PRETREATMENT OF DISPOSABLE NAPPIES TOWARDS VALORIZATION OF THE FERMENTABLE FRACTION THROUGH ANAEROBIC DIGESTION

K. Tsigkou[1], P. Tsafrakidou[2], C. Zafiri[2], M. Kornaros[1*]

[1]Department of Chemical Engineering, University of Patras, University Campus, Patras, 26504, Greece
[2] Green Technologies Ltd., 5 Ellinos Stratiotou Str., Patras, 26223, Greece
*Corresponding author email: kornaros@chemeng.upatras.gr, Tel.: +30 2610 997418, Fax: +30 2610 969584

ABSTRACT

Purpose: Disposable nappies represent around 1.7% of total Municipal European Wastes. A typical disposable nappy usually consists of nonwoven fabrics, a super absorbent polymer (SAP), and organic material, namely fluffy pulp, urine and/or excreta. An alternative approach to landfilling is targeted for used nappies in this study, i.e. energy recovery through anaerobic digestion and material recycling. More specifically, the aim of this work was the minimization of SAP volume, as this component can swell up to 1000 times its own mass by liquid absorbance, reducing thus the available bioreactor's volume and interfering with the biological processes.

Methods: Three reagents ($CaCl_2$, $MgCl_2$, $AlCl_3$) and a range of $CaCl_2$/$MgCl_2$ combinations were tested against their deswelling effeciency on SAP, the remaining reagent concentration (potential inhibitor of anaerobic digestion) and reagent cost. Physicochemical characterization of the nappies hydrolysate took place to estimate its adequacy as substrate for anaerobic digestion. The residual concentrations of added salts in the hydrolysate were quantified by atomic absorption spectroscopy.

Results: $CaCl_2$ provided the best results on SAP volume minimization, but the residual calcium concentrations were considered high enough for the subsequent bioprocess. Mixtures of $CaCl_2$/$MgCl_2$ could reduce 0.5g of SAP's volume less than 5ml with low residual salts in the hydrolysate and a mentionable low cost of treatment. Physicochemical characterization of hydrolysates resulted to an ideal COD:N:P ratio of 350:7:1.

Conclusions: The mixture of 20% $CaCl_2$ and 50% $MgCl_2$ w/w of SAP was concluded as the optimum combination for SAP deswelling with low residual cation concentrations and minimum cost.

Keywords: nappies, pretreatment, super absorbent polymer (SAP), optimization, anaerobic digestion

1. INTRODUCTION

A disposable nappy (diaper) can be defined as a type of underwear that has the ability to absorb urine and/or excreta and it is used by infants and adults with incontinence issues [1]. Generally, the components that form an unused nappy are: (i) polypropylene (PP) or polylactic (PLA) nonwoven fabrics that compose the top-sheet layer (inner), (ii) PP, PLA or polyethylene (PE) blends of nonwoven fabrics that form the acquisition and distribution layer (ADL), (iii) SAP and fluffy pulp that represent the absorbent core layer, (iv) the backsheet layer that provides a fluid impervious barrier so that moisture is contained within the structure and consists mainly of PE and finally (v) a small proportion of adhesives, dyes/prints and tapes [2]. Although, organic materials are present in a notable percentage in this type of waste they are still disposed of to landfills or led to incineration [3]. Due to this lack of waste management strategy of the biodegradable fraction, many environmental problems occur like methane emissions that contribute to global warming, possible groundwater contamination with leachate, land usage, noise and bad odors. Air pollution from incineration is also significant due to the formation of NO_x, SO_2, HCl, particles, dioxins etc. [4].

According to the European Directive 2008/98/EC [5] the following waste hierarchy should be applied: prevention, preparation for re-use, recycling, other recovery (such as energy recovery) and disposal, while Directive 1999/31/EC [6] of 31st April on the landfill of waste sets up significant restrictions on the disposal of biodegradable materials in landfills. Concerning this Directive, by 2016 the biodegradable municipal waste going to landfills should have been reduced to 35% of the total amount (by weight) of biodegradable municipal waste produced in 1995.

