1    **Synthetic zeolite materials from recycled glass and aluminium food packaging as potential oenological**

2                                                              **adjuvant**

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28    **Abstract**

29    Glass and aluminium packaging materials were recycled, in the perspective of circular economy, to synthetize

30    potassium and sodium zeolitic materials (Zeo-K and Zeo-Na) through an alkaline hydrothermal treatment.

31    Both materials were then tested as oenological adjuvants for the removal of riboflavin (300 µg L$^{-1}$) from a

32    model wine solution, to prevent the light-struck taste defect that can be caused in white and rosé wines by light

33    exposure during storage or consumption. Suspension tests revealed that Zeo-Na at 1 g L$^{-1}$ removed 15%

34    riboflavin in 16 h, similarly to what removed by a commercial bentonite at the same concentration. To reduce

35    the riboflavin concentration below the risk threshold, 50 g L$^{-1}$ Zeo-Na were required. Effectiveness of Zeo-K

36    was slightly lower compared to Zeo-Na, possibly due to the lower crystallinity, cation exchange capacity and

37    porosity of this zeolitic material. A higher removal efficiency and time saving were obtained by filtration using

38    columns packed with Zeo-Na. Weak bonding and physical entrapment are suggested as potential mechanisms

39    for riboflavin sorption by zeolites.

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41    Keywords: *white wine; riboflavin; light-struck taste; zeolite; circular-economy; packaging materials*

## 1. Introduction

Circular economy is based on the material cycling and 'waste-as-resource concept', where unwanted outputs of an industrial process or end-of-life products are used as raw materials in another industrial process or are recycled (Murray, Skene, & Haynes, 2017), thus reducing waste to a minimum (Stahel, 2016). Differently, in linear economy value chains are based on extracting resources, using them to make products, and then discarding products at their end-of-life (Stewart, Niero, Murdock, & Olsen, 2018).

Food packaging materials (FPMs) usually become end-of-life waste within a year (or much less), and the largest part of them is potentially available for recycling after use (Haas, Krausmann, Wiedenhofer, & Heinz, 2015). Nowadays, FPMs are causing rising concern for the environment due to their high production volume, short usage time, and problems related to waste management (Geueke, Groh, & Muncke, 2018).

Among FPMs, aluminium is widely used for the production of beverage cans (representing 90 % of beverage cans world-wide) and other types of food packaging (e.g., foils, trays, tubes, beverage cartons, and coffee capsules) (Geueke et al., 2018). Glass has also been used as food contact material for thousands of years in form of bottles or jars, and composes 0.6 % of municipal solid waste, while metal cans account for the 5.8 % (Consonni & Viganò, 2008). Aluminium and glass recovered from food packaging can be reused several times, as well as transformed into higher added-value products. For instance, glass can be recycled to produce concrete, mortar, glass wool, foamed glass, filtration media and many other goods (Ayadi, Stiti, Boumchedda, Rennai, & Lerari, 2011; Dyer, 2014; Ibrahim & Meawad, 2018). Among the numerous applications, Terzano, D'Alessandro, Spagnuolo, Romagnoli, and Medici (2015) developed a simple and cheap procedure to transform aluminium and glass FPMs into zeolites, through an alkaline hydrothermal treatment.

Zeolites are aluminosilicate minerals with a tectosilicate structure, characterized by a complex system of internal cavities (< 2nm) and channels, and by a high negative surface charge (Colella & Mumpton, 2000). Due to their microporous structure, high specific surface area and high cation exchange capacity, zeolites interact with cations and molecules through exchanging and sorption mechanisms. Zeolites are classified as 'non-toxic' by the International Agency for Research on Cancer (IARC,1997) and 'safe for human consumption' by the Food and Drug Administration (FDA, 2020). The Codex Alimentarius Commission listed zeolites among the substances approved for the organic food production and plant protection (Codex Alimentarius Commission, 2007). Natural zeolites have been extensively employed in many fields, such as in

70     agriculture for soil amendment and pesticide control (Cairo et al., 2017; Jakkula & Wani, 2018; Ming & Allen,

71     2001), in the agri-food for odor control and packaging (Adelodun et al., 2017; Alp-Erbay, Figueroa-Lopez,

72     Lagaron, Çağlak, & Torres-Giner, 2019; Boschetto, Lerin, Cansian, Pergher, & Di Luccio, 2012; Dogan,

73     Koral, & Inan, 2009; Lee, Lee, Jones, Sharek, & Pascall, 2011; Youssef, El-Naggar, Fouda, & Youssef, 2019),

74     as well as for soil and water remediation (Boros-Lajszner, Wyszkowska, & Kucharski, 2018; Reeve &

75     Fallowfield, 2018; Shi, Shao, Li, Shao, & Du, 2009), and mycotoxin control (Eroglu, Emekci, & Athanassiou,

76     2017; Tomašević-Čanović, Daković, Rottinghaus, Matijašević, & Duričić, 2003). Other industrial applications

77     of zeolites include catalysis in the petroleum industry, gas separations, domestic water treatment and nuclear

78     waste processing (Eroglu et al., 2017).

