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Published version:

DOI:10.1016/j.jclepro.2021.129236

Removal of sugars from food and beverage wastewaters by amino-modified SBA-15

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ABSTRACT

In the context of the removal of the biochemical oxygen demand (BOD_5) from food and beverages production wastewaters, this paper reports the capabilities of SBA-15 modified with (3-aminopropyl)-triethoxysilane (S-APTES) and N-[3-(trimethoxysilyl)propyl]aniline (S-Aniline) in the removal of glucose, fructose and sucrose at very high concentrations (350,000 mg/L for glucose, 350,000 mg/L for fructose and 170,000 mg/L for sucrose), i.e. the sugars most widely used as sweeteners in food and beverage manufacturing. After the determination of the main physico-chemical characteristics, the study of the effect of pH on the removal capabilities of S-APTES and S-Aniline allowed us to elucidate the main mechanisms involved. Based on the study of solid:liquid ratio, the optimal experimental conditions were defined to achieve a removal of BOD_5 in simulated soft-drink wastewater as high as 80 %. The results show that a lower adsorbent dosage is required in respect to current methodologies, representing an advantage especially for disposal procedures of the exhausted adsorbent. This work offers a proof of concept for the integration of amino-modified SBA-15 sorbents in industrial pre-treatment of wastewaters before discharging it in sewerage systems.

Keywords: Food and beverage wastewaters, sugars, SBA-15 mesoporous silica, amino group functionalization

1. Introduction

Sugars are present in food matrices both as additives or as natural components. Their presence poses some concerns in the field of environmental chemistry (Ozgun et al., 2012; Poddar and Sahu, 2017). In fact, sugars from food and beverage industrial wastewaters (e.g. sugar, carbonated soft-drink industries) can impact on the water quality with Biochemical Oxygen Demand (BOD_5) as high as 5,000-8,000 mg/L (Boguniewicz-Zabłocka et al., 2017). These BOD_5 values are far higher than the limits imposed by regulations for discharging into natural waters and in sewage systems, thus exceeding the capabilities of the local sewage treatment plant. Therefore, wastewaters from such industrial processes needs in-site treatment before being discharged in municipal sewerage systems. For encouraging the control of trade wastewaters by industrial consumers, some local quality water management offices, such as that of New South Wales, impose discharge fees calculated on the basis of BOD_5 concentration in the liquid trade waste discharged (Pagan and Prasad, 2007; Sydney Water, 2021), thus preventing the increase of BOD_5 by an a-priori strategy.

The treatment methods of wastewater effluents from sugar (Kushwaha, 2015), artificial sweeteners (Pang et al., 2020), confectionary (Zajda and Aleksander-Kwaterczak, 2019) and soft-drink (Boguniewicz-Zabłocka et al., 2017) industries are reviewed or discussed by several authors. The most used treatment approach to remove BOD_5 relies on biological processes. For example, in the wastewater treatment of soft-drink industries, the anaerobic stage can reduce BOD_5 from a few thousand to a few hundred mg/L, but additional aerobic treatment is still required for the effluent to meet the regulations (Seng et al., 2005). Chemical and physical treatment processes (e.g., coagulation and sedimentation/flotation) are also used to reduce the organic content before the wastewater enters the biological treatment. Various technological solutions (e.g. bio-reactors of nano-ceramic gel with deposited biofilm (Biogill, 2015)) are proposed in the market as stand-alone solutions for the pre-treatment of sugar wastewater.

On the other side, the reuse of wastewater for non-potable purposes is encouraged by many EU policies and has the advantage of being an economically viable solution. The treated effluent of food and beverages industries can be used as such or after dilution with other freshwater for irrigation purposes (Poddar and Sahu, 2017; Wang and Serventi, 2019) and for reutilization in industrial aqueducts (Kushwaha, 2015), provided that the presence of sugars is limited, as sugars provides nutrients to support bacterial growth responsible of microbial fouling on surfaces (Majewski et al., 2012).

Adsorption techniques based on different kinds of substrates like bentonite and lignite (Sunitha and Rafeeq, 2009), bagasse fly ash (Lakdawala and Oza, 2011) and silica (Majewski et al.,

2012) were identified as alternative economic approaches for pre-treatments of food and beverages wastewaters and they deserve further insights.

Ordered mesoporous silicas and organosilicas have been largely investigated as adsorbents (Bruzzoniti et al., 2000; Li et al., 2019; Wu and Zhao, 2011), due to their high specific surface area and uniform porosity, together with the possibility of tailoring their surface chemical properties through synthesis conditions and post-synthesis modification.

Mesoporous silica functionalized with amino groups was previously investigated for adsorption and removal of anionic pollutants in drinking and wastewater (Fiorilli et al., 2017; Rivoira et al., 2016).

The aim of this work is to show the capabilities of ordered mesoporous silica of SBA-15 family functionalized with primary and secondary amino groups (3-aminopropyl)-triethoxysilane and N-3-trimethoxypropylaniline, respectively) to be used for the removal of sugars. Glucose, fructose and sucrose, the disaccharide derivative of glucose and fructose, were chosen since they are commonly present in the food and beverage industry processes and since they are naturally contained in fruit. The SBA-15 was functionalized in laboratory and its physico-chemical properties were characterized. The adsorption behaviour towards glucose, fructose and sucrose at higher concentrations than those really found in soft-drink wastewaters was studied as a function of pH and sorbent amount.

As a proof of concept, the suitability of the use of amino modified SBA-15 as adsorbent for the reduction of the BOD_5 in industrial wastewaters was finally tested, simulating the typical composition of wastewater from a soft drink production process.

