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1 **Title:** Removal of biogenic amines from hydroalcoholic solutions by functionalized silica.

2

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6

7 **Running title:** Removal of biogenic amines from solutions by functionalized silica.

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13

14 **Abstract:**

15 The structure and the cation-exchange functional groups of hybrid silica materials were
16 evaluated for the effective detoxification of hydroalcoholic solutions containing eight toxic
17 biogenic amines (BA) usually found in fermented beverages. Results show the effectiveness
18 of the removal is related to the number of amino functions in the extracted molecule,
19 retention by the solid being more effective in the case of multiple amino groups, since
20 retention is stabilized through interaction with the material surface at several points. BA with
21 one amino function (isoamylamine, tyramine, β -phenylethylamine), in general, showed a
22 weak retention by the solids. For BA with more than two amine groups (spermine,
23 spermidine), the removal rate was close to 100% for all studied materials. For histamine,
24 cadaverine and putrescine, the removal percentages were higher with a lamellar structured
25 sulfonic acid functionalized material and with bifunctional materials (SBA-15 type and
26 macroporous) containing sulfonic/phosphonic acid groups obtained by co-condensation sol-
27 gel route.

28 **Keywords:** Detoxification; Biogenic Amines; Hydroalcoholic Solutions; Synthetic Wine;
29 Hybrid Silica.

30

31 **1. Introduction**

32 The application of adsorption processes for the removal of toxic compounds is
33 common in the industry. The effectiveness and selectivity requirements of the adsorption will
34 depend on the type of application, so searching for suitable adsorbents can be complex. In
35 the case of toxic compounds present in food products, the challenge is even more complex
36 since the process should be compatible with maintaining the properties and the quality of the
37 product (Kammerer, Carle & Kammerer, 2011; Nageeb Rashed, 2013).

38 In general, the origin of biogenic amines (BA) in food products is mainly due to the
39 action of microorganisms (decarboxylase enzyme activity) that produce these compounds by
40 the metabolism of the amino acids. Thus, amines such as histamine, putrescine, cadaverine,
41 spermine, spermidine, tyramine, tryptamine and β -phenylethylamine are very common in
42 cheese, fishery products and fermented beverages such as wine (Smit, du Toit & du Toit,
43 2008; Naila, Flint, Fletcher, Bremer & Meerdink, 2010).

44 Regarding the toxicity of BA, the human body can tolerate low amounts, in fact, most
45 of them are naturally present in the body due to the fact that they have numerous
46 physiological functions; however, at high levels they can cause negative effects on health. An
47 example is histamine, which is involved in the control of body temperature, learning and
48 memory, immune response and allergic reactions; however, at toxic levels it can produce
49 headaches, sweating, burning nasal secretion, facial flushing, bright red rashes, dizziness,
50 urticaria, respiratory distress, tachycardia and blood pressure disorders (Maynard &
51 Schenker, 1962; Ladero, Fernández & Álvarez, 2010). These negative effects can be
52 increased by the presence of ethanol, so its control in alcoholic beverages is justified, though
53 these are not the products with the highest contents in amines. (Maynard et al. 1962). For
54 this reason, in recent years, some countries have implemented regulations based on
55 maximum levels or maximum recommended levels in wine for some BA (for example,
56 maximum recommended levels for histamine in wine: France, 8 mg/L; Germany, 2 mg/L)
57 (Smit, Pflieginger, Binner, Grossmann, Horst & Lohnertz, 2014; Guo, Yang, Peng & Han,
58 2015).

59 BA present in wine can derive from the grape or be generated during fermentation or
60 aging. The final levels depend on viticulture and winemaking factors, such as soil fertilization,
61 indigenous microorganisms in the vineyard (bacteria, yeast and fungi) or the winemaking
62 technique (Kiss, Korbasz & Sass-Kiss, 2006; Moreno-Arribas & Polo, 2009; Smit et al, 2014).
63 In particular, the main origin of these BA in wines is the malolactic fermentation (MLF) that is
64 carried out by lactic acid bacteria (LAB) (Moreno-Arribas et al. 2009). Although inoculation
65 with lactic acid bacteria starters is less common compared with the inoculation of yeasts in
66 industrial winemaking, numerous studies have been carried out focusing on the selection of
67 bacteria starters with low production of BA (Beregal et al. 2017). However, the effectiveness
68 of this option is strongly dependent on the strain and the winemaking technique and
69 conditions (Beneduce et al. 2010; Ancin-Azpilicueta, Gonzalez-Marco & Jimenez-Moreno,
70 2010), since the production of BA is not controllable. On the other hand, another, less
71 studied, approach is the degradation of BA by specific LAB (Garcia-Ruiz, Gonzalez-
72 Rompinelli, Bartolome & Moreno-Arribas, 2011; Callejon, Sendra, Ferrer & Pardo, 2014) or
73 by other microorganisms such as fungi (Cueva et al. 2012). However, the addition of other
74 microorganisms could produce undesired effects due to the enzymatic activities and the
75 microorganisms' metabolism.

76 There is a further option which has been explored much less than the
77 aforementioned, an approach based on the removal of BA by selective adsorption by solids.
78 Vlasova and collaborators (Vlasova, Markitan & Stukalina, 2006; Vlasova, Markitan &
79 Golovkova, 2011) studied the removal of histamine, tyramine and tryptamine from water
80 solutions with non-functionalized silica and albumin-modified silica surface, evaluating the
81 effect of the solution pH. However, these authors observed the best results at high pH,
82 different from the typical pH of the wine (around 3.5). One of the most interesting studies,
83 published by Amghouz et al. (2014), is based on the chemical state of amines in wines (as
84 protonated substances), eliminating them through a cation exchange process with solids
85 based on zirconium phosphate. In this case, the authors worked on synthetic wine media and
86 obtained good extraction rates for putrescine, cadaverine and histamine. More recently,

87 Bettini, Santino, Valli and Giancane (2015) proposed the use of iron oxide nanoparticles
88 covered by a silica shell for the BA removal from alcoholic beverages. The results showed
89 good extraction for putrescine and 2-phenylethylamine, but in the case of the last compound
90 after application of several treatments. Moreover, they proposed the removal of the particles
91 from the liquid by using a weak magnetic field due to the paramagnetic character of the
92 particles.

