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# Functionalized Mesoporous Silica is a viable alternative to bentonite for wine protein stabilization

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#### **BACKGROUND AND AIM**

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The presence of grape-derived heat unstable proteins (TLPs and chitinases) can lead to haze formation in white wines [1], an instability prevented by removing these proteins by adding bentonite, a hydrated aluminum silicate that interacts electrostatically with wine proteins leading to their flocculation. Despite effective, using bentonite has several drawbacks as the costs associated with its use, the potential negative effects on wine quality, and its environmental impact, so that alternative solutions are needed. This project aimed at evaluating the effectiveness of functionalized mesoporous silica (FMS) in removing heat unstable proteins from white musts and wines, as well as its impact on wine composition.



#### PROTEIN REMOVAL

The protein profile and concentration of treated and untreated wines (**Table 2**) showed that the stabilizing effect of FMS was extremely similar to that of bentonite, and that it was attributable to the effective removal of both TLPs and chitinases in a dose dependent mode.

#### **Table 2.** Protein content assessed by RP-HPLC and expressed in mg/L.

| Treatment    | Sauvignon<br>Blanc 2019 |      | Friul<br>20 | Friulano<br>2019 |      | Zibibbo 2019 |      | Manzoni<br>bianco 2019 |      | Sauvignon<br>Blanc 2022 |      | Traminer<br>2022 |  |
|--------------|-------------------------|------|-------------|------------------|------|--------------|------|------------------------|------|-------------------------|------|------------------|--|
|              | TLPs                    | Chit | TLPs        | Chit             | TLPs | Chit         | TLPs | Chit                   | TLPs | Chit                    | TLPs | Chit             |  |
| Unfined wine | 179                     | 69   | 32          | 10               | 52   | 1            | 64   | 7                      | 65   | 15                      | 88   | 29               |  |
| FMS          | 17                      | 7    | 11          | 0                | 9    | 0            | 11   | 2                      | 10   | 1                       | 9    | 1                |  |
| Na-Bentonite | 26                      | 3    | 10          | 2                | 6    | 0            | 17   | 1                      | 14   | 2                       | 12   | 2                |  |

FMS treatments were benchmarked against a commercial Na-Bentonite in a series of experiments conducted on heat unstable white wines of different origin, vintage and variety, and on different scales (from few mL to 10 hL). The stabilizing properties of the fining agents were determined by analyzing the protein profiles of treated wines (by RP-HPLC), and by assessing protein stability via heat tests [3]. In addition, the treatments impact on other wine parameters (e.g. organic acid profiles, metal content, macromolecules, lees formation, sensory analysis) were determined.

#### FINING RATES

For each wine, the dose of bentonite and FMS needed to reach full protein stability was determined by fining rate trials (**Table 1**).

Table 1. Heat test of wines unfined, treated with Na-Bentonite or FMS. Wines considered heat stable with  $\Delta$ NTU values < 2.

| Treatment    | Sauvignon Friu<br>Blanc 2019 20 |      | iulano<br>2019 <sup>Zibibl</sup> |      | 0 2019 | Manzoni<br>bianco 2019 |     | Sauvignon<br>Blanc 2022 |     | Traminer<br>2022 |     |      |
|--------------|---------------------------------|------|----------------------------------|------|--------|------------------------|-----|-------------------------|-----|------------------|-----|------|
|              | NTU                             | g/hL | NTU                              | g/hL | NTU    | g/hL                   | NTU | g/hL                    | NTU | g/hL             | NTU | g/hL |
| Unfined wine | 38                              | 0    | 7.3                              | 0    | 15.4   | 0                      | 9.7 | 0                       | 93  | 0                | 193 | 0    |
| FMS          | 0.7                             | 130  | 1.2                              | 25   | 1.6    | 70                     | 1.9 | 90                      | 1.8 | 60               | 1.5 | 110  |
| Na-Bentonite | 1.8                             | 120  | 1.1                              | 20   | 1.8    | 80                     | 1.7 | 100                     | 1.8 | 60               | 1.4 | 100  |

#### IMPACT ON WINE COMPOSITION

**Table 3** shows that FMS did not cause modifications on wine composition in terms of organic acid profile, ethanol content (not shown), glycerol, volatile composition (not shown), and elemental content that, on the other hand, was always modified by bentonite fining that always led to an increase in Fe and Al (**Table 4**).