2. Material and methods

2.1 Reagents

Ordered mesoporous silica of the SBA-15 (ACS Material Advanced Chemical, Pasadena, CA, USA) was used. For functionalization of SBA-15, (3-aminopropyl) triethoxysilane (APTES, 99 %), N-[3-(Trimethoxysilyl)propyl]aniline, toluene (99.8 %) from Sigma Aldrich (Steinheim, DE) were used. D(+) glucose was from Merck (Darmstadt, DE), D(-), whereas fructose and sucrose were from J.T. Baker (Phillipsburg, NJ, USA).

Hydrochloric acid (35 % w/w, d = 1.187 g/ml) and NaOH (>98 %) were from Carlo Erba (Milano, IT). All reagents used were of analytical grade. For standard solution and eluent preparation, high-purity water (18.2 M Ω·cm resistivity at 25°C) produced by an Elix-Milli Q Academic system (Millipore, Vimodrone, MI, Italy) was used.

2.2 Preparation of sorbents

SBA-15 (1 g) previously washed with deionized water (50 mL), was stirred with toluene (200 mL) for 30 minutes, at room temperature. The functionalizing reagent (2 mL of APTES or N-[3-

(trimethoxysilyl)propyl]aniline) was added dropwise. The flask with the solution was heated to 110 ° C, after connection to a water-refrigerated system. The solution, kept under stirring for 24 hours at room temperature, was filtered and dried, according to previous work (Fiorilli et al., 2017; Rivoira et al., 2016).

For the sake of clarity, the sample functionalized with APTES is labelled as S-APTES and the sample functionalized with N-[3-(trimethoxysilyl)propyl]aniline as S-Aniline.*2.3 Physico-chemical characterization*

For the measurement of nitrogen adsorption-desorption isotherms, a Quantachrome AUTOSORB-1 (Boynton Beach, FL, USA) was used. Before measurement, S-APTES and S-Aniline samples were outgassed (393 K, 6 h). The BET specific surface areas (SSA_{BET}) were calculated in the relative pressure range 0.04-0.1; pore size distribution was determined through the NLDFT (Non Localized Density Functional Theory) method, using the equilibrium model for cylindrical pores.

TG analyses were obtained between 298 K and 1,073 K in air (flow rate: 100 mL/min, heating rate: 10 K/min) by a SETARAM 92 (Caluire, France) instrument.

Infrared spectroscopy characterization was carried out on powders pressed in self-supporting wafers. Spectra were recorded at room temperature with a Bruker Tensor 27 (Bruker, Billerica, MA, USA) spectrometer operating at 2 cm^{-1} resolution, after outgassing the sample at room temperature (residual pressure of 0.1 Pa).

2.4 Analysis of sugars

Sugar content was determined by ion-chromatography (ICS-3000 gradient pump, Thermo Fisher Scientific, Waltham, MA, USA), coupled to pulsed amperometric detection (AD40 Electrochemical Detector, Thermo Fisher Scientific), equipped with Ag/AgCl reference and a gold working electrode. The detection potential was 0.1 V (400 ms: 200 ms as delay time and 200 ms as determination time). The potential was then instantaneously set at -2 V (10 ms) and at 0.6 V (10 ms) to restore the gold oxide on the working electrode surface. The potential was finally set at -0.1V (60 ms).

The column used was a CarboPacPA10, 250x4 mm (100 μeq/column), Thermo Fisher Scientific. Sample loop was 10 μL. After optimization (data available upon request), the eluent concentration was 55 mM KOH.

Before injection, solutions were diluted in order to achieve a final concentration within 500 μg/L and 1 mg/L, so as to avoid column overload. Data were collected and managed by the Chromeleon v.6.80 software (Thermo Fisher Scientific).

2.4.1 Detection limits

Limits of detections (LOD) were expressed as s_m=s_m+3s_b, with s_m=average signal of blank, s_b= standard deviation of blank on 10 measurements and were 69, 56 and 11 µg/L for glucose, fructose and sucrose, respectively.

2.5 Simulated wastewater samples

As a proof of concept, the use of the amino-modified SBA-15 was tested in the treatment of wastewaters derived from the soft-drink industry. In detail, a simulated wastewater sample (SD-WW) was prepared according to the maximum levels of contamination reported for this type of effluent (Seng et al., 2005). Hence, the simulated soft-drink wastewater contained 70 mg/L K^+, 20 mg/L Fe^{3+}, 2500 mg/L Na^+, 300 mg/L NH_4^+, 5 mg/L Zn^{2+}, 2.5 mg/L Ni^{2+}, 8 mg/L Co^{2+}, 20 mg/L SO_4^{2-}, 40 mg/L PO_4^{3-}. In this matrix, the BOD_5 of 5000 mg/L was obtained in two different ways: (i) by adding 4500 ppm of sucrose (SD-WW-suc) and (ii) by adding a proper volume of a cola-like drink (SD-WW-cola) which original contained 10.9 g sugars. The final pH of the two samples was of 4.1 and 3.0, respectively.

2.6 Adsorption tests

Adsorption tests on simulated wastewaters were carried out in triplicate with a $6{\cdot}10^{-5}$ g:L adsorbent:solution ratio, at room temperature under stirring 1100 xg for 1 h.

Preliminary tests on sugars solution were also performed to investigate the role of parameters such as pH and solid:liquid ratio, by the one-variable at a time method.