79     Some researchers proposed natural zeolites as oenological adjuvants, for protein and tartaric stability

80     (Mercurio et al., 2010; Mierczynska-Vasilev, Wahono, Smith, Bindon, & Vasilev, 2019), phenolic off-odor

81     removal (Lisanti, Gambuti, Genovese, Piombino, & Moio, 2017), and volatile acidity abatement (Ciambelli &

82     Di Matteo, 1998). Recently, zeolite has been also tested for the prevention of light-struck taste in white wines,

83     which is recognisable as a distinctive and unpleasant sulphide-like aroma resembling onion and cooked

84     cabbage (Fracassetti et al., 2017). This defect, also known as sunlight flavour, is due to the volatile sulphur

85     compounds formed by the riboflavin-mediated photodegradation of methionine (Fracassetti, Limbo,

86     Pellegrino, & Tirelli, 2019; Grant-Preece, Barril, Schmidtke, Scollary, & Clark, 2017), and is caused by

87     exposure to light during wine storage, particularly on the shelves, as well as during wine consumption

88     (Arapitsas et al., 2020). Use of zeolite or other adsorbing materials able to reduce the riboflavin concentration

89     below 80–100 $\mu g\ L^{-1}$ may lower the risk of light-struck developing in wine (Fracassetti et al., 2017; Mattivi,

90     Monetti, Vrhovšek, Tonon, & Andrés-Lacueva, 2000). Although zeolites are not still included among the

91     adjuvants permitted by the Organisation Internationale de la Vigne et du Vin, they have been considered as a

92     possible replacement of bentonite for white wine stabilisation (Mercurio et al., 2010). In fact, use of bentonite

93     in oenological treatments may have some disadvantages (Mierczynska-Vasilev et al., 2019), such as the

94     removal of some flavour and aroma compounds in wine (Høj et al., 2000; Lubbers, Leger, Charpentier, &

95     Feuillat, 1993; Ribéreau-Gayon, Glories, Maujean, & Dubourdieu, 2006) or high disposal costs (Høj et al.,

96     2000; Tattersall et al., 2001). Conversely, current data show that the concentrations of the most representative

97     phenolic compounds do not change after the zeolite treatments, so that the quality traits related to these

98  compounds are not significantly modified (Cuenat & Wyss, 2005; Mierczynska-Vasilev et al., 2019).

99  However, the effect of zeolites on wine aroma compounds has never been evaluated.

100 Besides natural zeolites, also synthetic zeolites can be used for several agricultural and environmental

101 applications (Terzano, Spagnuolo, Medici, Tateo, & Ruggiero, 2005). A number of synthesis processes have

102 been developed in the last decades, in order to produce zeolites with specific and useful chemical and structural

103 properties (Querol et al., 2002; Zaarour, Dong, Naydenova, Retoux, & Mintova, 2014). Synthetic zeolites can

104 be easily produced also from different aluminium- and silicon-containing waste materials (e.g. coal and

105 biomass fly ashes, aluminium saline slags, alum sludge, crushed stone powder, porcelain waste, and many

106 other materials), thus reducing their production costs and making them competitive with natural zeolites

107 (Collins, Rozhkovskaya, Outram, & Millar, 2020; Yoldi, Fuentes-Ordoñez, Korili, & Gil, 2019). However, for

108 agri-food applications, "clean" starting materials must be used, not containing potentially toxic substances,

109 such as heavy metals or harmful organic compounds. In this sense, recycled aluminium and glass FPMs may

110 be ideal raw materials since they have been specifically produced to be used in contact with food and

111 beverages, without any risk for human health. In addition, natural zeolites are limited and non-renewable

112 resources and, therefore, environmental-friendly alternatives must be sought. Nevertheless, only few studies

113 have focused on the application of synthetic zeolites in the agri-food sector (Mercurio et al., 2010; Tzia &

114 Zorpas, 2012).

115 Within this context, this research aimed at testing two synthetic zeolite materials (a sodium zeolite, Zeo-Na,

116 and a potassium zeolite, Zeo-K), obtained by a simple and cheap alkaline hydrothermal treatment of glass and

117 aluminium recovered from drink and food packaging, as oenological adjuvants. In particular, the ability of

118 these materials to remove the photosensitizer riboflavin from a model wine system was assayed and compared

119 with the behaviour of bentonite, a natural mineral largely used for the wine treatment.

