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Article

Retention of Phthalates in Wine Using Nanomaterials as Chemically Modified Clays with H_{20}, H_{30}, H_{40} Boltron Dendrimers

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Abstract: The presence of phthalic acid esters in wines presents a major risk to human health due to their very toxic metabolism. In this paper, aluminosilicate materials were used, with the aim of retaining various pollutants and unwanted compounds in wine. The pollutants tested were di-butyl and di-ethyl hexyl phthalates. They were tested and detected using the gas chromatography–mass spectrometry (CG-MS) analytical technique. Nanomaterials were prepared using sodium bentonite, and were chemically modified via impregnation using three types of Boltron dendrimers of second, third and fourth generations ($NBtH_{20}$, $NBtH_{30}$ and $NBtH_{40}$). The synthesized nanomaterials were characterized using the Brunauer–Emmett–Teller (BET) method, Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analysis. In this paper, two aspects were addressed: the first related to the retention of phthalate-type pollutants (phthalic acid esters—PAEs) and the second related to the protein and polyphenol levels in the white wine of the Aligoté grape variety. The results obtained in this study have a major impact on PAEs in wine, especially after treatment with $NBtH_{30}$ and $NBtH_{40}$ (volumes of 250–500 µL/10 mL wine), with the retention of the pollutants being up to 85%.

Keywords: oenology; bentonite; dendrimers; phthalates; polyphenols; white wine

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1. Introduction

Wine is an alcoholic beverage made up of 80% water, 12–15% ethyl alcohol, and a minor amount of constituents, namely 3% (acetaldehyde, glycerol, tartric acid, lactic acid and malic acid) [1]. Other compounds that can be present in wine are as follows: organic acids, sugars, polyphenolic compounds, nitrogenous compounds, enzymes, vitamins, lipids, volatile compounds, etc. Among the minor compounds in white wine, the most important are organic acids and phenolic compounds [2]. They significantly affect the quality of the wine from an organoleptic point of view [2,3]. Some wine constituents are able to react with large amounts of oxygen, but polyphenols are the most prone to oxidation [4]. The concentration of flavonoids in wine is strongly affected by the following stages of winemaking: pressing and maceration. They can affect the degree of extraction from the skin of the grape berries, but especially from the seeds, due to the high content of proanthocyanidins. The contents of the previously mentioned compounds can be found in white wine up to the level of 100 mg·L^{-1} [4] White wines have a wide variety of bio-polymeric compounds in their composition. Obtaining stable wines is achieved by reducing, as much as possible, the bio-polymeric compounds, because they are responsible for the instability of the final product (wine). To solve this impediment, winemakers resort to different treatment processes using materials capable of absorbing the unwanted protein compounds from the wine.

Phthalates (PAEs) are among the desirable compounds found in the materials used in the wine industry, and have a disruptive effect [5]. PAEs are added to the mass of plastics due to their flexibility and durability [6]. The molecular weight of these compounds is small and they are formed via the reaction of phthalic anhydride with linear or branched alcohols [7]. Phthalate migration rate studies of polymer coatings in food environments have demonstrated that PVC and rubber retain their ability to release a phthalate even after a long period of use.

The migration rate of phthalates in plastics depends on the chemical composition of the extraction medium. Environments with high polarities are the most contaminated, especially in cases in which the thermal factor intervenes. Wines are among the most frequently affected [8,9]. It has been found that, of the variety of PAEs, the most common, both in wine and in other food products, are those of the di-ethyl hexyl phthalate type (DEHP, shown in Figure 1a) [10–15] and di-butyl phthalate type (DBP, shown in Figure 1b) [10,12–14,16–18].

They significantly affect the health of the consumer. In their 99% purified form, PAEs are in the form of viscous, transparent, low-volatile, colorless, odorless, hydrophobic organic liquids under normal conditions, are insoluble in water, and have a high affinity for alcoholic solutions [5]. The daily intake of PAEs tolerated and established by the European Food Safety Authority (EFSA) is 50 μg·kg^{-1}bw for DEHP [19] and 10 μg·kg^{-1}bw for DBP [20–22]. The most common method for the identification and quantification of low concentrations of phthalates in alcoholic beverages is gas chromatography coupled to mass spectrometry (GC–MS) [5,12,14,18,21,23].

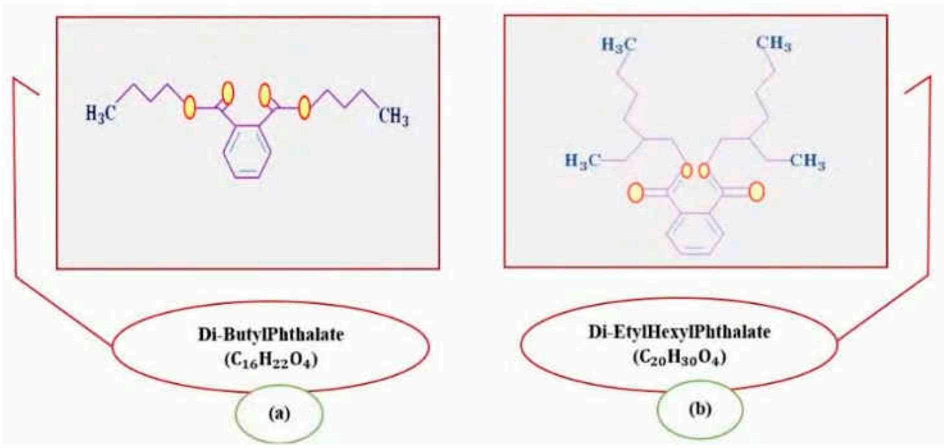

Figure 1. Representation of the chemical structure of Di-Butyl Phthalate (DBP) and (**a**) Di- Ethyl-Hexyl Phthalate (DEHP) (**b**) adapted from [22].