93 The different strategies for minimizing the contents of BA in wines present drawbacks
94 and advantages. The degradation of the BA by using microorganism or the inoculation of
95 selected starters of LAB presents the advantage that they are easy to integrate on the
96 winemaking process without complex operations. However, the main drawbacks are related
97 to the variable effectiveness and the possible generation of undesired compounds and/or
98 organoleptic deviations in the final products. On the other hand, the approaches based on
99 the removal of BA by the adsorption on solid presents the advantage that there is no risk of
100 generating undesired degradation products, however, the collateral removal of other
101 components could affect the characteristics of the final products. Moreover, depending on
102 the way to use the adsorbent (in batch or in packed columns), the process could be carried
103 out and integrate into common winery operations. However, due to the scarce bibliography
104 related the BA removal from finished wines, until now, the organization international of vine
105 and wine (OIV) has not approved any method or technique to this purpose.

106 Focusing on the removal of BA from finished wines, although the studies carried out
107 until now show the great potential of the use of solids (or functionalized solids), however, in
108 general, these works are focused on a single type of adsorbent and/or on minimal
109 modifications of these, so, really no systematic studies have carried out considering
110 structural and chemical aspects of the adsorbents. The main novelty of this study is the
111 approach for a systematic searching the adequate adsorbent for the BA removal considering
112 of two important characteristics of the adsorbents, its structure and the functional groups on
113 the surface. In addition, two methods for the introduction of the functional groups have been
114 considered in order to establish the most adequate synthesis method of the adsorbents.

115 Therefore, the aim this work was to evaluate different hybrid silica structures and
116 cation exchange functional groups for the removal of eight usual BA found in wines.

117

118 **2. Experimental Section**

119 2.1. Reagents

120 The eight BA studied in this work were (the size of the molecule is indicated in
121 brackets and expressed as the longer length (nm) (obtained from <http://molcalc.org/>))
122 (purity>97%): histamine (0.789), putrescine (0.783), cadaverine (0.777), spermidine (0.937),
123 spermine (1.062), 2-phenylethylamine (0.812), tyramine (0.875) and isoamylamine (0.673).
124 BA were obtained from TCI chemicals (Zwijndrecht, Belgium) and Across chemicals (Geel,
125 Belgium). Tetraethyl orthosilicate (TEOS) (98%) from Alfa-Aesar (Kandel, Germany), 3-
126 mercaptopropyltrimethoxysilane (MPTS) (95%), (Diethylphosphatoethyl)triethoxysilane
127 (DPETS) (95%) and 3-cyanopropyltriethoxysilane (CPTS) (95%) from Abcr.de (Karlsruhe,
128 Germany), were used as precursors for the synthesis of functionalized silica. Bis[3-
129 (silsequioxy)propyl] tetrasulfide was kindly donated by Sikemia (Montpellier, France).
130 Triblock copolymer Pluronic P123 (Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-
131 poly(ethylene glycol)) and cetyltrimethyl ammonium bromide (CTAB) (99%) from Aldrich (St.
132 Louis, USA), and polyethylenglycol (PEG) 20.000 from Alfa-Aesar, were used as surfactants
133 for the synthesis of silica by sol-gel route. Finally, hydrochloric acid (37%), ethanol (>99.8%),
134 and nitric acid (65%) and dichloromethane (>99.8%) from VWR (Fontenay sous Bois,
135 France), toluene (>99.7%) and sulfuric acid (98%), Triphenylphosphine (99%), dioxane
136 (99.8%) and meta-chloroperoxybenzoic acid (99%) from Sigma-Aldrich (Steinheim,
137 Germany), and ammonia (30%) from Carlo-Erba (Val de Reuil, France) were obtained.

138

139 2.2. Synthesis of materials

140 A scheme of the synthesis of the cation exchange materials used in this study is
141 presented in **Figure S1** in supplementary information section.

142

143 2.2.1. SBA-15 and mesoporous xerogel materials (direct synthesis sol-gel route)

144 For SBA-15 synthesis, TEOS or the adequate mixture of TEOS and the functionalized
145 precursors (DPETS and/or MPTS or CPTS) were added to a mixture of H₂O, HCl and P123
146 in the following molar ratio 1:140:13.3:0.015. The mixture was heated and stirred at 40 °C for
147 20 h. The aging process was carried out at 60 °C and 110 °C (depending on the type of silica
148 desired) for 24 h. After washing with water, surfactant was removed by soxhlet extraction
149 with ethanol (Margolese, Melero, Christiansen, Chmelka & Stucky, 2000; Mouawia, Mehdi,
150 Reye & Corriu, 2008; Pan et al. 2012).

151 For the synthesis of mesoporous xerogel materials, the ratio of H₂O and HCl was the
152 same than in the case SBA-15 at 60 °C but without surfactant. In addition, 1% of NaF (in
153 weight respect to TEOS) was added in order to accelerate the aging process (Tilgner,
154 Fischer, Bohnen, Rehage & Maier, 1995; Carre, Chuit, Corriu, Fanta, Mehdi & Reye, 1995).

155

156 2.2.2. MCM-41 materials (direct synthesis sol-gel route)

157 TEOS or the adequate mixture of TEOS and the functionalized precursors (DPETS)
158 were added to a mixture of H₂O, NaOH and CTAB in the molar ratio 1:100:0.3:0.12. The
159 mixture was stirred for 24 h at 30 °C and 20 h at 60 °C. After washing with water, ethanol and
160 acetone, the surfactant was removed by soxhlet extraction with acidified ethanol (HCl) (Qian
161 et al. 2012).

162

163 2.2.3. Macroporous xerogel materials (direct synthesis sol-gel route)

164 TEOS or the adequate mixture of TEOS and the functionalized precursors (DPETS
165 and MPTS) were added to a mixture (previously stirred 30 min in an ice bath) of H₂O, HNO₃
166 and PEG in the molar ratio 1:13.4:0.26:0.0013. The mixture was cooled in an ice bath and
167 stirred for 30 min and then was aged for 72 h. at 40 °C. The solid was washed with water and
168 then was treated with ammonium solution 0.1 M for 24 h at 40 °C. Surfactant was removed
169 by soxhlet extraction with ethanol (Galarneau et al. 2016).

170

171 2.2.4. Post-grafting route

172 For the addition of the second functional groups by post-grafting route, the dry
173 materials (functionalized solids obtained by sol-gel route) were treated with the adequate
174 precursor (MPTS or CPTS) in toluene for 24 h at 120 °C (under reflux). The precursor
175 percentage was fixed at 15% (in molar ratio). After reflux, solids were filtered, washed with
176 toluene and dried under vacuum at 80 °C (Chaudhuri, Dash & Sarkar, 2016).