120

121 **2. Materials and methods**

122 *2.1. Zeolite synthesis from beverage and food packaging*

123 *2.1.1.  Glass and aluminium*

124 Glass and aluminium were obtained from the separate collection of municipal solid waste. Aluminium derived

125 from cans of commercial soft drinks, and glass from colourless transparent bottles and food jars. According to

126  their composition (data not shown), glass can be classified as "common glass" while aluminium as Al-Mn

127  alloy (3004, International Alloy Designation System), being mainly composed of Al (97 %) and Mn (1.4 %).

128  Aluminium cans were cut into pieces of approximately 1 cm$^2$ with a scissor. Glass bottles and jars were

129  preliminary crushed into large pieces, then milled using a Pulverisette 1 (Fritsch, Germany) jaw crasher, and

130  finally passed through a 2 mm-sieve.

131  *2.1.2.  Zeolite synthesis*

132  Sodium (Zeo-Na) and potassium (Zeo-K) zeolites were obtained following the procedure developed by

133  Terzano et al. (2015), with slight modifications in order to produce a larger amount of zeolitic material. In

134  particular, 43.75 g of aluminium pieces were placed in a 10 L high-density polyethylene (HDPE) container

135  along with 7 L of a hyper-alkaline solution. The latter consisted of a 2.5M NaOH (pellets, ACS reagent grade,

136  Carlo Erba, Italy) solution for Zeo-Na, or a 5M KOH (pellets, ACS reagent grade, Carlo Erba, Italy) solution

137  for Zeo-K. After 2 h, the initial effervescence stopped and the vessel was closed and kept at room temperature

138  for 24 h. The aluminium solution was then filtered under vacuum with Whatman® 1 filter paper, in order to

139  remove the fragments of external coating remaining suspended in the solution. Then, 700 g of glass (Ø<2mm)

140  were added to the solution and the mixture was stirred for 2 h with an orbital shaker. The vessel was finally

141  placed in an oven at 60 °C (for Zeo-Na) or 90 °C (for Zeo-K) for 7 days, stirring it every day for 5 min with

142  an orbital shaker.

143  At the end of the incubation time, both Zeo-Na and Zeo-K samples were cooled to room temperature, and then

144  centrifuged at 5500 rpm for 15 min. Supernatant was discarded, whereas the pellet (containing the zeolitic

145  material) was washed three times with deionized water, using a pellet/water ratio of 1:5 (v/v) for each washing

146  step. Finally, the solid fraction was dried at 105 °C for 24 h and sieved at 500 µm to remove the residual coarse

147  glass fragments, which were reused in new synthesis processes.

148  All experiments were carried out using deionized water (Milli-Q system®, Merck Millipore, Germany).

149  *2.1.3.  Material characterization*

150  The mineralogical characterization of the zeolite materials produced was performed by X-ray powder

151  diffraction (XRPD), using a MiniFlex II X-ray diffractometer (Rigaku Corporation, Tokyo, Japan). The

152  instrument was equipped with a Cu-Kα X-ray source (30 kV, 15 mA, 450 W). An aliquot of both zeolitic

153  samples was finely pulverized using an agate mortar and pestle. A preliminary qualitative analysis was carried

154  out operating in the range 3-70° 2θ with a scan speed of 2° min$^{-1}$. In addition, for the semi-quantitative analysis,

155  each sample was added with 20 % (w/w) corundum (MicropolishTM II, 1 μm, Buehler, USA), used as internal

156  standard, and acquisitions were performed in the range 3-120° 2θ, using a step width of 0.02° and a counting

157  time of 3 s per step. Data elaboration was performed according to Gualtieri (2000), combining the Rietveld

158  and reference intensity ratio (RIR) methods. Diffraction data were refined using GSAS software and EXPGUI

159  as graphical user interface (Toby, 2001).

160  *2.2. Removal of riboflavin*

161  *2.2.1.  Model solution preparation*

162  The ability of the two zeolitic materials in reducing the concentration of riboflavin was assessed in a model

163  wine solution prepared with 5 g L$^{-1}$ tartaric acid (ACS reagent grade, Merck Millipore, Germany), 12 % ethanol

164  (v/v) (Carlo Erba, Italy), and corrected for pH at 3.2 with NaOH (Fracassetti et al., 2017). Riboflavin (≥ 98 %,

165  Supelco, Italy) was added at the concentration of 300 µg L$^{-1}$ considering that the riboflavin concentration in

166  European wines is around 100 µg L$^{-1}$, on average, but values exceeding 200 µg L$^{-1}$ may be also found

167  (Fracassetti et al., 2017; Mattivi et al., 2000). Riboflavin was preliminary dissolved in H$_2$O at a concentration

168  of 30 mg L$^{-1}$, then an aliquot of this solution was added to the model solution to obtain a final riboflavin

169  concentration of 300 µg L$^{-1}$.