An alternative approach to landfilling of used nappies is presented in this study, including energy recovery through anaerobic digestion of the biodegradable fraction and material recycling. More specifically, used nappies could be collected separately, cut in smaller pieces and chemically pretreated in order to separate the included components to three individual streams: a mixture of plastics, the treated SAP and a hydrolysate which includes the biodegradable material (excreta and cellulose). This hydrolysate could be anaerobically digested (or co-digested with other biodegradable organic substrates) while the mixture of plastics and the treated SAP could be recycled or re-used for other applications such as insulation materials, immobilization carriers etc.

In this work, the optimization of the chemical pretreatment of shredded nappies for SAP separation and recovery is presented. Our specific target was the minimization of SAP volume/SAP deswelling, as this component could swell up to 1000 times its own mass by liquid absorbance resulting to significant reduction of the available bioreactor's volume and interfere with the biological processes [7]. Previous studies, with similar polymers, suggest that these materials are highly recalcitrant to aerobic and anaerobic degradation probably due to their high molecular weight [8] and therefore should be removed before any biological treatment. Additionally, the optimization of the reagents' concentration as well as the reagents' combination was tested in order to avoid anaerobic digestion inhibition due to the remaining reagent in the hydrolysate. The physicochemical characterization of the produced hydrolysate is also presented.

According to literature, plenty of reagents/compounds as well as their combinations/mixtures seem to inhibit or favor the anaerobic digestion process [9]. The reagents' selection for testing SAP deswelling in this this study was based on anaerobic digestion's inhibition levels, atomic charge, manageability and cost. The optimization of the pretreatment process involved 3 parameters, namely minimization of volume of deswelled SAP, residual reagent concentration and reagent cost. Experiments using single reagents ($CaCl_2$, $MgCl_2$ and $AlCl_3$) and mixtures of $CaCl_2$ with $MgCl_2$ took place in order to measure the volume of the deswelled SAP and the residual concentration of the tested reagent in the hydrolysate.

2. METHODS

2.1 Materials

Unused nappies of two best-selling commercial brands in Greece (N1, N2) size 4+ were used to obtain SAP samples for the experiments. Nappies were cut manually to remove the adhesives and tapes using scissors [10]. After the separation of each layer, cellulose fibers and SAP segregation was achieved manually (visual observation) utilizing plastic laboratory spatulas and plastic beakers in order to avoid the static electricity of the fibers.

2.2 Deswelling optimization experiments

For the deswelling optimization experiments a standard weight of SAP (0.5g) with the addition of 10ml deionized water, in order to simulate the real conditions of used nappies (urine and excreta moisture), were used as reference for all the treatments. The reagents that were tested for their deswelling properties on SAP were $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$ and $AlCl_3$. Overnight drying at 105^oC was preceded, in order to secure anhydrous reagents [11]. Solutions containing 0.25-1% (w/v) of the tested reagent, or combinations of $CaCl_2$ (0.2-0.6%, w/v) and $MgCl_2$ (0.2-0.8%, w/v) to test their synergistic effect, were prepared [12]. Experiments were carried out into volumetric cylinders of 100(±1) ml at room temperature, using magnetic stirrers and magnetic stirring bars. Agitation was set at 1000rpm [13] as washing machine simulation [12]. 50ml of the tested solution was added into the volumetric cylinder and the volume of deswelled SAP was measured every 10, 20 and 30 minutes. After the treatment (30 minutes) the supernatant was separated from the deswelled SAP, and filtrated with nylon Whatman 0.2μm filters. The remaining concentrations of Ca^{2+}, Mg^{2+} and Al^{3+} were measured by atomic absorption spectroscropy (AAS, Perkin Elmer, AAnalyst 300). Cellulose, hemicellulose and lignin contents in the absorbent layer of the nappy were determined according to Sluiter et al. [14]. All experiments were carried out in triplicate under identical conditions.