2.6.1 Effect of pH. Tests were performed in triplicate on 0.25 g of sorbent (S-APTES/S-Aniline) put in contact with 4 mL solution containing a mixture of 350,000 mg/L glucose, 350,000 mg/L fructose and 170,000 mg/L sucrose, stirred at 1100 xg between 10 and 60 min. These concentrations can be considered representative of the sugar content in some kinds of fruit, i.e. strawberries (Castiglioni et al., 2021) and precautionary, about 70-folds higher, in respect to an average BOD_5 of wastewaters of sugary drink production (Castillo et al., 2017; Junior et al., 2021). Experiments were performed at pH 2.1, 5.0 and 8.5; for each pH value, experiments were performed in triplicate.

2.6.2 Solid:liquid ratio (effect of sorbent amount). Tests were performed in triplicate using different adsorbent amounts with the same sugar solution volume. In detail, amounts of adsorbent were 0.1 g and 0.25 g for the two tests. These amounts of adsorbent were put in contact with 4 mL of solution (pH 2.1) containing 350,000 mg/L glucose and fructose and 170,000 mg/L sucrose and kept under stirring between 10 and 60 min. The solid:liquid (S:L) ratios in the two tests were 1:16 and 1:40 for 0.1 g and 0.25 g of adsorbent, respectively. These values can be expressed as mg:L ratios, which are 0.025 mg/L and 0.06 mg/L.

3. Results and discussion

3.1 Physico-chemical features

S-APTES and S-Aniline were characterized by nitrogen adsorption-desorption isotherms (Figure 1). For both samples, isotherms are type IV according to IUPAC classification, which are typical of mesoporous materials. Hysteresis loops are type H1, revealing well-defined cylindrical-like pores. Figure 2 reports the pore size distributions, which appear narrow and unimodal for both materials, confirming their uniform porosity.

In respect to the pristine SBA-15 (SSA_{BET}=490 m^2/g, pore volume 0.92 cm^3/g, pore diameter 81 Å (Fiorilli et al., 2017; Rivoira et al., 2016), the textural properties of functionalized sorbents are in agreement with the grafting of the amino groups on the SBA-15 internal surface. Indeed, for S-APTES, SSA_{BET} is reduced to 325 m^2/g, pore volume is equal to 0.53 cm^3/g and pore diameter results 70 Å and for S-Aniline, the corresponding values are 299 m^2/g, 0.54 cm^3/g, and 68 Å, respectively.

The presence of functional groups in S-APTES and S-Aniline was confirmed by FTIR spectra (Fig. S1 of the Supplementary Material).

By TG analysis, the amount of amino groups in S-APTES and S-Aniline was estimated.

Figure 3 shows the percentage mass loss measured between 298 K and 1073 K in air flow. The first mass loss is observed between 298 K and 473 K which is ascribed to molecular water desorption. This loss is lower for S-Aniline (almost negligible) than for S-APTES (about 10 % w/w) revealing a lower hydrophilicity of S-Aniline than S-APTES in agreement with the more hydrophobic functional moiety.

The weight loss above 473 K was ascribed to the combustion of grafted amines and it is 26.9 % for S-Aniline and 25.6 % for S-APTES. Based on the molecular weight assumed for the removed species, these values of mass loss allowed to estimate the content of surface amines which resulted to be 2.23 mmol/g for S-Aniline and 4.41 mmol/g for S-APTES (corresponding to $7.5\cdot10^{-21}$ mmol/nm^2 and to $13.6\cdot10^{-21}$ mmol/nm^2, respectively).

3.2 Adsorption experiments

3.2.1 Effect of pH

The removal of sugars by the functionalized adsorbents was studied as a function of pH (2.1, 5.0 and 8.5) in view of a possible tuning of the removal conditions. It is worth mentioning that sugars are in the undissociated form at all the pH values investigated (pK_a=12.2 for glucose, 12.0 for fructose and 12.6 for sucrose).

As shown in Fig. 4, both S-APTES and S-Aniline are effective in the removal of sugars from water solution. This is ascribed to the interaction of sugar molecules with the amino groups grafted at the surface of SBA-15. Indeed, negligible adsorption of glucose from water solution was reported for bare SBA-15 by Majumdar et al. (Majumdar et al., 2016) and by Zhao and Shantz (Zhao and Shantz, 2011).

For S-APTES and S-Aniline removal capabilities decrease with the increase of pH: this may be explained considering the role of H-bonding between protonated amines (proton donor) and sugar molecules (proton acceptor) in the interaction between sugar molecules and adsorption sites (Ling et al., 2016). In fact, with the variation of the pH of the solution, a change of the protonated amine concentrations occurs. Increasing the pH, the population of protonated amines decreases, thus decreasing the population of H-bonding donor sites. It is worth noting that the decreasing of the removal capabilities upon increasing pH is larger for S-Aniline than for S-APTES. This may be due to the weaker basicity of propylaniline (pK_b 8.96) than propylamine (pK_b 3.5) so that the decrease of protonated amine population upon increasing pH is expected to be relatively larger in S-Aniline than S-APTES.

Since the highest removal yields were achieved at pH 2.1, further investigations were carried out at this pH value.

3.2.2 Solid:liquid ratio (effect of sorbent amount).

The choice of the most suitable S:L ratio is important for the correct dosage of adsorbent that minimize the mass of reagent required to achieve the desired performance, maximizing the cost-effectiveness of the approach. As shown by the data reported in Table 1, the use of higher S:L ratio 1:16 in respect to 1:40 improves removal performances. As a consequence, S:L=1:16 was used for the further removal tests. It is important to highlight that this S:L value, corresponding to $6 \cdot 10^{-5}$ g:L adsorbent:solution is seven orders of magnitude lower than the dosage reported for amorphous silica functionalized with APTES used to remove similar nominal amount of sucrose only (i.e. around 400 g/L ratio) (Majewski et al., 2012).