170  *2.2.2.  Removal of riboflavin by suspended zeolite materials*

171  An amount of 0.01 g of Zeo-Na or Zeo-K and 10 mL of the riboflavin-enriched wine model solution were

172  added to a 15 mL glass tube in order to have a zeolite concentration of 1 g L$^{-1}$ (Zeo-Na1, Zeo-K1). For

173  comparison, two commercial bentonites used for oenological applications (natural sodium bentonite Clarbent,

174  ENOLIFE s.r.l., Italy – Bent1; purified active bentonite Gelbentonite, Dal Cin Gildo spa, Italy – Bent2) were

175  also tested. Bentonites were preliminarily suspended in water at the concentration of 50 g L$^{-1}$ and stirred for

176  24 h, then an aliquot of this suspension was added to each sample to reach a final bentonite concentration of 1

177  g L$^{-1}$. Amounts of bentonites higher than 1 g L$^{-1}$ could result detrimental for wine sensory properties

178  (Fracassetti et al., 2017). A control without either zeolites or bentonites was also run. All the samples were

179  manually shaken and then stirred in the dark for 16 h at 25 °C, on a rotary shaker.

180  The effect of zeolite amount and contact time was also evaluated. For this purpose, each zeolite was added to

181  the riboflavin-enriched solution at the concentrations of 10 g L$^{-1}$ (Zeo-Na10, Zeo-K10), 25 g L$^{-1}$ (Zeo-Na25,

182    Zeo-K25) and 50 g L$^{-1}$ (Zeo-Na50, Zeo-K50). Controls without zeolites were also run, and all the samples

183    were stirred in the dark for 16 h at 25 °C, on a rotary shaker. Different contact times were also tested suspending

184    10 g L$^{-1}$ zeolites (Zeo-Na10, Zeo-K10) for 2, 4 and 16 h in the dark at 25 °C, on a rotary shaker. For each

185    treatment, a control without zeolites was also performed.

186    All the treatments were replicated three times.

187    *2.2.3.    Removal of riboflavin by filtration*

188    Zeolite materials were also tested as a filtration medium. For this aim, filtration columns were prepared using

189    5 ml plastic syringes and zeolite materials as a stationary phase. Initially, a polypropylene frit (commonly used

190    for SPE column) was inserted into the syringe. Then, 1 g of Zeo-Na or 1 g of Zeo-K, finely ground into an

191    agate mortar, was added into the syringe. Finally, another frit was inserted. As an alternative, two layers of

192    glass wool (50 mg for the base layer and 25 mg for the top layer) were used to replace frits. A light pressure

193    was applied to compact the layers of the syringe before use.

194    Vacuum manifold (Supelco, Italy) for SPE was used for filtration. The syringe, containing either Zeo-Na or

195    Zeo-K, was initially conditioned with 10 mL of ethanol and 10 mL of the wine model solution (without

196    riboflavin). Then the riboflavin-enriched model solution was added. In order to obtain a zeolite/solution ratio

197    of 10 g L$^{-1}$, 100 mL of the riboflavin-enriched model solution were filtered, using a flow rate of 1 mL min$^{-1}$.

198    *2.2.4.    Determination of riboflavin*

199    A high-pressure liquid chromatograph Agilent 1200 HPLC system (Agilent Technologies, Santa Clara, CA,

200    USA) equipped with G1311B quaternary pump, G1329B auto sampler (ALS, loop of 30 μL), G1316A

201    thermostated column compartment, and G1315D diode array detector (DAD) was used. The Openlab software

202    was used for data acquisition and processing. The riboflavin concentration in the model wine solution was

203    assessed using the method of Fracassetti et al. (2017), with some modifications. Specifically, samples were

204    filtered through a 0.45 μm cellulose acetate filter (Sartorius Stedim Biotech Gmbh, Germany), then 20 μL were

205    injected into a reversed-phase column RP C18 (Acclaim 120, 3 μm, 150 × 3 mm, Thermo Fisher, Waltham,

206    MA, USA) thermostatically controlled at 25 °C. The eluting solutions were as follows: (A) 90 % 50 mmol

207    citrate buffer at pH 2.5 and 10 % methanol (v/v), and (B) 10 % 50 mmol citrate buffer at pH 2.5 and 90 %

208    methanol (v/v). The gradient was from 100 % A to 30 % A (0-8 min), from 30 % A to 100 % A (8-9 min), 100

209    % A (9-15 min) at a flow rate of 0.6 mL min$^{-1}$. The detection wavelength was 440 nm. Under these conditions,

210    riboflavin was eluted with a retention time of 7.189 min. Calibration curves were prepared for a riboflavin

211    concentration in the range 15–600 μg L$^{-1}$, and riboflavin was quantified according to the external standard

212    method.