2.3 Pretreatment of used nappies and their physicochemical characterization.

Samples of used nappies (UN_1 and UN_2) were collected from two kindergartens (Halandri, Greece and Zamudio, Spain). 10 representative samples from each city were cut into small pieces (about 5cm^2) and treated using 30 liters of tap water and the optimum amount of reagents from the deswelling experiments. Agitation was adjusted properly, in order to facilitate the removal of plastics and other components.

Concerning the physicochemical characterization of used nappies, removal of solids from the hydrolysate took place using Whatman glass microfiber filters, grade GF/F in order to quantify soluble compounds such as carbohydrates, phenols etc. Off-line pH measurements were conducted using an electrode (Thermo Scientific, Orion ROSS Ultra Refillable pH/ATC Triode), while alkalinity, TS, VS, TSS, VSS, total and dissolved COD, TKN, ammonium nitrogen, total and dissolved phosphorus were determined according to *Standard Methods* [15]. For the carbohydrates determination, a colored sugar derivative was produced through the L-tryptophan, sulfuric and boric acid addition which was subsequently measured colorimetrically at 520 nm, as described by [16]. Total phenolic compounds were determined in the supernatant spectrophotometrically according to the Folin–Ciocalteu method [17]. Finally, Fats and Oils were measured after extraction with hexane using a Soxhlet extractor (Velp Scientifica, SER 148). All experiments were carried out in triplicate and mean values along with SD are presented in the results.

3. RESULTS

3.1 Deswelling optimization

The deswelling effect of the three tested salts ($CaCl_2$, $MgCl_2$ and $AlCl_3$) on SAP samples is shown on Fig. 1(a-c). Starting from a SAP volume of 50ml, the deswelling effect appears to increase with the increment on salts concentration up to a certain point where no further increment seems to affect the final volume of treated SAP. Comparing all three salts, there are similar results on final SAP volume and residual concentrations in the supernatant for both SAP samples (N1 and N2), concluding to the result that the raw material (SAP) has the same properties in both brands so there is no need for further research or different pretreatment when it comes to different nappy samples.

Among the tests with the reagents, $CaCl_2$ (Fig. 1a) presents a minimum final SAP volume of ~5ml at 60% w/w concentration, while for $MgCl_2$ (Fig. 1b) and $AlCl_3$ (Fig. 1c) concentrations range from 80% to 100% w/w, respectively, for the same final SAP volume (5 ml). Based on this observation, larger amounts of $AlCl_3$ are required for the pretreatment in comparison with the other two salts, implying a bigger environmental impact but also an increase of the final pretreatment cost. In addition, Al usage is rejected due to its potential toxicity, since it may cause eye and skin irritation and problems with lipids and proteins or DNA damage [19], and being thus included in the priority list of hazardous substances identified by The Agency for Toxic Substances and Disease Registry [20].

Concerning the other two salts, the used percentages to obtain the minimum SAP volume have a residual concentration of 400-700 mg/L. Such concentrations are considered high enough, because in combination with pre-existing salts in tap water could be inhibitory for the subsequent process of anaerobic digestion [9]. On this regard, salt mixtures of $CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$ were tested in various combinations to estimate their potential synergistic effect on deswelling and residual salt reduction. The combinations of salts, final SAP volume after a 30 min treatment, residual concentration of salts in the supernatant as well as final cost of reagents are shown in Table 1. As it was expected, there are various combinations that result to final SAP volumes ~5ml. Taking into account the residual concentrations for both salts and the final reagent cost, the optimum values are reached with the last combination (Test No15) where a mixture of 20% w/w $CaCl_2$ and 50% w/w $MgCl_2$ have a deswelling effect on 0.5g of SAP volume at 4.33±0.58 ml with low residual concentrations for both salts (160.13±7.67 mg Ca^{+2}/L and 276.50±14.55 mg Mg^{+2}/L) and low cost (0.151€). Unfortunately, there are no available data in literature regarding the type and amount of reagents used to achieve SAP deswelling to compare, due to an expired patent protection [12] or lack of information given on published studies [1].

