P* concentrations relative to the COD content in this wastewater were higher than the minimum nutrient requirements necessary for anaerobic digestion (COD/N/P ratio of 400/5/1) [25], suggesting that subsequent treatment in a UASB reactor should not be nutrient limited.

The spent zeolite was regenerated by aerobic nitrification during a period of two days. After an initial increase, the NH_4^+ concentration in the medium dropped steadily. At the same time, the NO_3^- concentration increased. After two days, the NH_4^+ concentration had dropped below 10 mg/L, and the NO_3^- content had risen to about 500 mg/L. The pH of the medium also decreased from 7.6 (initial) to 7.4 (end of day 1) to 6.9 (end of day 2). A regenerated zeolite removed typically approximately 55% of the TAN in the wastewater, as compared to fresh, unused zeolite, which exhibited an average removal efficiency of 58%.

In addition to the evaluation of a batch ion exchange system before the UASB system, the effectiveness of a zeolite column after the UASB reactor was evaluated during phase 3 of this study. The zeolite removal efficiency in this mode was much higher (average of $99\pm1\%$) and more stable than with the batch application.

This higher removal efficiency was the result of a longer exposure of the NH_4^+ to the zeolite as the UASB effluent percolated slowly through the column (the HRT in the column was 3.6 h versus 2 h in batch mode). This second option is preferable over the first one, not only because of its higher removal efficiency, but also because the removal of the NH_4^+ prior to the biological



Fig. 2. TAN concentrations of raw domestic wastewater (phases 1 and 2) and UASB effluent (phase 3) (\diamond), of zeolite-treated waste stream (zeolite treatment before UASB reactor for phases 1 and 2 and after UASB reactor for phase 3) (\blacksquare), and TAN removal efficiency (\blacktriangle).

treatment step in the UASB reactor for some waste streams may result in a concentration of NH_4^+ that is too low to support growth of the anaerobic biomass (see above). Furthermore, percolation of the UASB effluent through the zeolite column resulted in oxidation of residual organic material and produced an improved final effluent quality in terms of COD_t (average UASB effluent COD_t of 53±28 mg/L was decreased to an average COD_t value of 45±6 mg/L after the zeolite column). Completely spent zeolite can either be deposited on a landfill or applied as soil conditioner [33,34].

3.5. UASB reactor performance

The COD_t in the UASB reactor influent and effluent are shown in Fig. 1. The COD_t removal efficiency averaged $55 \pm 11\%$ during phase 1 with a B_v of 0.4 g COD/L. d, whereas the average COD_t removal efficiency rose to about $60 \pm 13\%$ during phase 2 when the B_v was increased to 0.7 g COD/L. d and a vitamin and mineral mix was added. When the vitamin and mineral mix addition was eliminated (phase 3), the COD_t removal efficiency averaged $57 \pm 10\%$ (B_v remained at 0.7 g COD/L. d). These removal efficiencies would be 62% and 61% for COD_t and COD_s removals, respectively, if one had to apply the direct approach used by many authors in evaluating COD removal efficiencies when treating domestic sewage with the UASB reactor (see materials and methods). In every case, however, the results are comparable to others cited in the literature for mesophilic UASB reactors treating domestic wastewater [35,18,28]. Although the results do not allow for a detailed analysis, the application of the vitamin and mineral mix appeared to have only a minimal impact on the COD_t removal efficiency.

The average COD_t and COD_s concentrations of the UASB influent were 140 ± 50 and 115 ± 14 mg/L, respectively. Average effluent COD_t and COD_s concentrations were 53 ± 28 and 45 ± 6 mg/L, respectively. Given the low SDs associated with these values and the COD_t profile shown in Fig. 1, it is clear that the effluent quality in terms of COD_t and COD_s was relatively constant and that the reactor generally exhibited stable performance throughout the experimental period. This is consistent with the observed effluent pH, which varied between 6.8 and 7.7, and the low effluent VFA concentrations (only acetate and propionate were generally detected at average concentrations of 16 ± 2 and 3 ± 1 mg/L, respectively). The mix of vitamins and minerals applied during phase 2 had no effect on the UASB operation, as no significant change could be detected with the reactor effluent (see Fig. 1). No higher dose was tried, since the treatment already proved adequate and the addition of vitamins and minerals would increase operating costs.