213    *2.3. Statistical analysis*

214    OriginPro 2020 (OriginLab Corporation, Northampton, MA, USA) was used for the statistical analysis. All

215    results were subjected to one-way analysis of variance (ANOVA), and means were separated by the Tukey's

216    HSD test ($P < 0.05$).

217

218    **3.    Results and discussion**

219    *3.1.    Zeolite synthesis from glass and aluminium FPMs*

220    The solid products obtained by the alkaline hydrothermal treatment of glass and aluminium FPMs were

221    characterized by XRPD and the diffractograms of the two zeolitic materials are shown in Fig. 1. The synthesis

222    carried out using NaOH as mineralising agent (Zeo-Na) produced a material containing 20 % zeolite-A

223    (characteristic peaks at 7.20, 10.19, 12.49, 16.14, 21.71, 24.04, 26.17, 27.18, 30.01, 34.26 and 52.72° 2θ,

224    corresponding to d-spacings of 12.267, 8.674, 7.082, 5.486, 4.089, 3.687, 3.402, 3.279, 2.975, 2.615 and 1.735

225    Å, respectively) and traces (<1 %) of faujasite (another zeolite with characteristic peaks at 13.83, 18.83, 24.16,

226    27.33 and 32.38° 2θ corresponding to d-spacings of 6.400, 4.710, 3.680, 3.260 and 2.763 Å, respectively). The

227    use of KOH during the synthesis (Zeo-K) caused the formation of 16% edingtonite (a zeolite mineral with

228    characteristic peaks at 12.82, 13.64, 25.81, 28.92, 30.43, 32.10, 40.31, 43.52 and 52.40° 2θ, corresponding to

229    d-spacings of 6.898, 6.488, 3.449, 3.085, 2.936, 2.786, 2.235, 2.078 and 1.745 Å, respectively). The broad

230    hump between 20° and 30° 2θ in XRPD patterns suggests the presence of a considerable amount of amorphous

231    phases, containing also cryptocrystalline and poorly ordered minerals. By using a similar synthetic procedure,

232    Terzano et al. (2015) synthesised aluminosilicate materials with a high cation exchange capacity (CEC)

233    containing 25–30 % of crystalline zeolites. According to Terzano et al. (2015), the synthetic zeolite A-

234    containing material was characterised by a CEC of 389.5 cmol$_{(+)}$ kg$^{-1}$, a surface area of 40.7 m$^2$ g$^{-1}$, a total

235    porosity of 67.5 % and a total pore volume of 2.88 mL g$^{-1}$, while the edingtonite-containing material by a CEC

236    of 259 cmol$_{(+)}$ kg$^{-1}$, a surface area of 42.2 m$^2$ g$^{-1}$,  a total porosity of 55.4 % and a total pore volume of 0.84

237    mL g$^{-1}$.

*3.2. Removal of riboflavin by zeolite suspension*

Results of riboflavin removal after suspending zeolite materials (1 g L$^{-1}$) in the riboflavin-enriched (300 µg L$^{-1}$) model solution for 16 h are reported in Fig. 2. Data revealed that the riboflavin concentration remained almost unchanged in the treatment with Zeo-K (Zeo-K1), whereas it significantly decreased in all the other treatments, compared to the control. In particular, Bent1 and Bent2 reduced riboflavin concentration by 14.7 % and 20.9 %, respectively, while Zeo-Na1 by 15.2 %. Fracassetti et al. (2017) obtained better performances with commercial bentonites, removing about 40 % of riboflavin in a model wine system containing a higher amount of photosensitizer (350 µg L$^{-1}$).

According to Terzano et al. (2015), synthetic sodium zeolite-materials are characterised by higher CEC values, total porosity and total pore volume than potassium zeolite-materials. Some of these better properties could explain the higher effectiveness of Zeo-Na in the removal of riboflavin (see Section 3.4). Moreover, Na-zeolites could be better wine adjuvants than K-zeolites, since potassium release from K-zeolites by cation exchange could favour the tartrate instability. This defect is caused by the crystallization of potassium tartrate salts occurring in super saturation states (Mercurio et al., 2010), and is negatively perceived by most consumers because it occurs after wine bottling and forms a clearly visible deposit of crystals (Lankhorst et al., 2017).