177

178 2.2.5. Lamellar sulfonic acid-functionalized material

179 Bis[3-(silsequioxy)propyl]-tetrasulfide was treated with triphenylphosphine and water
180 (molar ratio 1:6.5:8.1) in dioxane acidized with 10 drops of HCl (37%). The mixture was
181 stirred for 3 h at 40 °C under argon. The product was washed with dioxane and acetone and
182 then was treated with 2 equivalents of meta-Chloroperoxybenzoic acid in dichloromethane
183 for 12 h at room temperature. The lamellar sulfonic acid-functionalized material obtained was
184 washed with dichloromethane and was dried under vacuum (Alauzun, Mehdi, Mouawia,
185 Reye & Corriu, 2008).

186

187 2.2.6. Chemical transformations of functionalized materials

188 For the transformation of the thiol group of MPTS into sulfonic acid, 4.0 g of
189 synthesized solid were treated with 50 mL of H₂O₂ (33%) for 24 h at room temperature. After
190 that, the solid was treated with H₂SO₄ (2M) for 20 min at room temperature and then was
191 washed with water. For the transformation of the diethylphosphonate groups into phosphonic
192 acid, 4.0 g of the synthesized solid were treated with 80 ml of HCl (37%) at 110 °C for 24 h
193 (under reflux). After that, the solid was washed with water. For the transformation of nitrile
194 group of the CPTS into carboxylic acid, 4.0 g of synthesized solid were treated with 50 mL of
195 H₂SO₂ (9M) for 12 h at 130°C (under reflux) and then was washed with water. All products
196 were dried under vacuum at 60 °C.

197

198 2.3. Characterization of materials

199 Surface area and pore size of the materials were measured using the nitrogen
200 adsorption/desorption method on a Micromeritics TriStar instrument (Micromeritics
201 Instrument Co., Norcross, GA) at -196°C (77 K). Before analysis, all samples were
202 outgassed under vacuum at 100°C for 4 h.

203

204 2.4. Removal of BA from hydroalcoholic solutions by adsorption on solids

205 Concentrated individual solutions of each amine (between 1 and 5 g/L) were prepared
206 in HCl (0.1 M). For the experiments evaluating the effectiveness of the removal of BA by the
207 synthesized solids, a hydroalcoholic solution (12% ethanol v/v; 3.5 g/L of tartaric acid;
208 pH=3.5) were spiked with BA at a level of 8 mg/L for each one. Experiments evaluating the
209 BA removal capacity of each synthesized material (at a solid dose of 5 g/L) were carried out
210 in 5 mL vials by adding 4 mL of hydroalcoholic solution and 20 mg of the functionalized solid.
211 Extraction time was initially fixed at 24 h (with continuous stirring) in order to ensure reaching
212 the extraction equilibrium. After extraction time, samples were filtered (0.2 μm). 1 mL of
213 sample and 50 μL of internal standard solution of 160 mg/L (L-2-Aminoadipic acid (TCI
214 chemicals)) were added to a HPLC vial which was stored at 4°C until analysis. All
215 experiments were carried out in duplicate.

216 The study of the effect of the dose of solid was carried in vials of 5 mL with 4 mL of
217 synthetic solution (spiked with BA at a level of 8 mg/L) and increasing amounts of solid (from
218 5 to 12.5 g/L). After the extraction (24 h), the samples were prepared for HPLC analysis.

219 The evaluation of extraction kinetics was carried out with 80 mL of hydroalcoholic
220 solution spiked with 8 mg/L of each amine and a dose of 5g/L of solid (Macroporous xerogel
221 10% phosphonic acid). Samples of 1.5 mL were taken at different times (0, 0.5, 1, 3, 5, 8, 12,
222 24, 48 hours) and were prepared for HPLC analysis as previously described.

223

224 2.5. Biogenic amine Analysis.

225 Samples were analyzed by Liquid chromatography (LC) coupled to a mass
226 spectrometer detector (MS). LC-MS analysis were performed on an Ultimate 3000 UPLC

227 system (Thermo), equipped with a Biphenyl 50x2.1mm, 2.6 μ m column (Phenomenex)
228 Column temperature was 30 °C and 10 μ L of sample were injected. The elution gradient was
229 maintaining 100% of A (Formic acid 0.01%) for 3 minutes, then from 0 to 50% of B
230 (Acetonitrile + formic acid 0.01%) in 2 minutes, then from 50% to 100% of B in 1 minute,
231 100% of B is maintained for 2 minutes before returning to initial conditions. Flow rate was set
232 at 0.5 ml/min. Mass spectrometer coupled with the UPLC system was an AmaZon Speed Ion
233 Trap system (Bruker) with electrospray ionization source operating in SIM or MRM mode.
234 The m/z ions for SIM quantification and the MRM transitions were: histamine (112);
235 putrescine (89); isoamylamine (88); cadaverine (103 \rightarrow 86); spermidine (146 \rightarrow 129); spermine
236 (203 \rightarrow 129); tyramine (138 \rightarrow 121); 2-phenylethylamine (122 \rightarrow 105); L-2-aminoadipic acid
237 (162 \rightarrow 145). In these analytical conditions, acceptable and adequate repeatability and
238 linearity were observed in the concentration range 0 - 10 mg/L. BA contents were expressed
239 as relative peak area and the extracted percentage was calculated with respect to a
240 reference sample for each experiment.

241

242 2.6. Statistics

243 One way-ANOVA and least significant difference (LSD) were used to evaluate the
244 differences in amine removal results. STATISTICA program for Windows version 7.1 was
245 used for data processing (StatSoft, Inc., 2005, www.statsoft.com).

246

247 **3. Results and Discussion**

248 3.1. Structure and functionalization of the silica.

249 The selection of silica as base material was based on the possibility of easily
250 synthesizing different structures (with different functional groups) and on its chemical stability
251 at acid pH. In addition, thanks to the high stability of Si-C bond, the functionalization of the
252 silica was obtained by using organotrialkoxsilane precursors that allow generating very
253 stable immobilization of functional groups on the silica structure (Mehdi, Reye & Corriu,

254 2011; Borges & Volmer, 2015). Considering that BA at the pH of wine (around 3.5) are
255 protonated, the more logical interaction mechanism for its removal from wines would be the
256 cationic exchange. Preliminary experiments with non-functionalized silica or functionalized
257 with groups without cation exchange capacity (diethylphosphatoethyl group) showed a
258 practically null BA removal capacity from hydroalcoholic solutions (data not shown). These
259 results are in accordance with those obtained by Vlasova et al. (2006) that did not observe
260 amine removal capacity from water solutions at acid pH by non-functionalized silica.
261 Therefore, several functional groups (phosphonic, sulfonic and carboxylic acids) with cation
262 exchange capacity were considered in order to functionalize the silica. On the other hand,
263 taking into account the selectivity and effectiveness requirements of the removal process,
264 and to avoid the possible effects on the wine quality (color, aroma, etc.), several types of
265 structures of silica were considered (ordered hexagonal mesoporous silica materials (SBA-
266 15 and MCM-41), mesoporous and macroporous xerogels and lamellar structures).