The height of the sludge bed increased only slowly, from $13 \text{ cm} (255 \text{ cm}^3 \text{ of reactor volume})$ on day 0 to

33 cm (648 cm³) on day 300, and to 43 cm on day 400 (844 cm³). On day 400, the sludge bed height was decreased to 29 cm, by removing 274 cm³ of excess sludge. In a similar UASB reactor used for the treatment of raw domestic wastewater (without CEPT pretreatment), it was necessary to decrease the sludge bed height four times during an operational period of 400 days (unpublished data). This low rate of sludge production is certainly an advantage, as sludge handling in full-scale installations is expensive. The excess digested sludge can be a valuable commodity to be used in agriculture or for inoculating new reactors.

As expected, little or no biogas production was observed during the experimental period, because a substantial amount of the biogas produced during anaerobic treatment of domestic wastewater at low loading rates is dissolved in the effluent [4,15]. This implies that anaerobic treatment of low strength wastewater cannot be used as an energy recovery process and that this important benefit of anaerobic treatment in general cannot be achieved in the present application [36].

Low wastewater strength, low loading rates, and low biogas production can lead to substrate transfer limitation and cause inhibition of granulation or can make it difficult to maintain granules [25,16]. Consistent with this, the grain size of the granules used to inoculate the UASB system decreased over time (data not reported) and granulation was not observed during this study. However, the loss of granules and absence of granulation apparently did not affect the reactor performance.

3.6. Overall performance of the low investment sewage treatment (LIST) system

The combination of CEPT pretreatment using FeCl₃ as a coagulant followed by treatment in a UASB reactor was proposed by Kalogo and Verstraete [18] as an option for the treatment of domestic wastewater. In this study, this process was further optimized and evaluated and additional treatment steps were made for more efficient removal of suspended material, and to remove NH_4^+ . Fig. 3 shows an overall schematic of the LIST concept as proposed in this study and Table 1 provides a summary of overall performance characteristics.

It was possible to reduce the FeCl₃ coagulant dose of 70 mg/L used by Kalogo and Verstraete [18] to 50 mg/L through the addition of a flocculation step in the CEPT pretreatment. Furthermore, the average COD_s/VSS ratio of 5 reported by Kalogo and Verstraete [18] was increased to 6.8 in this study, resulting in a waste stream more suitable for treatment in a UASB reactor, since reactor space was not used by inactive solids [27,37, 38]. The coagulation/flocculation step produced a concentrated sludge (8.4% solids), which can be stabilized in a conventional anaerobic sludge digester in the mesophilic



Fig. 3. Overall schematic of the LIST treatment concept. If necessary, a polishing pond can be added to accomplish residual COD removal. The zeolite for TAN removal is preferably used in a column after the UASB reactor and is regenerated by biological nitrification. The regeneration water can be used for crop irrigation.

or thermophilic range. After stabilization, the sludge can be used as fertilizer in agriculture [4].

During CEPT pretreatment, phosphorus concentrations were reduced substantially. However, nitrogen removal was minimal and other options to remove this nutrient need to be explored if domestic wastewater is to be reused. In this study, an aluminosilicate (zeolite) was evaluated to remove NH_4^+ through ion exchange [39– 41]. As discussed above, the use of a zeolite-filled column after the UASB treatment step proved most beneficial, mainly because of a higher NH_4^+ removal efficiency and the oxidation of residual organic material. After regeneration by nitrification, a NO_3^- rich side stream results, which may be useful, for example, in crop irrigation.

The coupling of CEPT and UASB treatment removed on average 90% of COD_t. However, the corresponding average effluent UASB COD_t concentration $(53\pm28 \text{ mg/L})$ is too high for direct discharge in surface waters (e.g., Flemish standard = 50 mg/L COD_t). Percolation of the UASB effluent through the zeolite ion exchange column resulted in an improved effluent quality (average final effluent COD_t of $45\pm6 \text{ mg/L}$). Nevertheless, it is still possible that the overall LIST effluent characteristics do not meet standards for all discharge or reuse scenarios. If so, a passive flow of the LIST effluent through a shallow pond should decrease the residual organic matter to acceptable levels.

The side streams that emanate from the system can be disposed of in various ways. In this regard, ongoing work is investigating the stabilization of the CEPT sludge using conventional anaerobic sludge digestion, the product of which will be fit for application onto agricultural fields. The nitrate-enriched regeneration stream can be diluted appropriately and used for crop irrigation.