Zeo-Na1 treatment reduced riboflavin of an amount comparable with that of Bent1 treatment. Nevertheless, it should be considered that commercial bentonites for oenological use have a legal content of active crystalline aluminosilicates (montmorillonite) of at least 80 % (90-95 % in the tested bentonites). This value is much higher than the amount of crystalline zeolite contained in Zeo-Na (20 % zeolite A). Fracassetti et al. (2017) reported a decrease of riboflavin concentration by 40 % using a commercial zeolite. Commercial zeolites have usually a degree of crystallinity higher than that of the zeolites used in the present study, and this could explain the different performance of the two zeolitic materials. However, despite only 20 % of the synthesized zeolite material is crystalline, low structurally ordered aluminosilicates are also present (contributing for about 60% of the total CEC, as reported by Terzano et al. (2015)), that might contribute to the riboflavin removal.

To limit the risks of development of the so-called "light-struck" defect in wine, a riboflavin concentration lower than 80–100 µg L$^{-1}$ must be reached (Fracassetti et al., 2017), therefore none of the adopted treatments could be considered actually effective.

265  For this reason, an additional study varying the sorbent material concentration and contact time was performed.

266  The influence of zeolite material concentration was evaluated at 10, 25 and 50 g L$^{-1}$. Results are reported in

267  Fig. 3 and in Table 1. After 16 hours stirring, riboflavin concentration did not change in the control, while it

268  decreased significantly in all Zeo-Na and Zeo-K treatments. The riboflavin concentration decreased with

269  increasing concentrations of Zeo-Na or Zeo-K in the model wine solution. As for Zeo-Na, a linear decrease of

270  riboflavin concentration was observed increasing the amount of suspended zeolite. The linearity was highly

271  significant when excluding the control from the model. An amount of about 3.5 μg of riboflavin removed from

272  the wine model solution per each gram of Zeo-Na added can be calculated from the regression model equation

273  (Table 1). The treatment with 50 g L$^{-1}$ of Zeo-Na removed 68.7 % of riboflavin, obtaining a final riboflavin

274  concentration of less than 100 μg L$^{-1}$. As regards Zeo-K, the decrease of residual riboflavin followed a non-

275  linear, quadratic model. The treatment with 50 g L$^{-1}$ of Zeo-K removed 57.7 % of riboflavin, which corresponds

276  to a final riboflavin concentration of 130 μg L$^{-1}$. No treatment with Zeo-K decreased the concentration of

277  riboflavin below the target limit of 100 μg L$^{-1}$.

278  According to Fracassetti et al. (2017), riboflavin removal is affected by adjuvant concentration and reaches an

279  equilibrium within 2 h. The effect of contact time was also evaluated in the present study using 10 g L$^{-1}$ zeolite-

280  materials, and the results are presented in Fig. 4. Table 2 shows the parameters of the regression models of

281  riboflavin reduction as a function of contact time in the model wine system. Data are fitted by exponential

282  models. The highest removal of riboflavin occurred already within 2 h from the start of the experiment, but it

283  continued to increase up to 16 h of contact time. In the case of Zeo-Na, approximately 70 % of riboflavin was

284  removed within the first 2 h, but an apparent equilibrium was reached only after approximately 16 h.

285  A similar trend was also observed for Zeo-K, though the decrease in the initial phases was slightly less marked.

286  *3.3.  Removal of riboflavin by filtration*

287  Column filtration could be a more practical solution to remove riboflavin from wine, avoiding the step of

288  separating the adjuvant by centrifugation. Results obtained eluting 100 ml of wine model solution through 1 g

289  of zeolite material (corresponding to 10 g L$^{-1}$, as in the previous experiment) are shown in Fig. 5. Similar

290  results were obtained either using glass wool when preparing the columns (Fig. 5), or using frit (data not

291  shown). Columns containing Zeo-Na removed 33.4 % of riboflavin, whilst columns packed with Zeo-K

292  removed 22.6 %, thus confirming the higher effectiveness of Zeo-Na already observed in the suspension

293    experiments. When the filtration tests were compared with the suspension tests performed at the same

294    concentration of zeolitic material (10 g L$^{-1}$), the same riboflavin removal was obtained using Zeo-K (-22.6 %

295    vs -21.9 %). Conversely, the use of Zeo-Na appeared more effective in filtration than in suspension

296    experiments (-33.4% vs -21.3 %). Nevertheless, irrespective of the zeolitic material used, the residual

297    riboflavin concentration in the filtrate was still higher than the risk threshold, namely the value above which

298    the "light-struck" defect may occur.

299    Regardless of the type of zeolitic material used, filtration was more advantageous than suspension method due

300    to the shorter processing times. Indeed, to remove riboflavin from 100 mL of a model wine solution by

301    filtration, only 100 min were required instead of 16 h required by the suspension procedure. Possibly, the

302    further grinding of zeolites used for the filtration tests had increased the specific surface area of the zeolitic

303    materials and, consequently, their reactivity. Moreover, the removal mechanisms of zeolites towards riboflavin

304    (see Section 3.4) could be favoured during filtration compared to suspension.