267 A first set of materials functionalized with a 10% of phosphonic acid was obtained by
268 sol-gel co-condensation route (direct synthesis) and its characteristics are presented in
269 **Table 1**. As can be seen, the porosity ranged from less than 10 nanometers (SBA-15, MCM-
270 41 and mesoporous xerogel structures) to more than 500 nanometers (macroporous xerogel
271 structure). With the phosphonic acid set fixed as a primary functional group, the introduction
272 of other functional groups, such as carboxylic or sulfonic acids, was carried by co-
273 condensation and post-grafting. Taking into account the distortion of the porous structure that
274 the sulfonic acid precursor (hydrophilic character of thiol group that could distort the micelles)
275 can produce during sol-gel synthesis (Margolese et al. 2000), the post-grafting route of this
276 functional group was also considered using 5% phosphonic acid functionalized silica. The
277 reduction of the percentage of co-condensate phosphonic acid to 5% was based on avoiding
278 steric hindrance effects on the introduction of the second functional group by post-grafting.
279 Finally, a lamellar material functionalized with sulfonic acid was also considered. The
280 characteristics of the bi-functional materials synthesized are also presented in **Table 1**. As
281 can be seen, the introduction of a second functional group by co-condensation sol-gel route

282 and the variation of the percentages of the organic functions (for SBA-15 structures)
283 produced variations of the pore size, being more intense in the case of sulfonic acid
284 functionalization.

285

286 3.2. Removal of Biogenic Amines from hydroalcoholic solutions

287 3.2.1. Silica structure effect

288 For the first evaluation of the silica structure effect on BA removal, the 5 types of silica
289 (SBA-15^{60°C}, SBA-15^{110°C}, MCM-41, and macroporous and mesoporous xerogel structures)
290 functionalized with 10% of phosphonic acid were compared for the removal of the 8 BA from
291 a hydroalcoholic solution (with a dose of solid of 5 g/L). **Table 2** shows the removal
292 percentage for each amine. As can be seen, the extraction of spermine and spermidine was
293 close to 100 % for all solids assayed. However, histamine, putrescine and cadaverine
294 presented a clear effect of the silica structure. Thus, the solid with the narrow pores, MCM-
295 41, showed the lowest extractions for these three compounds. The maximum removal
296 percentage for putrescine, cadaverine and histamine ranged from of 85.6 to 96.3%. In the
297 case of monoamines, tyramine, isoamylamine and 2-phenylethyamine, removal was lower
298 than 35% and not showing statistical differences among solids.

299 These results show an effect of the type of amine; in particular, of the number of
300 amino functions in the molecules, polyamines being better retained by the solids than
301 monoamines. These differences between monoamines and polyamines have previously
302 observed by Amghouz et al. (2014) that suggested, in addition to the cationic exchange, the
303 interaction of N with the OH (of the functional group of the solid (zirconium phosphate sodium
304 salt)) that could stabilize the amine retention. Moreover, these authors also suggest the
305 interaction of tyramine is mainly due to hydrogen bonds. Considering our type of solid (silica)
306 and the type of functionalization (phosphonic acid), probably the interaction mechanisms of
307 BA would be similar to described by Amghouz et al. (2014). At the normal pH of wine,
308 between 3 and 4, silanol groups of silica are not dissociated, so an interaction by cation
309 exchange cannot be produced between them and the cationic amines (Vlasova et al. 2006).

310 However, hydrogen bond type interactions would be possible and could contribute to the
311 stabilization of the amine retention.

312 Regarding the differences observed due to the solid structure, taking into account the
313 size of BA molecules (< 1.1 nm of length) (section 2.1) and the pore size of the solids (> 2
314 nm), a steric hindrance effect due to pore size is perhaps not logical, considering the longest
315 molecules (spermine and spermidine) were the best retained by all solids. However, the
316 results suggest that the distance between functional groups and its distribution on the solids
317 and separation of the functional groups in the amine molecules could play an important role
318 in the stabilization of retained compounds (Mouawia et al. 2008; Amghouz et al. 2014).

319

320 3.2.2. Effect of the dose of the solid and extraction kinetics

321 According to the results of **Table 2**, no statistical differences were observed for BA
322 removal with SBA-15 and mesoporous and macroporous xerogels materials. In order to
323 evaluate the solid dose effect and the extraction kinetic, only one of them was chosen, the
324 macroporous xerogel material (10% phosphonic acid).

325 The study of the dose effect on the BA extraction for the range 5.0 to 12.5 g/L of solid
326 (**Figure 1**) showed almost total extraction in the case of spermine and spermidine for the
327 entire dose range evaluated. For the rest of amines, as expected, the increase of the dose of
328 solid produced an increase in the amount retained, but not in a totally proportional relation.
329 Monoamines were not removed from the solutions at percentages higher than 50% with the
330 highest dose (12.5 g/L), corroborating the slight interaction between these amines and the
331 functionalized solids. In the case of putrescine, cadaverine and histamine, the percentage
332 extracted showed a slight increase in relation to the dose added, achieving an increase of
333 the retention lower than 10% when the dose is doubled. Although the doses assayed in this
334 study are quite high, is important take into account that the application to BA removal in real
335 alcoholic beverages, for example wine, must consider the maximum legal limits (or
336 suggested limits) of each country for the amine content of wines. Therefore, depending on
337 the initial value of the beverage, the dose would be adapted and, in most cases, doses lower

338 than 5 g/L would probably be necessary. Considering that the treatment of real alcoholic
339 beverages must avoid affecting its organoleptic characteristics, the minimum dose (5 g/L)
340 was fixed for the following studies.