3.3 Sugar removal in simulated wastewaters

The functionalized S-APTES and S-Aniline were tested for real case applications on a simulated soft-drink wastewater (SD-WW) in which BOD_5 was obtained by adding sucrose (SD-WW-suc) or a cola-like beverage (SD-WW-cola) .

As an example, the chromatograms obtained for simulated wastewaters derived from the soft-drink industry (SD-WW-cola) before and after the treatment with S-APTES and S-Aniline is reported in Figure 5.

Figure 6A shows the abatement of BOD_5 (expressed as sucrose) in the simulated wastewater sample. In the case of SD-WW-suc, the abatement of BOD_5 is about 63 % (relative standard deviations, RSD, below 2 %) for both S-APTES and S-Aniline. For SD-WW-cola, the analysis allowed us to detect glucose, fructose and sucrose already present in the pristine cola-like drink. For this sample, the sugar removal capabilities for the two adsorbents were above (70 %, RSD< 7 %).

The differences observed for the two simulated wastewater samples is ascribed to the different pH values of the samples (pH 4.1 for SD-WW-suc; 3.0 for SD-WW-cola), as detailed in section 3.2.1. The S-Aniline adsorbent exhibits higher removal than S-APTES for the three sugars in the SD-WW-cola test (Fig. 6B). This result is in agreement with previous results on adsorption of polycyclic aromatic hydrocarbons (Castiglioni et al., 2021) and data in Fig. 3, showing higher removal for S-Aniline at low pH values (below pH 4). This effect cannot be ascribed to features such as SSA and concentration of adsorption sites which are both lower for S-Aniline (299 m^2/g and 2.23 mmol/g, respectively) than S-APTES (325 m^2/g and 4.41 mmol/g). The higher sugar removal observed for S-Aniline compared to that of S-APTES can be tentatively ascribed to its lower hydrophilicity, as revealed by molecular water loss in TGA analysis. This would cause a weaker competition of water molecules in the adsorption, so favouring the removal of organic solutes from water solution, similarly to what proposed for adsorption on activated carbons (Moreno-Castilla, 2004).

The organic load removal performance exhibited by S-Aniline and S-APTES are highly encouraging in respect to many processes reviewed by the literature.

Regarding other adsorption systems, the materials here proposed need lower adsorbent dosage (0.025 mg/L) and contact times (10 to 60 min) in respect to metakaolin or carbon (800 mg/L, for 180-240 min) to achieve comparable removal yields (Parande et al., 2009). Amino modified amorphous silica used by Majewski et al. (Majewski et al., 2012) proves to be capable to remove low organic load (BOD_5< 2 mg/L) with very high adsorbent dosage such as 100 g/L.

The BOD_5 removal by the proposed adsorbents demonstrates promising capabilities even towards the physico-chemical treatment (equalization and coagulation/flocculation) that usually precedes the biological treatment, which ensure BOD_5 removal of about 43 % (Seng et al., 2005). Worth to be mentioned that BOD_5 removal by S-Aniline and S-APTES could also compete with high rate aerobic processes, which are characterized by BOD_5 removal of about 64 % (Seng et al., 2005).

The use of lower dosages of adsorbent reduces the management/disposal procedures of the exhausted material. This feature is expected to introduce costs saving and advantages especially over physico-chemical treatment where high concentrations of coagulant (500 mg/L (Amuda et al., 2006)) or mixed coagulant/flocculant (100 mg/L / 25 mg/L) (Amuda and Amoo, 2007) are used to abate the organic load.

4. Conclusions

The ordered mesoporous SBA-15 modified with (3-aminopropyl)-triethoxysilane (S-APTES) and N-[3-(trimethoxysilyl)propyl]aniline (S-Aniline) allows to obtain adsorbents suitable for the removal of high concentrations of glucose, fructose, sucrose. This feature has been exploited to test them in the treatment of wastewater sample simulating the one derived from food process industry which are rich in the above-mentioned sugars and are characterized by high values of BOD_5.

The performance of S-APTES and S-Aniline adsorbents is pH dependent and is mainly ascribed to the formation of hydrogen bond which provide strong interactions with sugars. The better removal performance observed for S-Aniline is ascribed to the lower hydrophilicity of the functional group, which lead to weaker competition by water molecules. The efficient removal of BOD_5 by the modified SBA-15 adsorbents is achieved at an adsorbent dosage:solution ratio of $6\cdot10^{-5}$ g:L which is a far lower value than the ones usually reported in the literature with advantages even for disposal procedures at the end of the life cycle of the materials.

CRediT authorship contribution statement

Michele Castiglioni: Investigation, writing – original draft. **Luca Rivoira:** supervision, data validation. **Marta Gallo:** data validation and interpretation. **Irene Ingrando:** investigation; **Massimo Del Bubba:** visualization; **Barbara Onida:** data interpretation, review and manuscript editing. **Maria Concetta Bruzzoniti:** conceptualization, data interpretation, review and manuscript editing, funding acquisition.

Declaration of Competing Interest

No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication.

Acknowledgements

The authors acknowledge the financial supports from Ministero della Ricerca e dell'Università (MUR, Italy), PRIN 2017 (017PMR932) and Ex-60 %.

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Table 1. Removal performance of S-APTES and S-Aniline at different S:L ratios. Sugar concentrations: 350000 mg/L glucose-fructose, 170000 mg/L sucrose). Standard deviation (n=3) is also indicated.

