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Effect of clarification process on the removal of pesticide residues in white wine

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ABSTRACT

Presence of pesticides in wine is of great concern, due to their extensive use in viticulture. Seven clarifying agents (activated carbon, bentonite, polyvinylpolypyrrolidone, gelatin, egg albumin, isinglass, and casein) were examined in removing pesticides from white wine, fortified with single solutions and mixtures of pesticides. Solid phase extraction followed by GC-ECD was performed to analyse pesticide residues. The order of decreasing adsorbent effectiveness was: activated carbon 64% > egg albumin 23% ≥ gelatin 22% > PVPP 17% ≥ casein 16% > bentonite 8%. Isinglass showed 22% removal at the highest permitted concentration. The effect of the type of the clarifying agent and pesticide's chemical structure and properties (octanol-water partition coefficient and water solubility) on pesticide removal was studied. Distinct behavior is exhibited by each clarifying agent. Adsorption is increased by increasing hydrophobicity and decreasing hydrophilicity of pesticides. The removal of each pesticide from its single solution is generally higher than that from its mixtures, revealing the antagonistic and synergistic effects.

1. Introduction

The systematic use of pesticides causes serious problems on agricultural products with impacts on human health and environment. To date, crop protection with chemical methods is the common practice in viticulture in Europe, due to specificities of vine cultivation and its diseases and pests. In 2013 only 157,198 ha were fully converted to organic farming to produce grapes, while 3,121,070 ha were used to produce grapes conventionally (data from EUROSTAT), because producers are still skeptical about organic farming. Pesticide residues often detected in grapes and wine vary significantly every year, depending on climate conditions, quantity used in the field, way and number of applications and time from application to harvest. Fungicide residues were detected in red and white bottled wines by Calhelha, Andrade, Ferreira, and Estevinho (2006). Čuš, Česnik, Bolta, and Gregorčič (2010) analysed 25 bottled wines and reported that 82% of the samples contained pesticide residues. dos Anjos and de Andrade (2015) detected 11 pesticides, among 18 pesticides examined, in 19 white and rosé wine samples, with concentrations up to 65.3 μg/L. Nowadays, the aim of wine producers and consumers is the production of high quality wine, with no pesticide residues.

Pesticide reduction has been investigated during wine making process, including maceration, pressing, racking, clarification and filtration. Clarification is a basic step in winemaking. A variety of fining agents have been used to remove or reduce the concentration of one or more undesirable constituents, and enhance clarity, color, aroma, flavor, and/or stability modification (Zoecklein, Fugelsang, Gump, & Nury, 1999). Simultaneously, research activity on the removal of pesticide residues by clarification, beyond the above mentioned constituents, during clarification has been developed. Sala et al. (1996) examined the fate of 8 pesticides, determining a continuous residue decrease throughout the winemaking process, and reported persistence of 3 pesticides (procymidone, vinclozolin, iprodione) in bottled wine, being in some

Abbreviations: AEI (or SEI), antagonistic (or synergistic) effect index; C_c, capacity of each clarifying agent; K_{ow}, octanol-water partition coefficient; MPR, mean pesticide removal; MRL, maximum residue limit; MRSP, mean removal of significantly removed pesticides; PR, pesticide removal; S_c, selectivity of each clarifying agent; TAEI (or TSEI), total antagonistic (or synergistic) effect index; TC_c, total capacity of each clarifying agent.

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cases higher than the maximal levels established by law. Navarro, Barba, Oliva, Navarro, and Pardo (1999) achieved low to medium removal of 6 pesticides, using a mixture of bentonite (30 g/hL) plus gelatin (20 g/hL). Penconazole, chlorpyriphos, and vinclozolin showed low to medium reductions. Low pesticide (lindane and metalaxyl) removal by clarification of a white and a red wine was reported by Jimenez, Bernal, del Nozal, Bernal, and Toribio (2007), using mixtures of gelatin plus bentonite and casein plus bentonite respectively. González-Rodríguez, Cancho-Grande, and Simal-Gándara (2011) estimated the effectiveness of white winemaking process in reducing 13 fungicides, reporting that pressing and settling proved the most important steps. The reduction rate of almost all fungicides was very high, up to 99%. Alister et al. (2014) reported that the concentration of 6 pesticides decreases gradually at every oenological step, mainly during alcoholic and malolactic fermentations and bottled wine storage, while the removal effectiveness of other steps (e.g. clarification) could vary, depending on pesticide type.

For better understanding of pesticide removal, clarification has been studied separately, as a single process, using either individual pesticide solution or mixture of pesticides. As far as the removal of a single pesticide is concerned, the recent research is briefly described below. Cabras et al. (2001) reported the high effectiveness of charcoal, in reducing fenhexamid content by 91%, and the ineffectiveness of bentonite, gelatin, K caseinate and PVPP. Čuš et al. (2010) investigated boscalid removal and observed significant reduction after fining with a mixture of bentonite, casein, PVPP, and diatomaceous earth, while bentonite itself showed very low efficiency. Likas and Tsiropoulos (2011) reported that bentonite, casein, PVPP, and gelatin–silicon dioxide mixture did not remove significantly tebufenozide residues from wine, while charcoal removed 95% of the pesticide. The removal of a mixture of pesticides by clarification has, also, been investigated. In a review article, Paolo Cabras and Angioni (2000) reported the complete elimination of most pesticides by activated carbon, particularly when residues are low (ranging between 0.05 and 0.39 mg/L), while bentonite, gelatin, PVPP, potassium caseinate, and colloidal silicon dioxide showed no significant pesticide removal. Fernández, Oliva, Barba, and Cámara (2005) and Oliva, Paya, Camara, and Barba (2007) examined the removal of 4 or 3 different fungicides respectively, using the same clarifying agents at the same doses (charcoal, blood albumin, egg albumin, bentonite plus gelatin or charcoal and PVPP), which were proven selectively effective. Angioni, Dedola, Garau, Schirra, and Caboni (2011) examined the removal of a mixture of 3 pesticides; bentonite, casein, and gelatin were selectively effective in adsorbing the pesticides.