341 With the same macroporous xerogel silica (10% phosphonic acid) (at a dose of 5 g/L),
342 a study of the adsorption kinetics was carried out in synthetic media from 30 min to 48 hours
343 of extraction time. The behaviors for all studied compounds are presented in **Figure 2**. As
344 expected, spermine and spermidine showed extractions higher than 98% from the first 30
345 min of treatment. For other amines, the extraction equilibrium was reached, in general, after
346 1 or 2 hours of contact with the solid. At a practical level, for the use of the solid in batch
347 applications, the characteristics of the solid should allow a suspension of the solid for
348 sufficient time to permit the equilibrium to be reached.

349

350 3.2.3. Effect of silica functionalization on BA removal

351 **Table 3** shows BA removal percentages for the different bifunctional materials
352 synthesized, based on the structure of SBA-15^{110°C} (phosphonic acid + sulfonic acid or
353 carboxylic acid), the initial SBA-15^{110°C} (10% phosphonic acid) and the lamellar sulfonic
354 material. As can be seen, the effect of the introduction of a second functional group
355 depended on the type of amine and the type of functional group. In general, the introduction
356 of carboxylic acid group showed less extraction of BA than in the case of sulfonic acid group.
357 In the particular case of the lamellar sulfonic material, for 2-phenylethylamine, isoamylamine
358 and tyramine, the removal percentages were much higher than those obtained with the other
359 materials. This fact is probably related to the different structure of this lamellar material in
360 comparison with the others.

361 With regard to the polyamines spermine and spermidine, both of them presented
362 removal percentages close to 100% for all solids, showing no statistical differences between
363 them. Histamine only showed extraction percentages lower than 99% for the initial 10%
364 phosphonic, and putrescine presented the best extractions with all solids that contain sulfonic
365 acid functions. A similar trend to putrescine was observed for cadaverine, although there

366 were no statistical differences. In general, there were no important differences between
367 removal percentages of mixtures of phosphonic/sulfonic acids obtained by co-condensation
368 and post-grafting.

369 Although in some cases, the lamellar sulfonic material showed the best removal
370 capacities, it is important to take into account that this type of material could extract other
371 compounds in the wine and therefore could strongly affect quality. In fact, the use of
372 bentonite (a lamellar clay material) is very common in white winemaking for the removal of
373 proteins in order to avoid turbidity after bottling. In this sense, the negative effect that high
374 bentonite doses produce on wine aroma due to the removal of volatile compounds is well-
375 known (Waters et al. 2005). For this reason, to achieve higher selectivity of BA removal
376 based on the controlled pore structure and pore size, the two structures sulfonic and
377 phosphonic acid mixtures have also been chosen as the most adequate solids.

378 Thus, in addition to these bifunctionalized (phosphonic + sulfonic acids) mesoporous
379 SBA-15^{110°C} materials, the two macroporous xerogel equivalent structures have been
380 synthesized in order to evaluate if the structural differences (for example the distances
381 between active functional groups) affect the effectiveness of BA removal. **Figure 3** shows the
382 BA removal results for the mesoporous (SBA-15^{110°C}) and macroporous xerogel
383 bifunctionalized materials. As can be seen, all monoamines (isoamylamine, 2-
384 phenylethyamine and tyramine) showed no statistical differences between materials,
385 although it is possible to observe a trend indicating better extractions with SBA-15^{110°C}
386 structures than with macroporous xerogels ones. As commented in the previous section, the
387 interaction of these monoamines with the functional groups is not strong enough and this fact
388 could lead to a greater influence of environmental conditions during extraction. By contrast,
389 spermine and spermidine showed extractions higher than 99% for all materials. For
390 histamine, cadaverive and putrescine, on the other hand, statistical differences were
391 observed for BA removal with the different solids. Thus, macroporous xerogel materials
392 synthesized by post-grafting of sulfonic acid showed a lower capacity of extraction than the
393 other three solids. These results suggest, once again, that the distribution of the functional

394 groups on the solids and the distance between them could play an important role in the
395 stabilization of the retained molecules (Mouawia et al. 2008; Amghouz et al. 2014).
396 Moreover, in the post-grafting treatments of the materials, in addition to the possible steric
397 hindrance due to phosphonic groups, the distribution obtained are probably less
398 homogeneous than in the case of the co-condensation sol-gel process (Lim & Stein, 1999),
399 and this also could explain the lower BA removal with the post-grafted materials.

400

401 **Conclusions**

402 The results obtained establish the hybrid silica functionalized with phosphonic and/or sulfonic
403 acids as an interesting option to remove the biogenic amines from hydroalcoholic solutions.
404 In addition, the more open structures such as mesoporous SBA-15, macroporous and
405 mesoporous xerogels, and lamellar materials, showed a better amine removal capacity. On
406 the other hand, the effectiveness of the removal strongly depended on the number of amino
407 functions in the molecule, retention by the solid being more effective in the case of multiple
408 amino functional groups. In the same way, extraction kinetics also depended on the number
409 of amine functions in the biogenic amine molecule, achieving faster equilibrium for the
410 molecules with more than 2 amino functions. With regard to the way to synthesize the
411 bifunctionalized materials (phosphonic and sulfonic acid functions), ordered hexagonal
412 mesoporous (SBA-15) and macroporous xerogel structures obtained by co-condensation
413 achieved greater effectiveness in amine removal than post-grafted structures. Taking into
414 account the selectivity needs to avoid undesired effects in the application in real wines, this
415 study supply valuable information about the characteristics of the hybrid silica structures for
416 its evaluation in real wine samples. In addition, the synthesis of this type of materials is not
417 expensive and, depending on the way to its build, also would allow different approaches for
418 its application, from discontinuous batch application to continuous processes by using
419 packed columns.

420

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425 Authors declare no competing interests.

426

427 **Supplementary Information description**

428 **Figure S1** shows a scheme of the synthesis of the hybrid silica functionalized with cation

429 exchange groups used in this study.