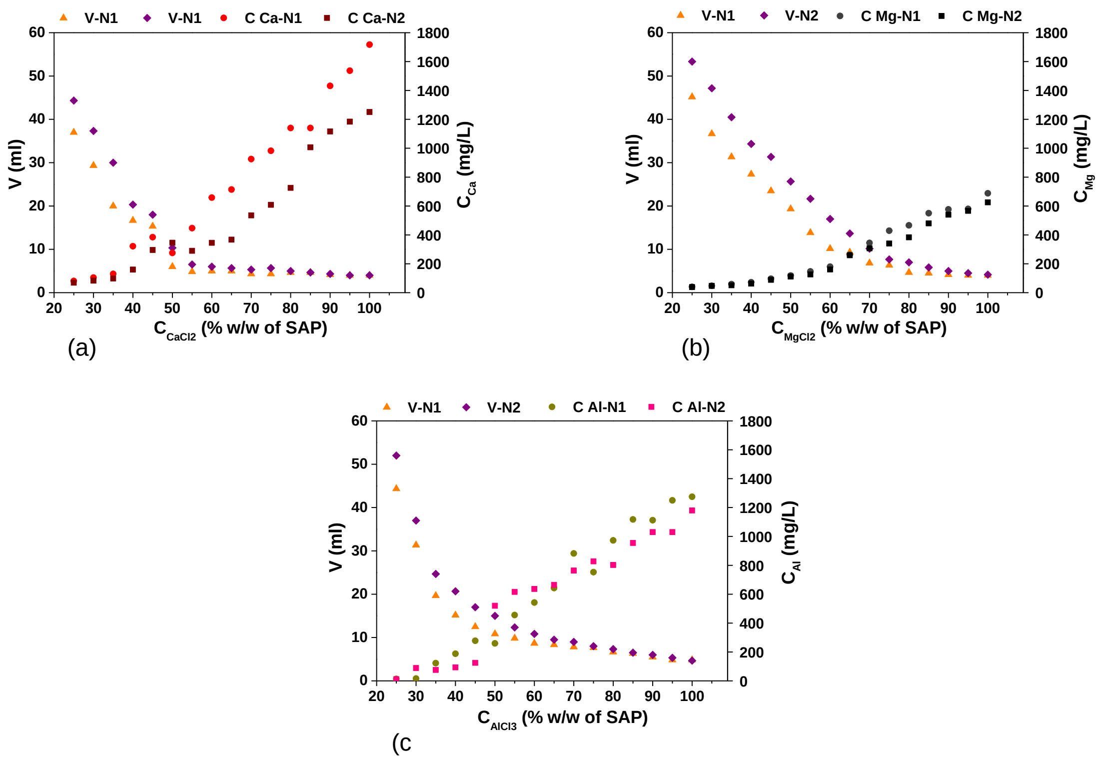

Fig. 1 Volume of SAP (left) in correlation with different added concentrations of: (a) $CaCl_2$, (b) $MgCl_2$ (c) $AlCl_3$ and residual cation concentration in the bulk solution (right)

Table 1
Mixture combinations of $CaCl_2$ and $MgCl_2$ concentrations for SAP deswelling optimization treatments, final SAP volume after a 30 min treatment, residual concentration of salts in the supernatant and final cost of reagents. Data are mean values ±SD (n=3).

Test No	$CaCl_2$ (% w/w of SAP)	$MgCl_2$ (% w/w of SAP)	SAP (ml) ± SD	Residual Ca^{+2} (mg/L) ± SD	Residual Mg^{+2}(mg/L) ± SD	Final Cost (€)/g treated SAP
1	20	20	25.00 ± 1.00	59.30 ± 10.98	44.32 ± 1.65	0.1874
2	20	40	7.00 ± 0.00	84.92 ± 8.84	99.73 ± 4.95	0.2638
3	20	60	4.33 ± 0.58	169.67 ± 16.40	374.33 ± 9.09	0.3402
4	20	80	4.00 ± 0.00	262.00 ± 27.75	563.50 ± 31.22	0.4166
5	40	20	5.33 ± 0.58	353.42 ± 94.71	80.88 ± 3.06	0.2984
6	40	40	4.00 ±0.00	467.83 ± 59.10	184.83 ± 7.42	0.3748
7	40	60	4.00 ±0.00	702.83 ± 108.16	511.33 ± 21.00	0.4512
8	40	80	4.33 ±0.58	487.00 ± 118.30	582.50 ± 22.49	0.5276
9	60	20	5.33 ±0.58	671.83 ± 64.73	139.27 ± 9.58	0.4094
10	60	40	4.83 ±0.29	969.00 ± 56.76	373.17 ± 20.68	0.4858
11	60	60	5.00 ±0.00	898.00 ± 407.08	555.83 ± 54.00	0.5622
12	60	80	4.50 ±0.50	1224.83 ± 76.29	704.33 ± 38.39	0.6386
13	60	50	4.17 ±0.29	666.67 ± 21.69	455.33 ± 50.58	0.5240