Analysis of fecal coliform levels also showed that the LIST system provided good hygienization. Indeed, the fecal coliform levels in the LIST effluent had decreased to 8% of the amount present in the raw wastewater (Table 1).

3.7. Preliminary economic evaluation

Using the combination of CEPT and UASB treatments, excess UASB reactor sludge production can be minimized, as discussed above. Thus, the coupling of these two treatment steps is a more economical option compared to conventional anaerobic treatment alone because the cost of treatment and disposal of the CEPT sludge is lower than for UASB reactor sludge. The difference in sludge treatment and disposal costs is primarily due to the differences in solids content (8.4% for CEPT sludge versus 2.5% for UASB biomass). An important difference in dewaterability also arises, as a chemical sludge is generally easier to dewater than a biological sludge [42].

A significant fraction of the operational costs of the various treatment steps can be estimated by considering the costs of the different chemicals and additives. FeCl₃.6H₂O costs € 0.21/kg, resulting in an operational expense of about $\in 0.01/m^3$ of raw wastewater treated for the 50 mg/L dosed. Similarly, Allied Colloids E 10 costs € 3.75/kg, and thus the flocculation step would contribute an operational cost of € 0.04/m³ of raw wastewater handled, considering the 10 mg/L of flocculant used. Zeolite costs $\in 0.2/kg$ and this material can be obtained for $\in 0.7/m^3$ of raw wastewater treated. Furthermore, zeolite is a natural mineral that is widespread in many sedimentary basins and volcaniclastic regions in developing countries [43], from where it can be mined cheaply, thus eliminating a substantial fraction of the investment cost in developing countries. The inoculum used for nitrification (ABIL) sells for $\in 10/L$ and, considering that 0.1 L was used per kg of zeolite, the continued use of ABIL would add $\in 10/m^3$ of wastewater treated. However, since ABIL is a biological inoculum, it would only be used during the initial startup of the regeneration system in full-scale applications. Finally, the vitamin and mineral additive was obtained for $\in 1.6/\text{kg}$ and dosed at 10 mg/L, resulting in a cost of $\notin 0.016/\text{m}^3$ of wastewater treated. Thus, the

total cost of chemicals and additives was estimated at \notin 0.07–0.1/m³ wastewater treated. The operating costs for other items (e.g., electricity) have not been included yet in this initial cost analysis, but should remain relatively low, in the order of \notin 0.1/m³, because of the simplicity of the LIST system. The analyzed costs compare favorably with overall operational expenditures for treating domestic wastewater in conventional activated sludge systems, which are in the order of \notin 0.65 /m³ [44].

The construction costs of a UASB are about $\in 250/m^3$ reactor; hence the low HRT of the proposed LIST system (approximately 5h) should keep the capital expenditure quite low.

4. Conclusions

In this study, an integrated concept for the treatment of domestic wastewater was evaluated, consisting of a coagulation/flocculation pre-sedimentation step to remove suspended material and phosphorus, followed by treatment in a UASB reactor to remove soluble organics. In addition, NH_4^+ could be removed by a zeolite ion exchange system preferably placed after the UASB system. This ion exchange system can be regenerated by biological nitrification.

The integrated system effectively decreased the TSS in the raw wastewater by 88%, the COD_t by more than 90%, and the COD_s by more than 70%. Nitrogen and phosphorus levels were decreased by 99% and 94%, respectively. Fecal coliform levels fell to 8% of the input, indicating a good removal of putative undesired bacteria. Furthermore, the system can operate at low costs, making it suited for developing countries and rural areas. The final effluent from the system can be used for crop irrigation, or be discharged.

The recycling, reuse or disposal of the side streams generated should be explored further and evaluated in future research, together with the energy potential of the CEPT sludge.

Acknowledgements

This research was sponsored by a grant from the Ghent University, Belgium. Gratitude is expressed to Prof. Mario Kruz E. of the University of Havana-Cuba. Funding for LR was provided by the Flemish Science Foundation (Fonds voor Wetenschappelijk Onderzoek [FWO]—Vlaanderen). Fruitful interactions with Xu Hui, Mariane VanWambeke, Geert Lissens, Ying Zhang, and Jeroen De Rudder are acknowledged.