Table 3. Organic acid composition of the three wines treated with 4 fining regimes (n = 3).

|                  | CITRIC ACID (g/L) |                   |       |  |  |  |
|------------------|-------------------|-------------------|-------|--|--|--|
| WINE TYPE        | Untreated         | Bentonite         | FMS   |  |  |  |
| Grüner Veltliner | 0.22              | 0.22              | 0.18  |  |  |  |
| Traminer         | 0.12              | 0.11              | 0.11  |  |  |  |
| Manzoni          | 0.04              | 0.04              | 0.04  |  |  |  |
|                  |                   | TARTARIC ACID (g/ | ′L)   |  |  |  |
|                  | Untreated         | Bentonite         | FMS   |  |  |  |
| Grüner Veltliner | 2.70              | 2.68              | 2.40  |  |  |  |
| Traminer         | 1.81              | 1.71              | 1.80  |  |  |  |
| Manzoni          | 1.65              | 1.64              | 1.67  |  |  |  |
|                  |                   | MALIC ACID (g/L)  |       |  |  |  |
|                  | Untreated         | Bentonite         | FMS   |  |  |  |
| Grüner Veltliner | 2.95              | 2.92              | 2.02  |  |  |  |
| Traminer         | 0.11              | 0.06              | 0.10  |  |  |  |
| Manzoni          | 0.09              | 0.08              | 0.07  |  |  |  |
|                  |                   | LACTIC ACID (g/L  |       |  |  |  |
|                  | Untreated         | Bentonite         | FMS   |  |  |  |
| Grüner Veltliner | 0.17              | 0.16              | 0.17  |  |  |  |
| Traminer         | 3.51              | 3.22              | 3.44  |  |  |  |
| Manzoni          | 3.05              | 3.07              | 3.11  |  |  |  |
|                  |                   | GLYCEROL (g/L)    |       |  |  |  |
|                  | Untreated         | Bentonite         | FMS   |  |  |  |
| Grüner Veltliner | 7.77              | 7.72              | 7.83  |  |  |  |
| Traminer         | 10.95             | 9.20              | 10.82 |  |  |  |
| Manzoni          | 10.73             | 10.71             | 10.97 |  |  |  |

FMS allowed to reach wine heat stability at addition rates in line with those of bentonite, with a small variability attributable to differences in wine composition.

### ELEMENTAL ANALYSIS

**Table 4.** Element analysis on a Sauvignon Blanc fined with two types of bentonite and FMS at addition rates sufficient to fully stabilize it.

| Element   | Control wine | Wine after<br>bentonite A (1g/L) | Wine after bentonite B<br>(1.3 g/L) | Wine after FMS<br>(1.5 g/L) |  |  |
|-----------|--------------|----------------------------------|-------------------------------------|-----------------------------|--|--|
| Ca (mg/L) | 64           | 67 +4%                           | 71 +11%                             | 60 -6%                      |  |  |
| Na (mg/L) | 6.6          | 16.1 +151%                       | 11.4 +73%                           | 6.3 -5%                     |  |  |
| Fe (mg/L) | 0.20         | 0.40 +100%                       | 0.26 +30%                           | 0.18 -10%                   |  |  |
| Al (µg/L) | 227          | 1741 <b>+669%</b>                | 499 +120%                           | 223 -2%                     |  |  |
| Ba (µg/L) | 27           | 255 +840%                        | 180 +560%                           | 25 -7%                      |  |  |
| Si (mg/L) | 4.9          | 10.6 +116%                       | 5.2 +6%                             | 4.9 =                       |  |  |

### IMPACT ON WINE SENSORY QUALITY

A sensory analysis conducted by triangle test (Table 5) on two white wines (Sauvignon blanc and Traminer, both vintage 2022) stabilized with FMS or bentonite at similar addition rates (see **Table 1**) revealed the lack of significant differences between the two stabilization treatments.

#### **Table 5.** Results of the triangle tests, n = 39 responses.

| TEST  | TOTAL<br>ANSWERS | CORRECT<br>ANSWERS | P-Value | Significance    |
|---|------------------|--------------------|---------|-----------------|
| Sauvignon BENT (0.6 g/L)<br>VS<br>Sauvignon FMS (0.6 g/L) | 39               | 13                 | 0.5599  | Not significant |
| Traminer BENT (1.0 g/L)<br>VS<br>Traminer FMS (1.1 g/L)   | 39               | 17                 | 0.1184  | Not significant |

In general, FMS, a material currently under OIV scrutiny for approval for winemaking, showed to effectively stabilized wines at addition rates similar to those of bentonite, without causing major compositional modification, nor detectable sensory impacts  $\rightarrow$ FMS is a candidate to become a viable bentonite alternative.

#### References

1. Van Sluyter, S.C.; McRae, J.M.; Falconer, R.J.; Smith, P.A.; Bacic, A.; Waters, E.J.; Marangon, M. Wine Protein Haze: Mechanisms of Formation and Advances in Prevention. J. Agric. Food Chem. 2015, 63, 4020-4030.

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