305    *3.4. Interaction mechanisms between riboflavin and zeolitic materials*

306    No information is reported in literature about the interaction between riboflavin and zeolites. The only few

307    information concerns the interaction between riboflavin and clay minerals, such as smectites and vermiculite

308    (Mortland & Lawless, 1983). In the light of the physico-chemical properties of the two zeolitic materials

309    synthesized, the riboflavin properties, and the outcomes obtained by suspension and filtration experiments,

310    potential mechanisms for the riboflavin removal can be suggested. Riboflavin is a very weak acid, with a pKa

311    of 9.69 (Kisler, Dähler, Stevens, & O'Connor, 2001), a polar behaviour (log Kow = -1.46) and a molecular

312    size of approximately 12.5 Å (Yasuda, Tamai, Ikeuchi, & Kojima, 1997). According to Brzezińska,

313    Mielczarek, and Pająk (2008), riboflavin is neutral in a very large range of pH ranging from 0 to about 10.

314    Therefore, at the pH of wine model solution, riboflavin cannot be adsorbed by zeolites through cation exchange

315    reactions with the negative charges on the surfaces and in inner cavities of zeolites but rather through dipolar

316    van der Waals interactions and hydrogen bonding between hydroxyl or nitrogen-containing functional groups

317    of riboflavin with the hydroxyl groups on the zeolite inner and outer surfaces. The size of riboflavin (12.5 Å)

318    is considerably lower than the average pore size reported by Terzano et al. (2015) for Zeo-Na (1.25 µm) and

319    Zeo-K (0.13 µm), and therefore riboflavin may enter the microporous structure of both zeolitic materials. The

320    hydrophilic environment created on the external surface of zeolites by hydrated cations is necessary for the

321 bond formation between zeolites and polar organic molecules (Colella, 2007; Mercurio et al., 2010). Indeed,

322 Mortland & Lawless (1983) proved that hydrogen bonding and physical interactions were the main

323 mechanisms for riboflavin adsorption by smectites, whereas cation exchange was negligible. Therefore,

324 similarly to what observed for smectites, also for zeolites weak bonding and physical "entrapment" are the

325 main mechanisms responsible for riboflavin removal from the wine model solution. The higher adsorption

326 capacity of Zeo-Na compared to Zeo-K can thus be explained not by its higher CEC, but rather by the higher

327 number of reactive sites and higher porosity of Zeo-Na, which can trap higher amounts of riboflavin within its

328 pores and channels.

329 *3.5. Considerations about the zeolitic materials sustainability*

330 Both procedures adopted in this study to synthetize the two zeolitic materials were cheaper and more

331 competitive (in terms of zeolite yields) than other methods reported in the literature (Terzano et al., 2015). In

332 particular, synthesis of Zeo-Na and Zeo-K required temperatures below 100°C and no fusion pre-treatment,

333 differently from most of the methods synthetizing zeolite starting from waste materials. In general, the whole

334 process was conceived to reduce to the minimum the energy consumption during the different steps, from

335 wastes preparation to synthesis (Terzano et al., 2015). Moreover, some additional features could be

336 implemented to make the process even more sustainable. For example, the heat released by the exothermic

337 reactions of NaOH or KOH solubilization might be recovered and/or used to reduce the energy consumption

338 during the hydrothermal treatment; the heat and hydrogen gas developed by the Al dissolution might also be

339 exploited to produce energy, in order to auto-sustain the whole synthesis process (Hiraki, Yamauchi, Iida,

340 Uesugi, & Akiyama, 2007; Terzano et al., 2015). A very recent publication (López-Delgado, Robla, Padilla,

341 López-Andrés, & Romero, 2020) showed how this type of process can be also carried out at pilot scale without

342 generation of solid residues, including recycling of liquid effluents (consequently saving water) and recovering

343 gases generated in the process to be used for other applications.

344 At last, in the respect of circular economy principles, zeolitic materials can be recovered at the end of the

345 adsorption process, washed with desorbing solutions and reused for further cycles of riboflavin removal, at

346 least until the zeolite structure is preserved. Residual zeolites could be also reintroduced in the hydrothermal

347 process and reused for the synthesis of new zeolites or, at least for what concerns Zeo-K, could be used as soil

348 amendment in agriculture.