430

431 **References**

- 432 Alauzun, J., Mehdi, A., Mouawia, R., Reye, C., & Corriu, R. J. P. (2008). Synthesis of new
433 lamellar materials by self-assembly and coordination chemistry in the solids. *Journal of*
434 *Sol-Gel Science and Technology*, 46, 383-392. [https://doi.org/10.1007/s10971-008-1710-](https://doi.org/10.1007/s10971-008-1710-7)
435 7
- 436 Amghouz, Z., Ancin-Azpilicueta, C., Burusco, K. K., García, J. R., Khainakov, S. A., Luquin,
437 A., Nieto, R., & Garrido, J. J. (2014). Biogenic amines in wine: Individual and competitive
438 adsorption on a modified zirconium phosphate. *Microporous and Mesoporous Materials*,
439 197, 1387-1811. <https://doi.org/10.1016/j.micromeso.2014.06.006>
- 440 Ancin-Azpilicueta, C., Gonzalez-Marco, A., & Jimenez-Moreno, N. (2010). Comparative study
441 of the amine concentration in wines obtained from the traditional fermentation and from a
442 more anaerobic fermentation method. *LWT- Food Science and Technology*, 43, 771-776.
443 <https://doi.org/10.1016/j.lwt.2009.12.013>
- 444 Beneduce, L., Romano, A., Capozzi, V., Lucas, P., Barnavon, L., Bach, B., Vuchot, P.,
445 Grieco, F., & Spano, G. (2010). Biogenic amine in wines. *Annals of Microbiology*, 60, 573-
446 578. <https://doi.org/10.1007/s13213-010-0094-4>
- 447 Berbegal, C., Benavent-Gil, Y., Navascues, E., Calvo, A., Albors, C., Pardo, I., & Ferrer, S.
448 (2017). Lowering histamine formation in a red Ribera del Duero wine (Spain) by using an
449 indigenous *O. oeni* strain as a malolactic starter. *International Journal of Food*
450 *Microbiology*, 244, 11-18. <https://doi.org/10.1016/j.ijfoodmicro.2016.12.013>
- 451 Bettini, S., Santino, A., Valli, L., & Giancane, G. (2015). A smart method for the fast and low-
452 cost removal of biogenic amines from beverages by means of iron oxide nanoparticles.
453 *RSC Advances*, 5, 18167-18171. DOI: 10.1039/C5RA01699A
- 454 Borges, E. M., & Volmer, D. A. (2015). Silica, hybrid silica, hydride silica and non-silica
455 stationary phases for liquid chromatography. part II: chemical and thermal stability.
456 *Journal of Chromatographic Science*, 53, 1107–1122. DOI:10.1093/chromsci/bmu173

457 Callejon, S., Sendra, R., Ferrer, S., & Pardo, I. (2014). Identification of a novel enzymatic
458 activity from lactic acid bacteria able to degrade biogenic amines in wine. *Applied*
459 *Microbiology and Biotechnology*, 98, 185-198. <https://doi.org/10.1007/s00253-013-4829-6>

460 Carre, F. Chuit, C., Corriu, R. J. P., Fanta, A., Mehdi, A., & Reye, C. (1995). Use of the 2,6-
461 bis[(dimethylamino)methyl]phenyl ligand for the study of nucleophilic substitution at
462 hexacoordinate silicon centers. Evidence suggestive of a heptacoordinate silicon
463 transition state. *Organometallics*, 14, 194-198. DOI: 10.1021/om00001a030

464 Chaudhuri, H., Dash, S., & Sarkar, A. (2016). SBA-15 functionalised with high loading of
465 amino or carboxylate groups as selective adsorbent for enhanced removal of toxic dyes
466 from aqueous solution. *New Journal of Chemistry*, 40, 3622-3634. DOI:
467 10.1039/C5NJ02816G

468 Cueva, C., Garcia-Ruiz, A., Gonzalez-Rompinelli, E. M., Bartolome, B., Martin-Alvarez, P. J.,
469 Salazar, O., Vicente, M. F., Bills, G. F., & Moreno-Arribas, M. V. (2012). Degradation of
470 biogenic amines by vineyard ecosystem fungi. Potential use in winemaking. *Journal of*
471 *Applied Microbiology*, 112, 672-682. <https://doi.org/10.1111/j.1365-2672.2012.05243.x>

472 Galarneau, A., Sachse, A., Said, B., Pelisson, C. H., Boscaro, P., Brun, N., Courtheoux, L.,
473 Olivi-Tran, N., Coasne, B., & Fajula, F. (2016). Hierarchical porous silica monoliths, a
474 novel class of microreactors for process intensification in catalysis and adsorption.
475 *Comptes Rendus Chimie*, 19, 231-247. <https://doi.org/10.1016/j.crci.2015.05.017>

476 Garcia-Ruiz, A., Gonzalez-Rompinelli, E. M., Bartolome, B. & Moreno-Arribas, M. V. (2011).
477 Potential of wine-associated lactic acid bacteria to degrade biogenic amines. *International*
478 *Journal of Food Microbiology*, 148, 115-120.
479 <https://doi.org/10.1016/j.ijfoodmicro.2011.05.009>

480 Guo, Y. Y., Yang, Y. P., Peng, Q., & Han, Y. (2015). Biogenic amines in wine: a review.
481 *International Journal of Food Science & Technology*, 50, 1523-1532.
482 <https://doi.org/10.1111/ijfs.12833>

483 Kammerer, J., Carle, R., & Kammerer, D.R. (2011). Adsorption and ion exchange: basic
484 principles and their application in food processing. *Journal of Agricultural and Food*
485 *Chemistry*, 59, 22-42. <https://pubs.acs.org/doi/abs/10.1021/jf1032203>

486 Kiss, J., Korbasz, M., & Sass-Kiss, A. (2006). Study of amine composition of Botrytized
487 grape berries. *Journal of Agricultural and Food Chemistry*, 54, 8909-8918.
488 <https://pubs.acs.org/doi/abs/10.1021/jf061578g>

489 Ladero, V. C. E., Fernández, M., & Álvarez, M. A. (2010). Toxicological effects of dietary
490 biogenic amines. *Current Nutrition & Food Science*, 6, 145-156.
491 <https://doi.org/10.2174/157340110791233256>

492 Lim, M. H., & Stein, A. (1999). Comparative studies of grafting and direct syntheses of
493 inorganic–organic hybrid mesoporous materials. *Chemistry of Materials*, 11, 3285-3295.
494 <https://pubs.acs.org/doi/10.1021/cm990369r>

495 Margolese, D., Melero, J. A., Christiansen, S. C., Chmelka, B. F., & Stucky, G. D. (2000).
496 Direct syntheses of ordered SBA-15 mesoporous silica containing sulfonic acid groups.
497 *Chemistry of Materials*, 12, 2448-2459. <https://pubs.acs.org/doi/abs/10.1021/cm0010304>

498 Maynard, L. S., & Schenker, V. J. (1962). Monoamine oxidase inhibition by ethanol in vitro.
499 *Nature*, 196, 575-576. <https://doi.org/10.1038/196575a0>