14	40	50	4.10 ±0.22	595.70 ± 108.08	401.50 ± 36.31	0.4130
15	20	50	4.33 ±0.58	160.13 ± 7.67	276.50 ± 14.55	0.3020

Fig. 2 presents the percentages of cellulose, hemicellulose and lignin contents in the absorbent layer of the unused nappies (N1, N2). Others refer to plastics, adhesives or SAP that wasn't removed and other components that may be present in this specific layer. There is a difference between the two samples regarding their cellulosic content, but in both cases the percentage is higher than 50%. Cellulose and hemicellulose content is important since it is the biodegradable fraction of the nappy.

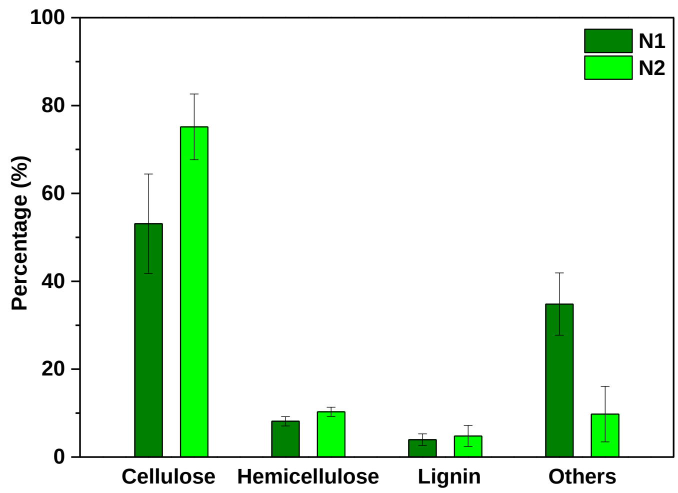

Fig. 2 Cellulose, hemicellulose and lignin content in the absorbent layer of unused nappies

Before SAP removal, the two samples of unused nappies (N1, N2) were separated to their layers and they were weighted in order to compare the brands and identify possible differentiations. As shown in Fig. 3, the samples had a slightly different weight distribution between their layers, particularly in layer 2 (nonwoven fibers) and layer 3 (fluffy pulp and SAP). However, the total weight of unused nappies didn't present significant differences.

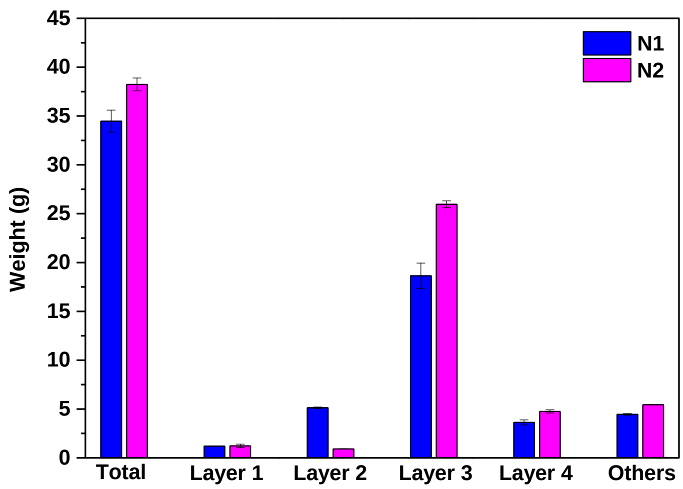

Fig. 3 Weight (g) of unused nappies' layers

The differences in the weight of layer 3 (Fig. 3) and the cellulosic content (Fig. 2) between the samples are also evident in Fig. 4, which shows that the percentage of fluffy pulp in N2 is higher than N1. Despite these facts, the physicochemical characterization of the used nappies after the pretreatment did not present significant differences on the amount of total and dissolved carbohydrates.