The selection of an appropriate adsorbent is of great importance, due to the variety of pesticides and fining agents used. Therefore, data on the correlation of pesticide removal to its octanol-water partition coefficient - K_{ow} and water solubility are useful and welcome. Few data on this topic have been recently reported. Sen, Cabaroglu, and Yilmaz (2012) could only correlate the removal of 6 pesticides to their water solubility (ranging 0.078–180 mg/L) during clarification using activated carbon, casein, bentonite, PVPP, and kieselsol plus gelatin. However, they couldn't correlate pesticide removal to pesticides' log K_{ow} (ranging from 3 to 4.61). Pazzirota, Martin, Mezcua, Ferrer, and Fernandez-Alba (2013) observed during winemaking (using a mixture of bentonite plus gelatin) that generally the higher the log K_{ow} (for 14 pesticides tested), the higher the pesticide removal, while the opposite behavior was observed for pesticide solubility. It should be noted that log K_{ow} ranges from 0.8 to 4 and water solubility from 2 to 23,800 mg/L Alister et al. (2014) reported the effect of log K_{ow} (ranging from 0.57 to 6.9), solubility (ranging from 0.005 to 4200 mg/L) and water DT_{50} on the removal of 6 pesticides in 2 winemaking processes (red and white wine). (Cabras, Garau, Melis, Pirisi, and Tuberoso, 1995), (Fernández et al., 2005), (Ruediger, Pardon, Sas, Godden, & Pollnitz, 2004), and (González-Rodríguez, Cancho-Grande, & Simal-Gándara, 2009) have reported a relationship between pesticide removal and pesticides' water solubility, whereas the lower the solubility, the greater the pesticide removal during fining. Oliva et al. (2007) did not find any correlation between pesticide removal and pesticides' properties, examining 3 fungicides (with log K_{ow} 3.24–4.65 and water solubility 0.011–2.6 mg/L), and using activated carbon, PVPP, egg albumin, blood albumin, silica gel and mixture of bentonite plus gelatin.

Winemakers are interested in an appropriate clarifying agent, which should combine the enhancement of clarity, color, aroma, etc. to pesticide removal. Thus, improvement of hygienic and sanitary quality of wines would be achieved. In addition, the effectiveness data provided are useful for the preparation of directives on maximum residues limits (MRL) in wines, which might include correction factors for the winemaking processes employed (Fernández et al., 2005). The study of pesticide removal from wines by clarification could be useful for similar water-systems contaminated with pesticides, beyond wines. MRLs have not been established in wine by the EU, but only in wine grape (EC–European Commission, 2005). Also, pesticide minimum requirement for drinking water is set at 0.1 μg/L for each pesticide and 0.5 μg/L for total pesticides (EC–European Commission, 1998).

The aim of this experimental work was to determine the effectiveness of 7 clarifying agents [activated carbon, bentonite, polyvinylpolypyrrolidone (PVPP), gelatin, egg albumin, isinglass (fish glue), and casein] at 2 doses to remove pesticides (selected with a wide range of log K_{ow} and water solubility, and belonging to 11 chemical groups) from a white wine, fortified with two pesticides mixtures or a single pesticide solution. In addition, the effect of K_{ow} and water solubility of pesticides on the outcome of clarification was determined. In the present research, the systematic and simultaneous examination of a great number and various mixtures of pesticides, and fining agents differs to that of previous reported studies in type, number, or mixtures of pesticides and clarifying agents tested. Also, this different approach, compared to that of previous researches, allows the confirmation of the relationship between pesticide hydrophobicity and fining effectiveness at every pesticide mixture for all the adsorbents tested. In addition, the antagonistic or synergistic effect among pesticides is revealed in pesticide mixtures. So, the results of this research enrich the data on the field of pesticide removal during wine clarification.

2. Materials and methods

2.1. Materials

A non-clarified and non-filtered wine, produced from a white Greek variety (Savvatiano), was used. The wine has the following characteristics: pH = 3.26, alcohol 11.75% v/v, volatile acidity 0.22 g/L (expressed as g/L tartaric acid), total acidity 5.2 g/L (expressed as g/L acetic acid), reducing sugars 1.1 g/L, SO2 free 29 mg/L, SO2 total 95 mg/L. Wine is a multicomponent acidic aqueous solution, and it is, due to its composition, an acidobasic ‘buffer’ solution, i.e. a modification in its chemical composition produces only a limited variation in pH (Ribereau-Gayon, Glories, Maujean, & Dudourdieu, 2006).

Seven clarifying agents were studied. Activated carbon extra pure food grade was purchased from Merck (Darmstadt, Germany). Bentonite, polyvinylpolypyrrolidone (PVPP), gelatin, egg albumin, isinglass (fish glue), and casein were purchased from Laffort (Bordeaux, France). Fining agents were added to the wine at 2 doses (Table 1) according to supplier's instructions, usually applied in