References

- Boschier JA. Criteria for assessing appropriate technology for sewage treatment and disposal. Water Sci Techol 1993;27(1):11–8.
- [2] Lansdell M. Fifteen years of practical sewage treatment in Venezuela. Water Sci Technol 1996;33(3):39–46.
- [3] Lettinga G, Hulshoff Pol LW. UASB process design for various types of wastewaters. Water Sci Technol 1991;24(8):87–107.
- [4] Van Haandel AC, Lettinga G. Anaerobic sewage treatment: a practical guide for regions with a hot climate. New York: Wiley; 1994.
- [5] Van Haandel A, Catunda PFC, Application and perspectives of anaerobic waste water treatment in Latin America; Sustainable rural environment and energy network, 5th FAO/SKEN workshop, anaerobic conversion for environmental protection, sanitation and reuse of residues, 24–27 March, 1997.
- [6] Kalogo Y, Verstraete W. Potentials of anaerobic treatment of domestic sewage under temperate climate conditions. In: Lens P, Zeeman G, Lettinga G. editors. Decentralized sanitation and reuse: concepts, systems and implementations, IWA Publishing; 2001.
- [7] Lettinga G, Van Lier JB, Van Buren JCL, Zeeman G. Sustainable development in pollution control and the role of anaerobic treatment. Water Sci Technol 2001;44(6):181–8.
- [8] Foresti E, Anaerobic treatment of domestic sewage: established technologies and perspectives. Proceedings of the Ninth world congress of anaerobic digestion—anaerobic conversion for sustainability, Antwerp, Belgium, Sept 2–6, 2001.
- [9] Harleman D, Murcott S. An innovative approach to urban wastewater treatment in the developing world. Water 2001;21:44–88.
- [10] Parker DS, Barnard J, Daigger G, Tekippe RJ, Wahlberg EJ. The future of chemically enhanced primary treatment: evolution not revolution. Water 2001;21:49–56.
- [11] Gnanadipathy A, Polpraset C. Treatment of a domestic wastewater with UASB reactors. Water Sci Technol 1993;27(1):195–203.
- [12] De Souza JT, Foresti E. Domestic sewage treatment in an upflow anaerobic sludge blanket—sequencing batch reactor system. Water Sci Technol 1996;33(3):73–84.
- [13] Schellinkhout A, Collazos CJ. Full-scale application of the UASB technology for sewage treatment. Water Sci Technol 1992;25(7):159–66.
- [14] Tawfik A, Klapwijk B, el-Gohary F, Lettinga G. Treatment of anaerobically pre-treated sewage by a rotating biological contactor. Water Res 2002;36:147–55.
- [15] Lettinga G, De Man A, Van der Last ARM, Wiegant W, Van Kippenberg K, Frijns J, Van Buren JCL. Anaerobic treatment of domestic sewage and wastewaters. Water Sci Technol 1993;27(9):67–73.
- [16] Aiyuk SE, Verstraete W. Sedimentological evolution in an UASB treating SYNTHES, a new representative synthetic sewage, at low loading rates. Biores Technol 2004;93(3):269–78.
- [17] Tchobanoglous G, Burton FL, Metcalf and Eddy-wastewater engineering: treatment, disposal and reuse, 3rd ed., New York: McGraw-Hill, Inc.; 1991. p. 1334.