500 Mehdi, A., Reye, C., & Corriu, R. (2011). From molecular chemistry to hybrid nanomaterials.
501 Design and functionalization. *Chemical Society Reviews*, 40, 563–574. DOI:
502 10.1039/B920516K

503 Moreno-Arribas, M. V., & Polo, M.C. (2009). Amino acids and biogenic amines, In Moreno-
504 Arribas, M.V., & Polo, M.C. (Eds), *Wine chemistry and biochemistry* (pp 163-189). New
505 York: Springer. DOI: 10.1007/978-0-387-74118-5

506 Mouawia, R., Mehdi, A., Reye, C., & Corriu, R. J. P. (2008). Bifunctional ordered
507 mesoporous materials: direct synthesis and study of the distribution of two distinct
508 functional groups in the pore channels. *Journal of Materials Chemistry*, 18, 4193–4203.
509 DOI: 10.1039/B807793B

510 Nageeb Rashed, M. (2013) Adsorption technique for the removal of organic pollutants from
511 water and wastewater. In Nageeb Rashed, M. (Ed.), *Organic Pollutants: Monitoring, Risk*
512 *and Treatment* (pp 167-194). London: IntechOpen. DOI: <http://dx.doi.org/10.5772/54048>

513 Naila, A., Flint, S., Fletcher, G., Bremer, P., & Meerdink, G. (2010). Control of biogenic
514 amines in food--existing and emerging approaches. *Journal of Food Science*, 75, 139-
515 150. <https://doi.org/10.1111/j.1750-3841.2010.01774.x>

516 Pan, Y. C., Tsai, H. H. G., Jiang, J. C., Kao, C. C., Sung, T. L., Chiu, P. J., Saikia, D., Chang,
517 & Kao, H. M. (2012). Probing the nature and local structure of phosphonic acid groups
518 functionalized in mesoporous silica SBA-15. *The Journal of Physical Chemistry C*, 116,
519 1658-1669. <https://pubs.acs.org/doi/10.1021/jp206017j>

520 Qian, X. F., Li, B., Hu, Y. Y., Niu, G. X., Zhang, D. Y. H., Che, R. C., Tang, Y., Su, D. S.,
521 Asiri, A.M., & Zhao, D. Y. (2012). Exploring meso-/microporous composite molecular
522 sieves with core-shell structures. *Chemistry – A European Journal*, 18, 931-939.
523 <https://doi.org/10.1002/chem.201102505>

524 Smit, A. Y., du Toit, W. J., & du Toit, M. S. (2008). Biogenic amines in wine: understanding
525 the headache. *South African Journal for Enology and Viticulture*, 29, 109-127.
526 <http://dx.doi.org/10.21548/29-2-1444>

527 Smit, I., Pfliehringer, M., Binner, A., Grossmann, M., Horst, W. J., & Lohnertz, O. (2014).
528 Nitrogen fertilisation increases biogenic amines and amino acid concentrations in *Vitis*
529 *vinifera* var. Riesling musts and wines. *Journal of the Science of Food and Agriculture*, 94,
530 2064-2072. <https://doi.org/10.1002/jsfa.6525>

531 Tilgner, I. C., Fischer, P., Bohnen, F. M., Rehage, H., & Maier, W. F. (1995). Effect of acidic,
532 basic and fluoride-catalyzed sol-gel transitions on the preparation of sub-nanostructured
533 silica. *Microporous Materials*, 5, 77-90. [https://doi.org/10.1016/0927-6513\(95\)00045-B](https://doi.org/10.1016/0927-6513(95)00045-B)

534 Vlasova, N. N., Markitan, O. V., & Golovkova, L. P. (2011). Adsorption of biogenic amines on
535 albumin-modified silica surface. *Colloid Journal*, 73, 24-27.
536 <https://doi.org/10.1134/S1061933X1006102X>

537 Vlasova, N. N., Markitan, O. V., & Stukalina, N. G. (2006). The adsorption of biogenic amines
538 on the surface of highly dispersed silica from aqueous solutions. *Colloid Journal*, 68, 384-
539 386. <https://doi.org/10.1134/S1061933X06030185>

540 Waters, E. J., Alexander, G., Muhlack, R., Pocock, K. F., Colby, C., O'Neill, B. K., Hoj, P. B.,
541 & Jones, P. (2005). Preventing protein haze in bottled white wine. *Australian Journal of*
542 *Grape and Wine Research*, 11, 215-225. [https://doi.org/10.1111/j.1755-](https://doi.org/10.1111/j.1755-0238.2005.tb00289.x)
543 [0238.2005.tb00289.x](https://doi.org/10.1111/j.1755-0238.2005.tb00289.x)

544

545 **Figure captions**

546 **Figure 1.** Effect of the dose of the solid (functionalized silica) on the biogenic amine removal
547 from hydro-alcoholic solutions. Solid type: Macroporous xerogel (10% phosphonic acid).
548 Different letters indicate statistics differences in ANOVA ($p < 0.05$) and the LSD test. Removal
549 values of 100 ± 0 indicate that the amine was not detected in the treated sample.

550 **Figure 2.** Adsorption kinetic of each biogenic amine on the functionalized silica material from
551 hydro-alcoholic solutions. Solid type: Macroporous xerogel (10% phosphonic acid). Solid
552 dose: 5 g/L.

553 **Figure 3.** Biogenic amine removal (%) from hydro-alcoholic solutions with SBA 15^{110°C} and
554 Macroporous xerogel silica materials functionalized with sulfonic (sulf) and phosphonic (pho)
555 acids. (1) Co-condensation sol-gel route. (2) Post-grafting route. Different letters indicate
556 statistics differences in ANOVA ($p < 0.05$) and the LSD test. Removal values of 100 ± 0
557 indicate that the amine was not detected in the treated sample.

558

Table 1. Characteristics of the synthesized functionalized silica materials.

