Food Chemistry 275 (2019) 154–160

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Magnetic separation technology: Functional group efficiency in the removal of haze-forming proteins from wines

Agnieszka Mierczynska-Vasilev[a,b,*], Pawel Mierczynski[c], Waldemar Maniukiewicz[c], Rahul M. Visalakshan[b], Krasimir Vasilev[d], Paul A. Smith[a,e]

[a] The Australian Wine Research Institute, Waite Precinct, Hartley Grove cnr Paratoo Road, Urrbrae (Adelaide), PO Box 197, Glen Osmond, SA 5064, Australia
[b] Future Industries Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes, SA 5095, Australia
[c] Institute of General and Ecological Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland
[d] School of Engineering, University of South Australia, Mawson Lakes Campus, Mawson Lakes, SA 5095, Australia
[e] Wine Australia, P.O. Box 660, Kent Town, SA 5071, Australia

ARTICLE INFO

Keywords:
Acrylic acid
Allylamine
Haze
Magnetic nanoparticles
2-Methyl-2-oxazoline
Plasma polymerization
Protein removal
White wine

ABSTRACT

Magnetic nanoparticles were modified by plasma polymerization, using allylamine, acrylic acid and 2-methyl-2-oxazoline as precursor to produce amine, carboxyl and oxazoline functional group rich surfaces. The nanoparticles were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and zeta potential measurements. The capacity of nanoparticles carrying different surface properties to remove haze-forming proteins from Sémillon and Sauvignon Blanc unfined wines was examined by high-performance liquid chromatography (HPLC). The protein capture efficiency of the modified surfaces decreases in the following order: COOH > POx > NH_2. This study will help optimising the design of this new technology for the selective removal of haze proteins from white wines.

1. Introduction

In today's competitive global wine market, it is critical for wine to be visually appealing to consumers, meaning the wine need to be clear and sediment free. Protein instability, together with microbial instability and tartrate instability are most commonly responsible for development of haze in wine (Ribereau-Gayon, Glories, Maujean, & Dubourdieu, 2000). Currently, microbial instability is managed in the wine industry by sulfur dioxide addition and filtration (Du Toit & Pretorius, 2000); tartrate instability by cold stabilization, ion exchange resins or electrodialysis (Lasanta & Gomez, 2012); protein instability is currently managed by protein removal through bentonite addition (Achaerandio, Pachova, Güell, & López, 2001; Ferreira, Piçarra-Pereira, Monteiro, Loureiro, & Teixeira, 2002; Høj et al., 2000; Waters et al., 2005). Bentonite fining to remove haze-forming proteins is a key step in the production of white and rosé wines, however, it has drawbacks including wine losses and issues with waste disposal (Høj et al., 2000; Majewski, Barbalet, & Waters, 2011; Tattersall et al., 2001). Over the last two decades several alternative techniques to bentonite fining have been studied such as ultrafiltration (Van Sluyter et al., 2015), flash pasteurization (Pocock, Hoj, Adams, Kwiatkowski, & Waters, 2003), proteases (Esti, Benucci, Liburdi, & Garzillo, 2011; Marangon et al., 2012; Waters, Wallance, & Williams, 1992) and various adsorbents (e.g. carrageenan, zirconium dioxide) (Sarmento, Oliveira, & Boulton, 2000; Van Sluyter et al., 2015; Vincenzi, Polesani, & Curioni, 2005). However, the results obtained to date have not led to widespread uptake by the wine industry and bentonite continues to be the predominant process for protein stabilisation.

In our recently published work (Mierczynska-Vasilev, Boyer, Vasilev, & Smith, 2017), we reported a new magnetic separation technology that allows for selective removal of pathogenesis-related proteins such as thaumatin-like proteins (TLPs) and chitinases from wines. The process utilizes magnetic nano-beads with carefully tuned surface functionalities that capture haze proteins (TLPs and chitinases) and which can be subsequently removed by applying an external magnetic force (Mierczynska-Vasilev et al., 2017). The surface chemistry of magnetic particles was tailored *via* plasma deposition of acrylic acid using a custom engineered technology for encapsulation of

* Corresponding author at: The Australian Wine Research Institute, Waite Precinct, Hartley Grove cnr Paratoo Road, Urrbrae (Adelaide), PO Box 197, Glen Osmond, SA 5064, Australia.
E-mail addresses: agnieszka.mierczynska-vasilev@awri.com.au (A. Mierczynska-Vasilev), pawel.mierczynski@p.lodz.pl (P. Mierczynski), waldemar.maniukiewicz@p.lodz.pl (W. Maniukiewicz), rahul.madathiparambil_visalakshan@mymail.unisa.edu.au (R.M. Visalakshan), krasimir.vasilev@unisa.edu.au (K. Vasilev), Paul.Smith@wineaustralia.com (P.A. Smith).

https://doi.org/10.1016/j.foodchem.2018.09.046
Received 4 May 2018; Received in revised form 26 July 2018; Accepted 8 September 2018
Available online 08 September 2018
0308-8146/

particulates (Cavallaro & Vasilev, 2015). In addition to removing protein from model solutions, the particles were also successfully tested in heat-unstable wines. This novel separation technology is simple and very effective in removing both pathogenesis-related protein families, TLPs and chitinases from white wines. Importantly, the phenolic content of the wines was not altered by the protein removal treatment via these magnetic nanoparticles.