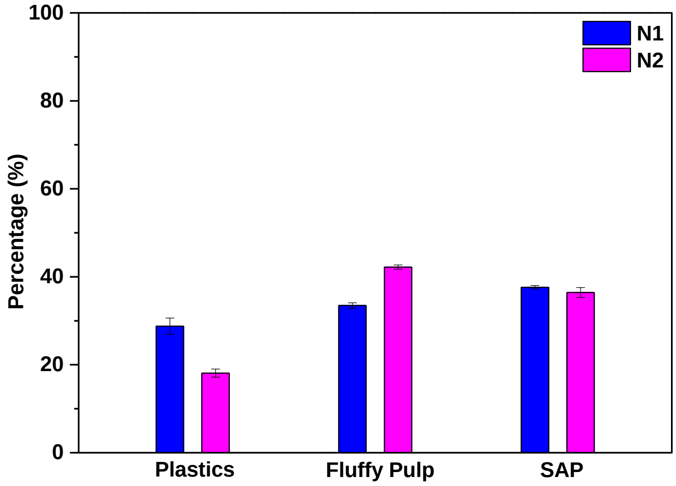

Fig. 4 Percentages of plastics, fluffy pulp and SAP in unused nappies.

3.2 Pretreatment of used nappies and their physicochemical characterization.

The optimum concentrations of salts in order to obtain the maximum SAP deswelling effect, that were determined on unused nappies, were used to pretreat the samples from Halandri and Zamudio (UN1 and UN2). The addition of 20% w/w $CaCl_2$ and 50% w/w $MgCl_2$ in the nappies' hydrolysate led to the precipitation of SAP and its successful separation from the hydrolysate. Residual concentrations of cations were 0.12±0.01 mg/L and 0.14±0.00 mg/L in UN1 hydrolysate and 0.17±0.01 mg/L and 0.11±0.02 mg/L in UN2 hydrolysate for Ca^{+2} and Mg^{+2} respectively (Table 2). It should be noted that the residual concentrations quantified in UN1 and UN2 hydrolysates were lower in comparison with the corresponding ones from the optimization experiments. This observation is probably due to variations on the sizes of the nappies and their contents. Samples of UN were obtained from kindergartens and nappies' sizes ranged from +3 to +6 and therefore the contained quantity of SAP was different, while the deswelling optimization experiments were carried out with nappies' size +4, as was considered the prevailing size in kindergartens according to data obtained (data not shown).

After the chemical pretreatment and the recovery of SAP, a physicochemical characterization of the used nappies' hydrolysate took place in order to assess its possibility to be used as feedstock for anaerobic digestion. As shown in Table 2, the hydrolysates of UN1 and UN2 are characterized by a neutral to alkaline pH value (7.77 ± 0.04 and 7.51±0.05). These values can be attributed to water and the presence of urine which has a high pH value when stored due to the decomposition of urea and urate [18]. Furthermore, total carbohydrates do not show significant differences between the two hydrolysates. The absence of soluble carbohydrates leads to the conclusion that cellulosic fibers from the nappies are the main source of carbohydrates. As far as t-COD is concerned, values are of the same order of magnitude (5.87±1.26 g/L for UN1 and 2.56±0.11 g/L for UN2) but present a difference probably due to different amount of excreta.

In addition, it is obvious that the total amount of quantified nitrogen is derived from ammonia, while both hydrolysates present an ideal COD:N:P ratio of 350:7:1. By ensuring that there will be no significant deviations of the aforementioned ratio, in order to prevent inhibition from high ammonia concentrations, these hydrolysates could be used without any limitation in the anaerobic digestion process.