Sorbent	***Sugar***	***Removal %***	
		S:L	
		1:40	**1:16**
S-APTES	Glucose	13.4 ± 3.0	65.2 ± 1.5
	Fructose	10.3 ± 1.1	67.4 ± 1.7
	Sucrose	14.4 ± 1.6	66.6 ± 1.6
S-Aniline	Glucose	11.7 ± 0.0	88.1 ± 2.3
	Fructose	12.8 ± 0.7	88.6 ± 4.6
	Sucrose	14.7 ± 1.0	89.7 ± 5.8

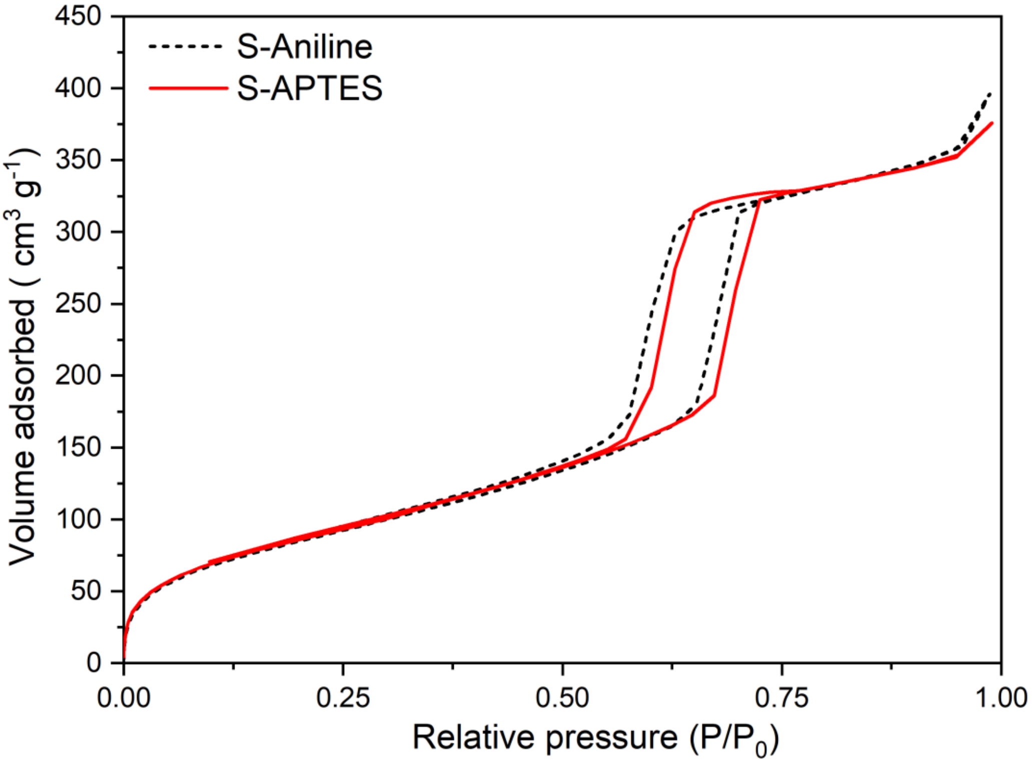

Figure 1. Nitrogen adsorption-desorption isotherms at 77 K of S-Aniline and S-APTES