## 4. Conclusions

Two synthetic zeolite materials, obtained by an alkaline hydrothermal treatment of glass and aluminium recovered from drink and food packaging, were tested for the first time as possible oenological adjuvants on model solutions, with the aim to reduce the levels of the photosensitizer riboflavin and to prevent the light-struck taste of white and rosé wines. Both materials resulted able to partially remove riboflavin during suspension and filtration tests. Riboflavin removal was higher and faster in the filtration tests compared with suspension tests using the same relative amount of zeolite materials. Sodium zeolite material appeared more effective than potassium zeolite, and its use may reduce the risks of tartrate instability in wine. The amount of zeolite material needed to reduce the concentration of riboflavin below the limit of 80–100 $\mu g\ L^{-1}$, after which the development of the so-called "light-struck" defect in wine can occur, is still quite high and likely not applicable on real scale. Additional efforts should be done to increase the crystallinity of zeolite materials synthesized from recycled FPMs in order to reduce the amount of adjuvant added to wine. Starting from the same raw materials, a synthetic process based on the use of ultrasound waves was also developed in order to shorten the crystallization times and increase the yields, however this procedure did not appear successful. Additional costs required by the use of higher energetic inputs and new technologies should be also considered, in order to ensure the economic sustainability of zeolite synthesis. Further experiments are also needed to evaluate their effectiveness in real wine matrices and possible secondary effects on wine properties (e.g. taste, smell) or wine safety (e.g. potentially toxic elements concentration).

## 5. Conflicts of interest

There are no conflicts of interest to declare.

## 6. Authors contribution

Mirella Noviello: investigation; formal analysis; writing – original draft. Concetta Eliana Gattullo: supervision; methodology; investigation; writing – review and editing. Ignazio Allegretta: investigation; data curation. Roberto Terzano: conceptualization; resources; writing – review and editing. Giuseppe Gambacorta: supervision; resources; writing – review and editing. Vito Michele Paradiso: conceptualization; project administration; writing – review and editing

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547
548

549 **Figure captions**

550

551 **Fig. 1.** Diffraction patterns of zeolite materials obtained from the alkaline hydrothermal treatment of glass and

552 aluminium FPMs using NaOH (Zeo-Na) or KOH (Zeo-K) as mineralising agents. A: zeolite-A; EDI:

553 edingtonite; F: faujasite.

554

555 **Fig. 2.** Residual concentration of riboflavin in a model wine solution containing 300 µg $L^{-1}$ riboflavin after 16

556 h of suspension with bentonites (Bent1 or Bent2) or synthetic zeolite-materials (Zeo-Na1 or Zeo-K1), added

557 at 1 g $L^{-1}$. Control (without bentonites and zeolites) is also shown. Data are reported as means ± standard

558 deviation (n = 3). Different letters on the error bars indicate a significant difference (P < 0.05).

559

560 **Fig. 3.** Residual concentration and regression models of riboflavin in a model wine solution containing 300 µg

561 $L^{-1}$ riboflavin after 16 h of suspension with different amounts of Zeo-Na (left graph) or Zeo-K (right graph)

562 synthetic zeolite-materials. Data are reported as means ± standard deviation (n = 3). Data labels indicate the

563 average riboflavin reduction as percentage.

564

565 **Fig. 4.** Residual concentration and regression models of riboflavin in a model wine solution containing 300 µg

566 $L^{-1}$ riboflavin treated for different times with 10 g $L^{-1}$ of Zeo-Na (left graph) or Zeo-K (right graph) synthetic

567 zeolite-materials. Data are reported as means ± standard deviation (n = 3). Data labels indicate the average

568 riboflavin reduction as percentage.

569

570 **Fig. 5.** Residual concentration of riboflavin in a model wine solution containing 300 µg $L^{-1}$ riboflavin after

571 filtration tests with synthetic zeolite-materials (Zeo-Na or Zeo-K) at 10 g $L^{-1}$. Control (without zeolites) is also

572 shown. Data are reported as means ± standard deviation (n = 3). Different letters on the error bars indicate a

573 significant difference (P < 0.05).

574

**Table 1** Parameters of the regression models of riboflavin reduction as a function of zeolitic materials suspended in the model wine system

|  | Zeo-Na | Zeo-K |
| --- | --- | --- |
| Equation | y = a - bx | y = a - bx + cx$^2$ |
| Intercept (a) | 272.927 ± 2.930 | 307.225 ± 0.916 |
| b | -3.499 ± 0.135 | -7.393 ± 0.151 |
| c | - | 0.077 ± 0.003 |
| Residual sum of squares | 1.510 | 0.354 |
| R$^2$ (C.O.D.) | 0.99701 | 0.99993 |

575    .

**Table 2**

Parameters of the regression models of riboflavin reduction as a function of contact time in the model wine system.

| | Zeo-Na | Zeo-K |
|---|---|---|
| Equation | $y = a \times x^b$ | $y = a \times x^b$ |
| a | $264.397 \pm 1.901$ | $280.238 \pm 0.168$ |
| b | $-0.035 \pm 0.006$ | $-0.055 \pm 0.000$ |
| $R^2$ (C.O.D.) | 0.97018 | 0.99998 |

576