Although the biodegradable content of a used nappy is considerable (cellulose fibers plus excreta), yet the hydrolysates present rather low concentrations of nutrients and organic carbon. This result is attributed to the high dilution ratio, which is needed for the pretreatment. With this composition and in order to fully exploit its biodegradable fraction, the hydrolysates could be used in co-digestion anaerobic treatments of substrates with low humidity and high TS, COD values in order to dilute them. Co-digestion has been previously reported, by several researchers as an efficient method for biogas production and an effective way to balance nutrient concentrations or avoid inhibition from specific compounds [1, 21, 22].

Table 2
Physicochemical characterization of used nappies' hydrolysates following SAP recovery. Data are mean values ±SD (n=3).

	UN1 Hydrolysate	UN2 Hydrolysate
Parameter	Value ± SD	Value ± SD
pH	7.77 ± 0.04	7.51 ± 0.05
Humidity (%)	99.19 ± 0.10	99.29 ± 0.13
Alkalinity (g $CaCO_3$/L)	0.53 ± 0.08	0.44 ± 0.02
t-Carbohydrates (g/L)	1.37 ± 0.13	1.52 ± 0.17
d-Carbohydrates (g/L)	0.24 ± 0.01	0.16 ± 0.02
Phenols (g/L)	0.04 ± 0.00	0.01 ± 0.00
t-COD (g/L)	5.87 ± 1.26	2.56 ± 0.11
d-COD (g/L)	1.51 ± 0.22	1.32 ± 0.23
Fats and Oils (g/L)	0.06 ± 0.01	0.02 ± 0.00
t-Phosphorus (g/L)	0.024 ± 0.00	0.04 ± 0.00
d-Phosphorus (g/L)	0.017 ± 0.00	0.02 ± 0.00
TKN (g/L)	0.26 ± 0.02	0.07 ± 0.04
NH_3-N (g/L)	0.26 ± 0.02	0.07 ± 0.03
TSS (g/L)	4.45 ± 0.18	3.52 ± 0.05
VSS (g/L)	4.30 ± 0.32	3.44 ± 0.03
TS (g/L)	8.07 ± 0.97	7.06 ± 0.67
VS (g/L)	4.99 ± 0.98	4.56 ± 0.48
Ca^{2+} (g/L)	0.12 ±0.01	0.17 ± 0.01
Mg^{2+} (g/L)	0.14 ±0.00	0.11 ± 0.02

4. CONCLUSIONS

Among the three tested salts, namely $AlCl_3$, $MgCl_2$ and $CaCl_2$, the later resulted in better deswelling of SAP at 60 % w/w concentration. $AlCl_3$ was rejected due to health risks at high concentrations and poor deswelling performance. The combination of 20% w/w $CaCl_2$ and 50% w/w $MgCl_2$ resulted to SAP volume of 4.33±0.58 ml (for 0.5g SAP) with residual concentrations 160.13±7.67 mg $Ca^{2+/}$L and 276.50±14.55 mg $Mg^{2+/}$L and a final cost of 0.3020€/g treated SAP. The pretreatment was satisfying for the successful deswelling of SAP and its removal from the used nappies samples with even lower residual concentrations than expected, while the physicochemical characterization of the hydrolysate indicates that it can be used as substrate in co-digestion anaerobic processes without limitations and risk of inhibition in the subsequent anaerobic digestion.

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REFERENCES
1. Torrijos, M., Sousbie, P., Rouez, M., Lemunier, M., Lessard, Y., Galtier, L., Simao, A., Steyer, J.P.: Treatment of the biodegradable fraction of used diapers by co-digestion with waste activated sludge. Waste Manage. 34, 669-675 (2014)
2. EDANA: Sustanability Report 2015. EDANA, ISBN 2-930159-73-1, D/2011/5705/1.http://www.sustainability.edana.org/Objects/10/Files/sustainabilityReport2011.pdf (2015). Accessed 14 May 2017
3. Colón, J., Ruggieri, L., Sánchez, A., González, A., Puig, I.: Possibilities of composting disposable diapers with municipal solid wastes. Waste Manage. Res. 29, 249-259 (2010)