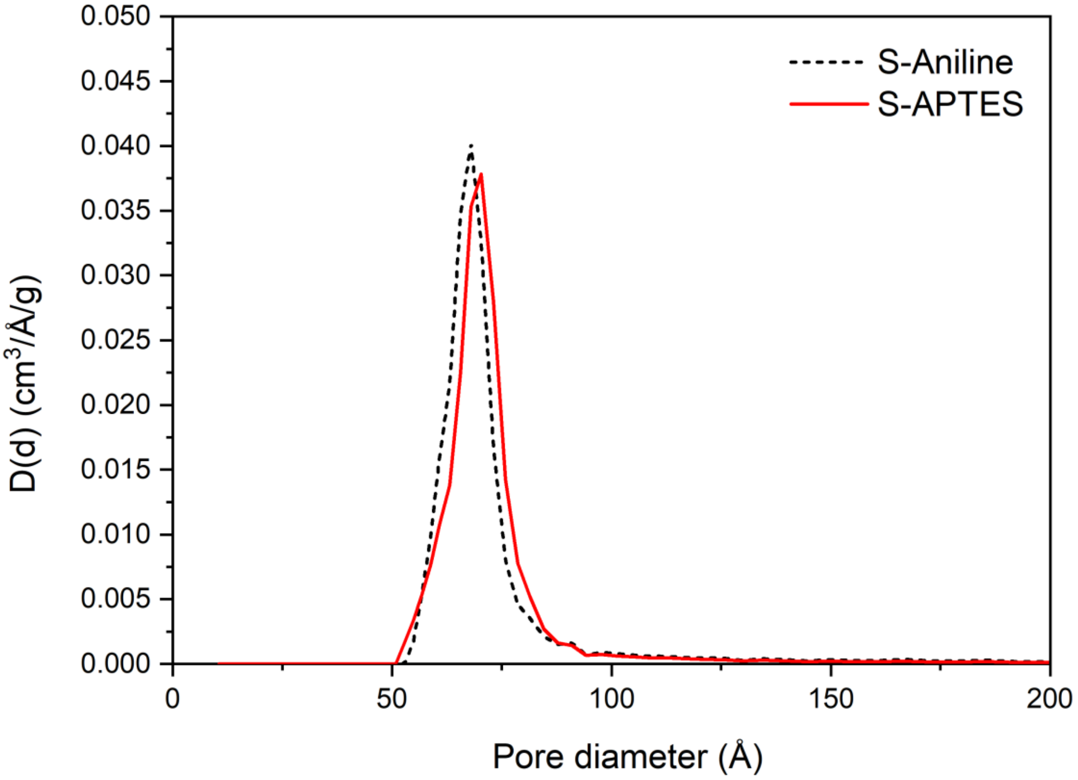

Figure 2. Pore size distributions (NLDFT) of S-Aniline and S-APTES

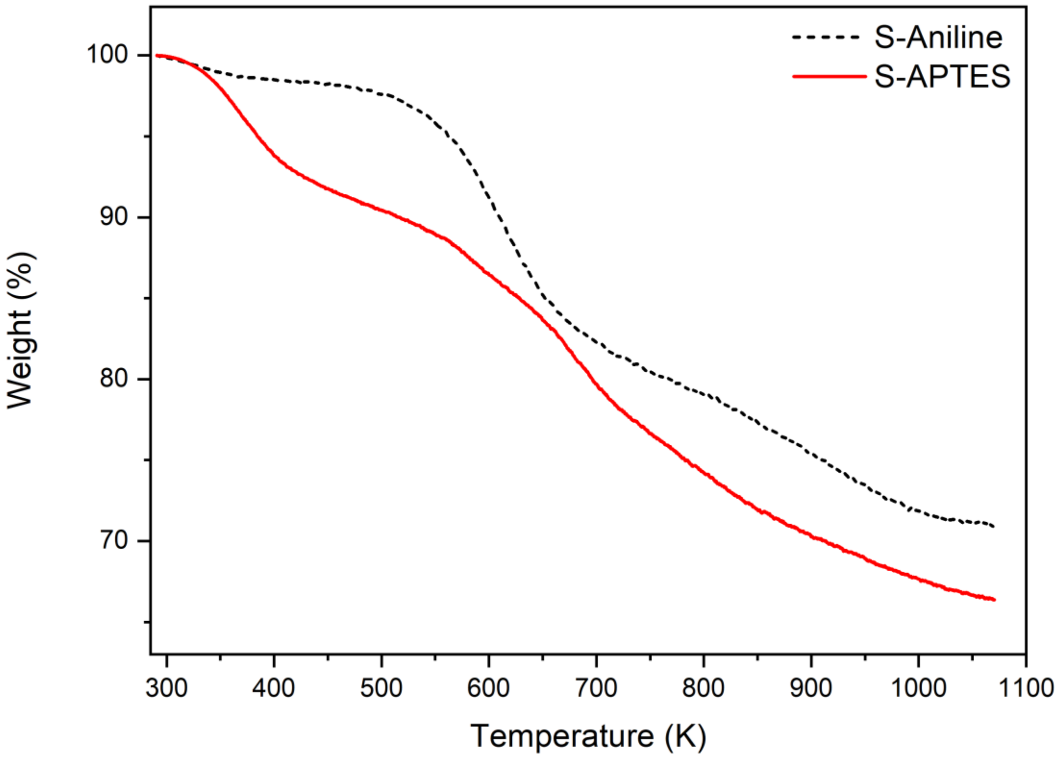

Figure 3. Thermogravimetric analysis of S-Aniline and S-APTES

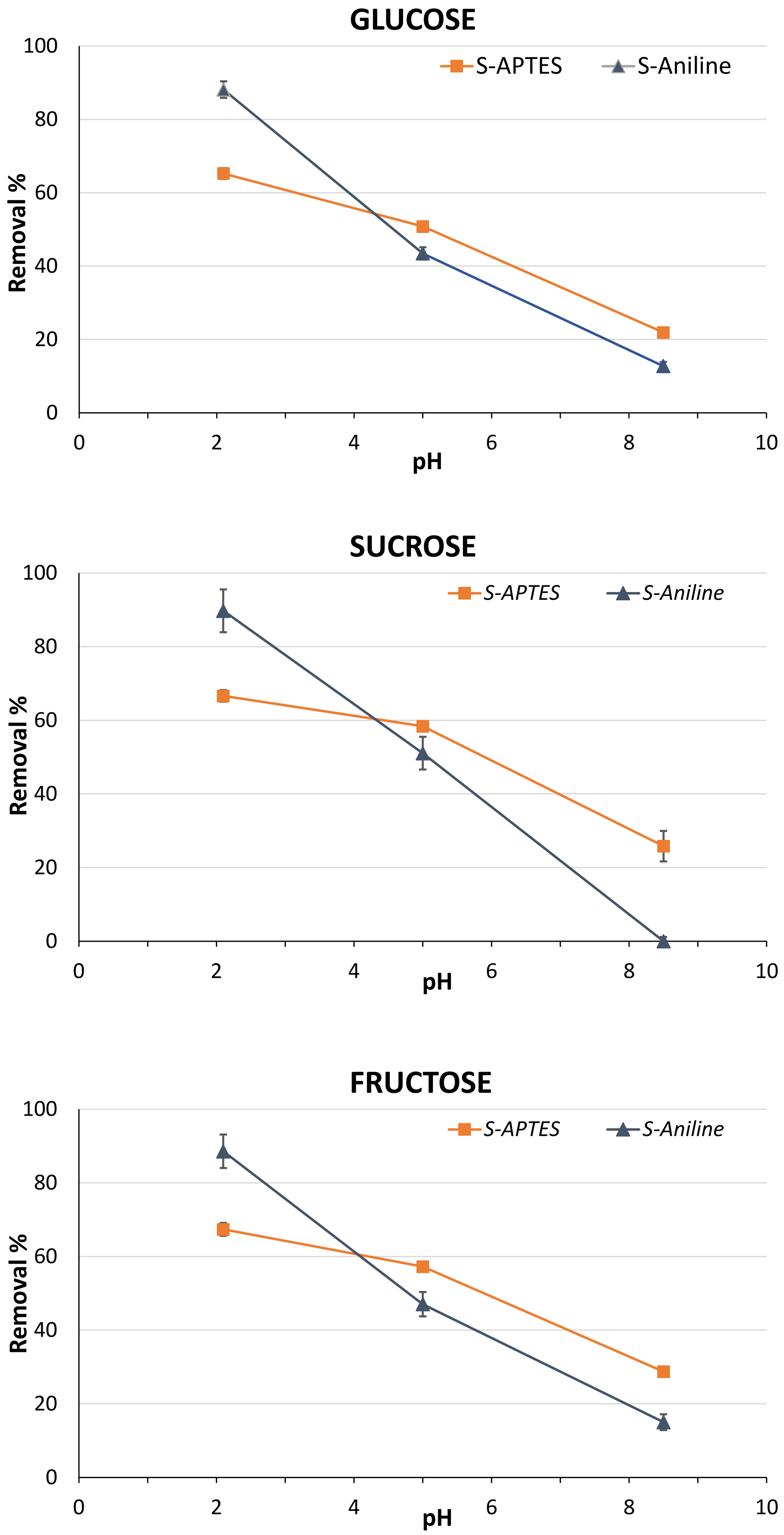

Figure 4. Effect of pH on sugar removal by S-APTES and