Materials ^a	Synthesis method and precursors ^b	Surface Area (m ² /g)	Pore diameter (nm)	Pore Volume (cm ³ /g)
10% phosphonic acid functionalized materials				
<i>SBA 15</i> ^{60°C} _{10% Pho (1)}	DS: TEOS (90%), DPETS (10%)	560.3	≈ 6.2	0.662
<i>SBA 15</i> ^{110°C} _{10% Pho (1)}	DS: TEOS (90%), DPETS (10%)	557.5	≈ 7.5	0.922
<i>MCM 41</i> _{10% Pho (1)}	DS: TEOS (90%), DPETS (10%)	840.4	≈ 2.5	0.877
<i>Macroporous X</i> _{10% Pho (1)}	DS: TEOS (90%), DPETS (10%)	681.7	>500	1.179
<i>Mesoporous X</i> _{10% Pho (1)}	DS: TEOS (90%), DPETS (10%)	603.6	≈ 7	0.942
Bi-functionalized materials				
<i>SBA 15</i> ^{110°C} _{10% Pho (1) 10% Sulf (1)}	DS: TEOS (80%), DPETS (10%) MPTS (10%)	587.4	≈ 4.0	0.549
<i>SBA 15</i> ^{110°C} _{5% Pho (1) Sulf (2)}	DS: TEOS (95%), DPETS (5%). P: MPTS.	526.7	≈ 8.5	0.867
<i>SBA 15</i> ^{110°C} _{10% Pho (1) 10% Carbox (1)}	DS: TEOS (80%), DPETS (10%), CPTS (10%)	569.3	≈ 5.0	0.512
<i>Macroporous X</i> _{10% Pho (1) Sulf (1)}	DS: TEOS (80%), DPETS (10%) MPTS (10%)	601.2	> 500	0.788
<i>Macroporous X</i> _{5% Pho (1) Sulf (2)}	DS: TEOS (95%), DPETS (5%). P: MPTS.	506.1	> 500	1.299

^a Pho: Phosphonic acid. Sulf: Sulfonic acid. Carbox: Carboxylic acid. X: xerogel. (1) indicate functional group introduced by direct synthesis (2) indicate functional group introduced by post grafting.

^b Precursors: Tetraethyl orthosilicate (TEOS), 3-mercaptopropyltrimethoxysilane (MPTS), (Diethylphosphatoethyl)triethoxysilane (DPETS) and 3-cyanopropyltriethoxysilane (CPTS). DS: indicate direct synthesis sol-gel route. Percentage in brackets indicate the molar ratio in direct synthesis. P: indicate post-grafting route (15% molar ratio for the MPTS precursor).

Table 2. Removal of BA by the 10% phosphonic acid functionalized silica materials^a (expressed as removed %)^b.

Biogenic Amine	<i>SBA 15</i> _{10% Pho.} ^{60°C}	<i>SBA 15</i> _{10% Pho.} ^{110°C}	<i>MCM 41</i> _{10% Pho.}	<i>Macro. X.</i> _{10% Pho.}	<i>Meso. X.</i> _{10% Pho.}
Histamine	96.3 ± 0.8 c	95.0 ± 0.4 bc	70.6 ± 2.8 a	92.4 ± 0.5 b	95.5 ± 0.2 bc
Putrescine	77.3 ± 0.6 b	82.0 ± 3.9 b	64.2 ± 2.3 a	77.0 ± 2.4 b	85.6 ± 9.0 b
Cadaverine	88.8 ± 3.1 b	88.7 ± 3.9 b	68.8 ± 9.6 a	88.0 ± 5.3 b	90.5 ± 2.2 b
Spermidine	100 ± 0	100 ± 0	98.2 ± 1.0	99.3 ± 0.5	99.7 ± 0.3
Spermine	100 ± 0	100 ± 0	100 ± 0	100 ± 0	99.9 ± 0.1
2-Phenylethylamine	32.3 ± 3.1	22.1 ± 8.1	25.7 ± 2.5	27.1 ± 1.9	33.1 ± 0.6
Tyramine	20.0 ± 1.3	13.3 ± 8.8	13.2 ± 3.9	10.9 ± 8.5	21.0 ± 2.0
Isoamylamine	33.5 ± 4.7	23.8 ± 9.5	21.9 ± 3.0	24.4 ± 3.0	31.5 ± 0.5

^a Obtained by direct synthesis (co-condensation) sol-gel route. Pho: phosphonic acid. Macro. X: Macroporous Xerogel.

Meso: X.: Mesoporous Xerogel. Removal values of 100 ± 0 indicate that the amine was not detected in the treated sample.

^b Different letters indicate statistics differences in ANOVA (p < 0.05) and the LSD test.

Table 3. Removal of BA from hydro-alcoholic solutions by silica material functionalized with different types of functional groups (expressed as removed %)^a

Solid Type Functionalization and route of synthesis ^b	Mesoporous materials based on SBA15 ^{110°C}				Lamellar
	<i>SBA 15</i> ^{110°C} 10% <i>Pho</i> (1)	<i>SBA 15</i> ^{110°C} 10% <i>Pho</i> (1) 10% <i>Sulf</i> (1)	<i>SBA 15</i> ^{110°C} 5% <i>Pho</i> (1) <i>Sulf</i> (2)	<i>SBA 15</i> ^{110°C} 10% <i>Pho</i> (1) 10% <i>Carbox</i> (1)	<i>Lamellar</i> _{<i>Sulf</i>}
Histamine	95.0 ± 0.4 a	99.9 ± 0.1 c	99 ± 0.1 b	99.2 ± 0.0 bc	99.6 ± 0.5 bc
Putrescine	82.0 ± 3.9 a	97.6 ± 1.6 b	94.9 ± 0.1 b	86.6 ± 3.0 a	98.0 ± 0.3 b
Cadaverine	88.7 ± 3.9	97.7 ± 2.0	91.0 ± 0.9	81.4 ± 8.0	96.5 ± 5.0
Spermidine	100 ± 0	100 ± 0	99.7 ± 0.3	99.7 ± 0.2	99.9 ± 0.2
Spermine	100 ± 0	100 ± 0	100 ± 0	100 ± 0	99.9 ± 0.1
2-Phenylethylamine	22.1 ± 8.1 a	46.5 ± 3.0 a	37.9 ± 0.2 a	33 ± 2.2 a	78.9 ± 1.1 b
Tyramine	13.3 ± 8.8 a	23.6 ± 6.5 c	22.3 ± 5.4 bc	10.0 ± 0.4 b	58.3 ± 2.7 d
Isoamylamine	23.8 ± 9.5 a	37.9 ± 6.0 b	34.3 ± 1.2 ab	21.5 ± 1.3 a	66.5 ± 4.5 c

^a Removal values of 100 ± 0 indicate that the amine was not detected in the treated sample. Different letters indicate statistics differences in ANOVA (p < 0.05) and the LSD test. ^b Pho: Phosphonic acid. Sulf: Sulfonic acid. Carbox: Carboxylic acid. (1) Direct synthesis (co-condensation) sol-gel route. (2) Post-grafting route (15% molar ratio for the post-grating process).