- [18] Kalogo Y, Verstraete W. Technical feasibility of the treatment of domestic wastewater by a CEPS-UASB system. Environ Technol 2000;21:55–65.
- [19] Mihelcic JR, Hand DW. Fundamentals of environmental engineering. New York, USA: Wiley; 1999.
- [20] Torres LG, Jaimes J, Mijaylova P, Ramirez E, Jimenez B. Coagulation-flocculation pretreatment of high-load chemical-pharmaceutical industry wastewater: mixing aspects. Water Sci Technol 1997;36(2–3):255–62.
- [21] Lees EJ, Noble B, Hewitt R, Parsons SA. The impact of residual coagulant on downstream treatment processes. Environ Technol 2001;22:113–22.
- [22] APHA, Standard Methods for the Examination of Water and Wastewater, 18th ed. American Public Health Association (APHA)/American Water Works Association (AWWA)/Water Environment Federation (WEF), Washington DC, USA, 1992.
- [23] Holdeman LV, Cato EP, Moore WEC. Anaerobic laboratory manual. Virginia polytechnic institute and state university, Blacksberg, Virginia, 1977.
- [24] Valcke D, Verstraete W. A practical method to estimate the acetoclastic methanogenic biomass in anaerobic sludge. J Water Pollu Cont Feder 1983;52:720–9.
- [25] Thaveesri J, Liessens B, Verstraete W. Granular sludge growth under different reactor liquid surface tensions in lab-scale upflow anaerobic sludge blanket reactors treating wastewater from sugar-beet processing. Appl Microbiol Biotechnol 1995;43:1122–7.
- [26] Kuai L, Kerstens W, Verstraete W. Low-cost and smallscale sewage treatment system. 5th FAO/SREN workshop on anaerobic conversions for environmental protection, sanitation and re-use of residues, Ghent, Belgium, 1997.
- [27] Verstraete W, Tanghe T, De Smul A, Grootaerd H. Anaerobic biotechnology for sustainable waste treatment. In: Sayler, editor. Biotechnology in the sustainable environment. New York: Plenum Press; 1997. p. 343–59.
- [28] Seghezzo L, Guera RG, Gonzalez SM, Trupiano AP, Figueroa ME, Cuevas CM, Zeeman G, Lettinga G. Removal efficiency and methanogenic activity profiles in a pilot-scale UASB reactor treating settled sewage at moderate temperatures. Proceedings of the Ninth world congress of anaerobic digestion—anaerobic conversion for sustainability, Antwerp, Belgium, Sept 2–6, 2001.
- [29] Harleman D, Murcott S. Chemically enhanced primary treatment: challenging the status quo. Water 2001;21:57–9.
- [30] Jørgensen SE. Ammonia removal by use of clinoptilolite. Water Res 1976;10:213–24.
- [31] Demir A, Gunay A, Debik E. Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite. Water SA 2002;28(3):329–35.
- [32] Nguyen ML, Tanner CC. Ammonia removal from wastewaters using natural New Zealand zeolites. N Z J Agri Res 1998;41(3):427–46.
- [33] Dwairi IM. Evaluation of Jordanian zeolite tuff as a controlled slow-release fertilizer for NH₄⁺. Environ Geol 1998;34(1):1–4.
- [34] Perrin TS, Drost DT, Boettinger JL, Norton JM. Ammonium loaded clinoptilolite: a slow-release nitrogen fertilizer for sweet corn. J Plant Nutr 1998;31(3): 255–9.

- [35] Agrawal LK, Ohashi Y, Mochida E, Okui H, Ohashi A. Treatment of raw sewage in a temperate climate using a UASB reactor and the hanging sponge cubes process. Water Sci Technol 1997;36(6–7):433–40.
- [36] Uemura S, Harada H. Treatment of sewage by a UASB reactor under moderate to low temperature conditions. Biores Technol 2000;72(3):275–82.
- [37] Rozzi A, Verstraete W. Calculation of active biomass and sludge production vs. waste composition in anaerobic contact processes. Trib Cebedeau 1981;455(34):421–7.
- [38] De Smedt M, Van Ermen S, Koning J. Influence of particulate matter on UASB reactor performance: pilot and full scale studies. Proceedings of the Ninth world congress of anaerobic digestion—anaerobic conversion for sustainability, Antwerp, Belgium, Sept 2–6, 2001.
- [39] Semmens MJ, Martin WP. The influence of pre-treatment on the capacity and selectivity of clinoptilolite for metal ions. Water Res 1988;22(5):537–42.
- [40] Rozic M, Cerjan-Stefanovic S, Kurajica S, Vancina V, Hodzic E. Ammoniacal nitrogen removal from water by treatment with clays and zeolites. Water Res 2000;14:3675–81.
- [41] Inglezakis VJ, Papadeas CD, Loizidou MD, Grigoropoulou HP. Effects of pretreatment on physical and ion exchange properties of natural clinoptilolite. Environ Technol 2001;22:75–82.
- [42] Mequipco, 2003, http://www. mequipco. com/FilterPress. Htm.
- [43] Tucker ME. Sedimentary petrology: An introduction to the origin of sedimentary rocks, 2nd ed. London: Blackwell Scientific Publications; 1991.
- [44] AQUAFIN, 2002, http://www. aquafin.be.