S-Aniline. Error bars (n=3) are also reported. For experimental conditions, see text.

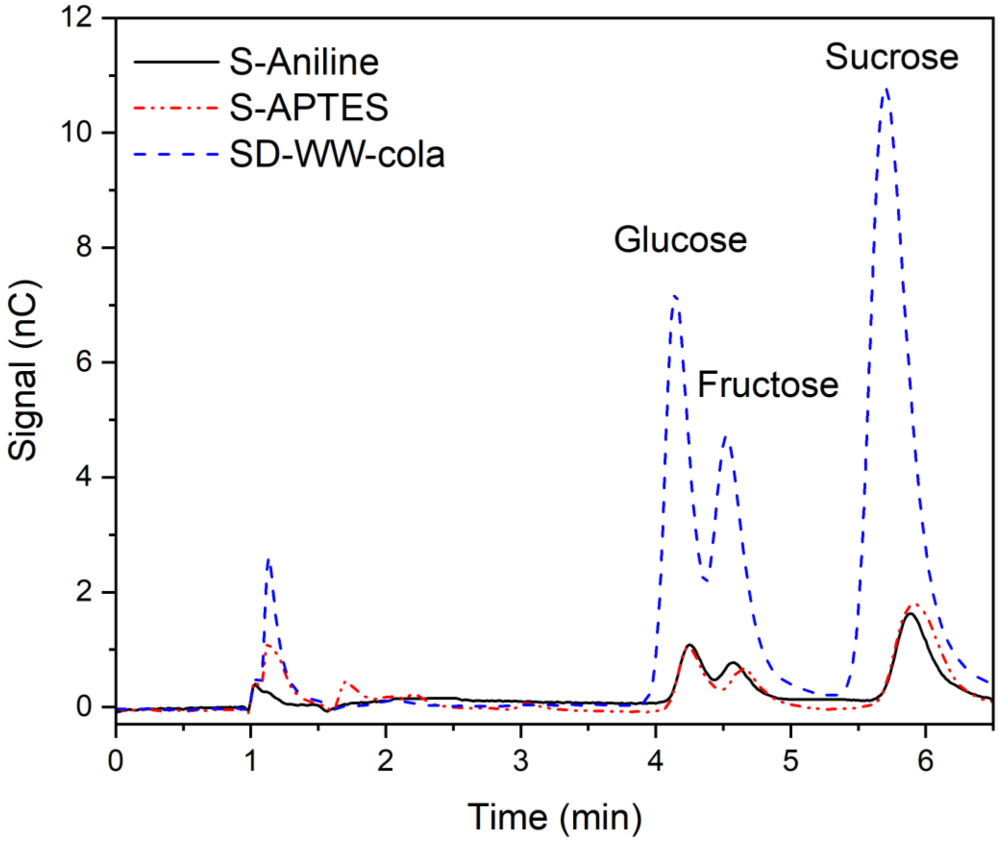

Figure 5. Chromatograms of simulated wastewaters derived from the soft-drink industry (SD-WW-cola) before (blue line) and after the treatment with S-APTES (red line) and S-Aniline (black line).