4. Colón, J., Mestre-Montserrat, M., Puig-Ventosa, I., Sánchez, A.: Performance of compostable baby used diapers in the composting process with the organic fraction of municipal solid waste. Waste Manage. 33, 1097-1103 (2013)
5. Directive 2008/98/EC on waste (Waste Framework Directive). http://ec.europa.eu/environment/waste/framework/. Accessed 14 May 2017
6. Directive 1999/31/EC on the landfill of waste. http://eur-lex.europa.eu/legal-content/EL/TXT/?uri=CELEX%3A31999L0031. Accessed 14 May 2017
7. Horie, K., Báron, M., Fox, R.B., He, J., Hess, M., Kahovec, J., Kitayama, T., Kubisa, P., Maréchal, E., Mormann, W., Stepto, R.F.T., Tabak, D., Vohlídal, J., Wilks, E.S., Work, W.J.: Definitions of terms relating to reactions of polymers and to functional polymeric materials (IUPAC recommendations 2003). Pure Appl. Chem. 76, 889-906 (2004)
8. El-Mamouni, R., Frigon, J.C., Hawari, J., Marroni, D. : Combining photolysis and bioprocesses for mineralization of high molecular weight polyacrylamides. Biodegradation 13, 221–227 (2002)
9. Chen, Y., Cheng, J.J., Creamer, K.S.: Inhibition of anaerobic digestion process: A review. Bioresour. Technol. 99, 4044-4064 (2008)
10. Raghuram, B.: Synthesis of Non-Toxic and Biodegradable Flame Retardant Using Diapers, IJESC. 6, 2223-2227 (2016)
11. Perrin, D.D., Armarego, W.L.F., Perrin, D.R.: Drying of Solvents and Laboratory Chemicals, Purification of Laboratory Chemicals, Pergamon Press (2nd Ed) (1980)
12. Conway, M.E., Francois, J., Michael, D.S.: Treatment of absorbent sanitary paper products, U.S. Patent No. 5.558.745, (1996)
13. De, H.P.: Laundry washing and drying machine, U.S. Patent No. 3.927.542. (1975)
14. Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D.: Determination of Structural Carbohydrates and Lignin in Biomass, Laboratory Analytical Procedure (LAP), National Renewable Energy Laboratory (2008)
15. American Public Health Association (APHA), Standard Methods for the Examination for Water and Wastewater (19th edition), Byrd Prepess Springfield, Washington (1995)
16. Dareioti, M.A., Dokianakis, S.N., Stamatelatou, K., Zafiri, C., Kornaros, M.: Biogas production from anaerobic co-digestion of agroindustrial wastewaters under mesophilic conditions in a two-stage process. Desalination. 248, 891-906 (2009)
17. Waterman PG, Mole S: Analysis of phenolic plant metabolites, In: Lawton, J.H., Likens, G.E. (Eds.), Methods in Ecology, Blackwell Scientific Publications, Oxford (1994)
18. Kirchmann, H., Pettersson, S.: Human urine-Chemical composition and fertilizer use efficiency. Fert. Res. 40, 149-154 (1994)
19. Gonzalez, M.A., Alvarez, M.L., Pisani, G.B.: Involvement of oxidative stress in the impairment in biliary secretory function induced by intraperitoneal administration of aluminum to rats. Biol. Trace Elem. Res. 116, 329-48 (2007).
20. ATSDR (Agency for Toxic Substances and Disease Registry), Priority list of hazardous substances identified by ATSDR, Public Health Service, US Department of Health and Human Services, Atlanta, GA (2007).
21. Dareioti, M.A., Kornaros, M.: Effect of hydraulic retention time (HRT) on the anaerobic co-digestion of agro-industrial wastes in a two-stage CSTR system. Bioresour. Technol. 167, 407-415 (2014)
22. Ma, G., Neibergs, S., Harrison, J.H., Whitefield, E.M.: Nutrient contributions and biogas potential of co-digestion of feedstocks and dairy manure. Waste Manage. In Press (2017)