In this work we build on our first report and examine the influence of surface functionalities on the technology's efficiency for removal of haze-forming proteins from wine. We employ a range of surface coatings that possess positive or negative surface charges and provide different mechanism of interaction with proteins. A key selection criterion for the coatings is to be sufficiently hydrophilic to provide good discernibility of the nanoparticles. Allylamine, acrylic acid and 2-methyl-2-oxazoline monomers were used to produce plasma coatings rich in amine, carboxyl and oxazoline functional groups. The coatings were characterized in detail by X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and their surface charge was measured. The efficacy of the selected coatings in removing haze-forming proteins was examined using Sémillon and Sauvignon Blanc unfined wines.

2. Materials and methods

2.1. Chemicals

Allylamine (AA) (98%), acrylic acid (AcrA) (99%), 2-methyl-2-oxazoline (POx) (98%), NaOH pellets and NaCl were purchased from Sigma-Aldrich Australia and used as received.

Magnetic nanoparticles (316 L stainless steel grade) were supplied by SkySpring Nanomaterials, Inc. The chemical composition of the magnetic nanoparticles as well as their particle size were measured and reported previously (Mierczynska-Vasilev et al., 2017).

2.2. Wines and wine analysis

Two different unfined white wines were used. Sauvignon Blanc (SAB) and Sémillon (SEM) were kindly donated by Accolade Wines, Reynella, SA. Enological analyses and protein content in wines were analyzed following established methods previously described (Mierczynska-Vasilev et al., 2017) and are summarized in Table S1 (Supplementary Material). To analyse proteins in wines a Prozap Expedite C18 column was used with a solvent system of 0.1% TFA/H_2O (Solvent A) and 0.1%TFA/ACN (Solvent B), at 0.75 mL/min. The mobile phase gradient was: 0–1 min 10–20% Solvent B, 1–4 min 20–40% B, 4–6 min 40–80% B, 6–7 min 80% B, 7.01 min 10% B, and 7–10 min 10% B. Detection of proteins was achieved by Diode Array monitoring at 210 nm. Identification of proteins was achieved by comparing the retention times of sample peaks with isolated standards and quantitation was achieved by comparing the peak areas with those of a standard curve of thaumatin (Sigma, Australia).

The heat stability test was carried out according to Mierczynska-Vasilev et al. (2017). Wines were heated at 80 °C for 2 h, then cooled on ice for 2 h and analyzed after equilibration to room temperature. The heat stability was measured by calculating the difference between the heated and unheated samples in the absorbance values at wavelength of 540 nm using Cary 60 UV–vis spectrometer (Agilent Technologies). Samples were considered to be protein unstable when the haze (difference in absorbance between heated and unheated samples) was below 0.02 absorbance unit (au).

Metal content in wine before and after treatment with coated MNPs and two different bentonites was determined by inductively coupled plasma – optical emission spectrometry (ICP-OES) performed by AWRI Commercial Services.

2.3. Functionalisation of magnetic nanoparticles (MNPs) by plasma polymerization

Plasma polymerization of allylamine, acrylic acid and 2-methyl-2-oxazoline was carried out in bell-chamber reactor as described previously (Vasilev, Michelmore, Griesser, & Short, 2009; Vasilev, Poulter, Martinek, & Griesser, 2011). The reactor was equipped with agitation platform for coating of powder and particulate material (Cavallaro & Vasilev, 2015). All precursors were deposited at 2.3×10^{-1} mbar. Deposition time was 10 min in all cases (optimum plasma deposition time as estimated in our previous work (Mierczynska-Vasilev et al., 2017)). To achieve sufficient coating stability and functional group retention allylamine was deposited using power of 40 W, acrylic acid of 10 W and 2-methyl-2-oxazoline of 50 W.

2.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy spectra were recorded to confirm the modification of functional groups. XPS spectra were recorded on a SPECS SAGE spectrometer with a Mg Kα radiation source ($h\nu = 1253.6$ eV) operating at 10 kV and 20 mA. The elements present were identified from survey spectra recorded over the energy range 0–1000 eV at a pass energy of 30 eV and a resolution of 0.5 eV. All the binding energies were referenced to the C1s neutral carbon peak at 285 eV, to compensate for the effect of surface charging. CasaXPS software was used for spectra analysis.

2.5. Zeta potential measurements

The electrophoretic mobility of bare and plasma-coated magnetic nanoparticles was determined using Zetasizer Nano ZS (Malvern, UK) and transformed into zeta potential using the Smoluchowsky equation (Müller, 1991) for recognition. Measurements were carried out at 22 °C in 10^{-3} M NaCl.

2.6. Fourier transform infrared spectroscopy (FTIR)

IRTracer-100 FTIR (Shimadzu) spectrometer equipped with liquid nitrogen cooled MCT detector was used in all measurements. The measurements were performed using the Quest Single Reflection ATR Accessory (Specac) having a diamond ATR crystal. In all cases 128 scans (4 cm^{-1} resolution) were taken to achieve a satisfactory signal to noise ratio. ATR effect and atmospheric contributions from carbon dioxide and water vapour were corrected through the background made on an empty ATR accessory.

2.7. X-ray diffraction (XRD)

The room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer in the Bragg-Brentano reflection geometry. Copper Cu Kα radiation from a sealed tube was used. Data were collected in the 2θ range of 5–90° with a step of 0.0167° and exposure per step of 27 s. Since the raw diffraction data contain some noise, the background during the analysis was subtracted using the Sonneveld-Visser algorithm. The data were then smoothed using a cubic polynomial function.

3. Results

3.1. XPS analysis

Fig. S1 (Supplementary Material) shows XPS survey spectra of bare magnetic nanoparticles (bare MNPs) and magnetic nanoparticles coated with plasma polymer coatings deposited from vapour of acrylic acid (carboxyl MNPs), allylamine (amine MNPs) and 2-methyl-2-oxazoline (oxazoline MNPs).