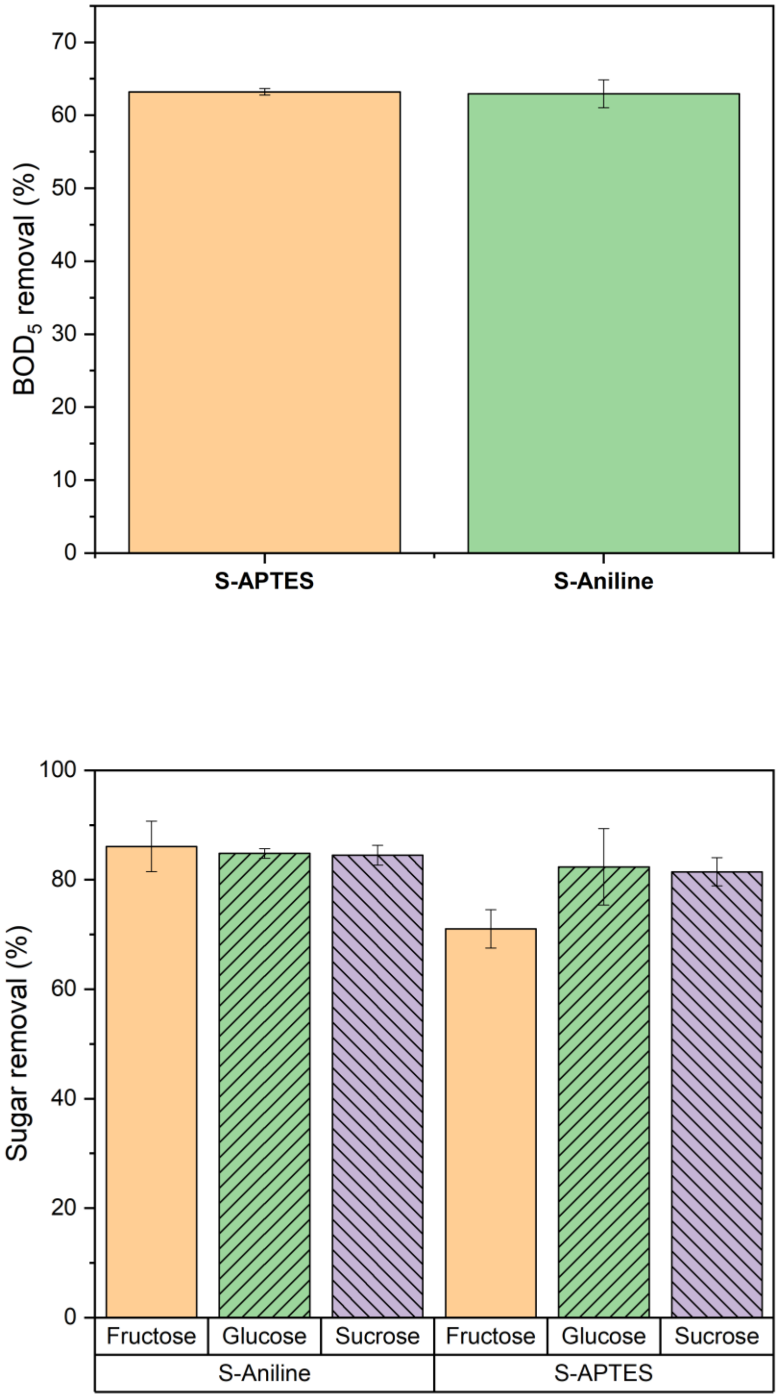

Figure 6. Removal of sugars from simulated wastewaters in which BOD$_5$ of 5000 mg/L was obtained by adding sucrose (SD-WW-suc, A) or a cola-like beverage (SD-WW-cola, B). Error bars (n=3) are also reported.

Supplementary Material

Removal of sugars from food and beverage wastewaters by amino-modified SBA-15

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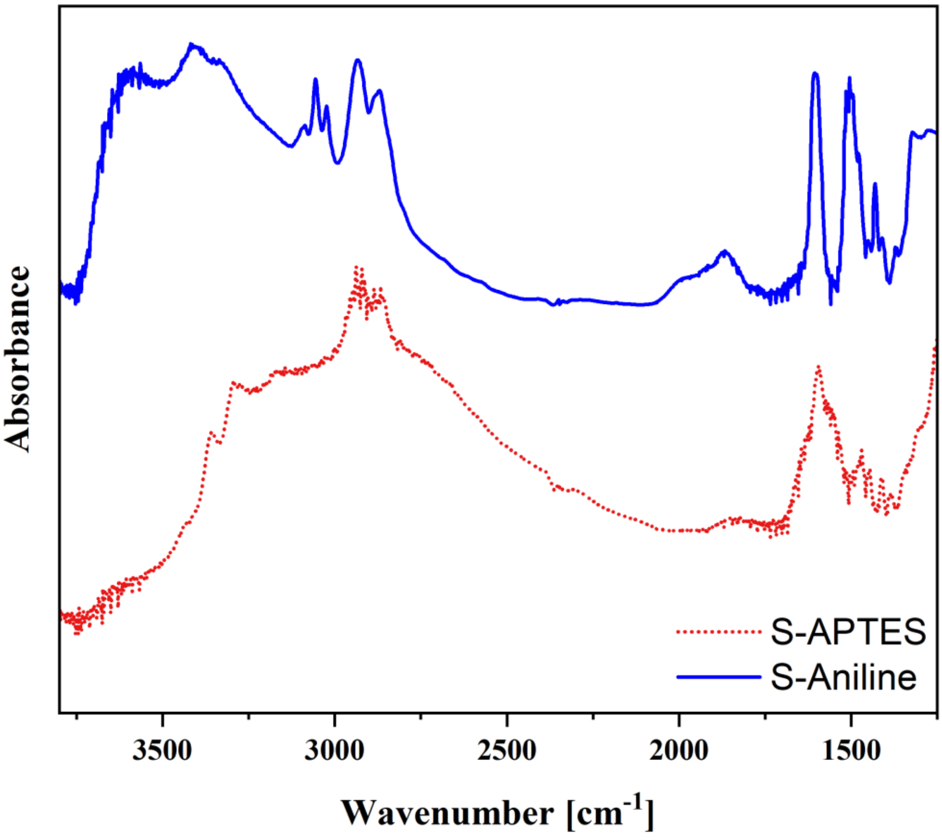

Figure S1. FT-IR Spectra of S-APTES (red dotted curve) and S-Aniline (blue curve).