Wine forms tartaric salts with potassium or calcium ions, and this factor leads to the formation of a wine defect from an aesthetic point of view [23]. A solution to prevent such wine breakdowns would be the use of clay-absorbent materials enhanced with different organic compounds such as dendritic polyols. Among the materials with a stabilizing role, aluminosilicates are the most common [24]. Sodium bentonite is frequently used at the industrial level [25–28]. In the final product (wine), in addition to proteins, other unwanted compounds are present, including tartaric acid, malic acid, etc. Via the contact of white wine with the different materials used during the fermentation and maturation processes (corks, gaskets from fermentation tanks, rubber hoses), there is a risk of changing the composition of the final product [23].

Boltron-type dendrimers are dendritic polymers characterized by an intensely branched architecture with a large number of functional groups. Dendrimer structures are differentiated by their core, which is represented by polyalcohols or hydroxy acids [29,30]. The basic compounds obtained from these complex structures are hydroxyl-functional dendritic polyesters [25,26]. These dendrimers are formed via the polymerization of the particular core and of 2,2-dimethylol propionic acid. These polymers are known as bis-MPA, aliphatic compounds with tertiary ester bonds [31]. Dendrimers present certain specific characteristics, such as high thermal and chemical properties, solubility, complexation capacity, and compatibility. All these characteristics of dendrimers indicate the possibility of their use in the wine industry. Dendrimers have been used in winemaking as encapsulating agents to capture and remove tartaric acid (TA) from white and red wines [28–30]. The formation of potassium or calcium tartrate salts leads to the obtainment of visible crystals in the wine, this aesthetic defect not being desirable in the final product. By binding tartaric acid to the interior of the dendritic polymer, a dendrimer–tartaric acid-type complex is formed; this can be removed from the wine via ultrafiltration or reverse dialysis [32]. More recently, dendrimers have been used as the stabilizers of anthocyanins in young red wines (e.g., malvidin-3-glucoside, cyanidin-3-glucoside) [33]. Another utility of polymers is in the identification of metal ions in red wines, such as Pb(II), Co(II), Cu(II), Fe(III), and Zn(II) [34]. This alternative has been used for the capture of tartaric acid from white wine using different organic solutions, with different dendrimers used as encapsulating agents [32,35–38].

The aim of this paper is to highlight the effect of chemically modified natural materials on the adsorption of phthalates from white wines. The raw material used for intercalation with Boltron dendrimers was sodium bentonite due to its availability in nature, its low operating cost, and its good ability to absorb the colloidal dispersions present in the wine [39–43]. The contact of the nanomaterials and their use in the retention of phthalates represent important goals in the application of advanced materials in the food industry. The novelty of this article is its use of a cationic clay intercalated with Boltron dendrimers of different generations (second, third and fourth generations) (Figure 2), employed in the food industry as advanced materials that retain the phthalates present in alcoholic beverages such as white wine.

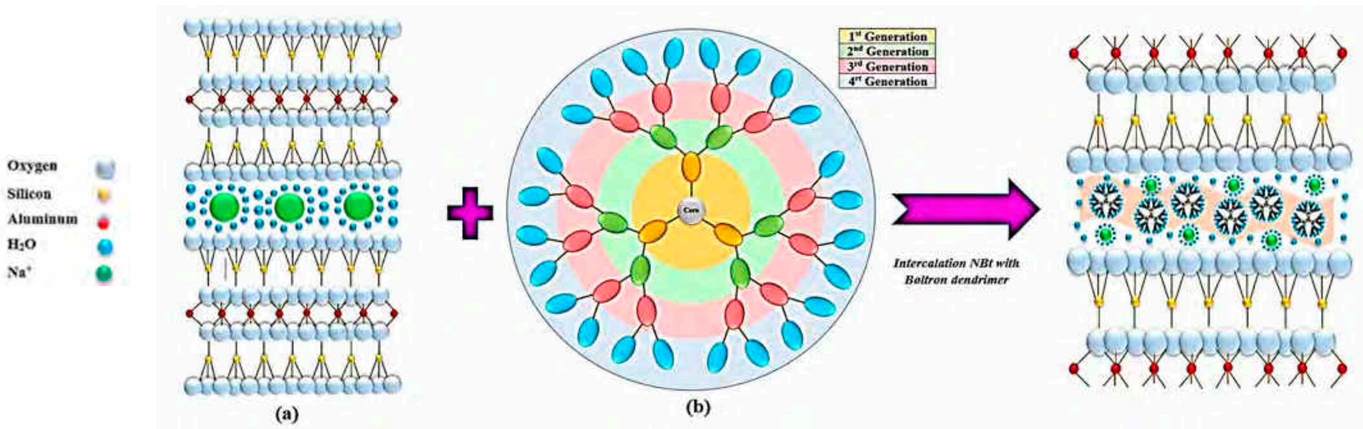

Figure 2. General representation of the impregnation of sodium bentonite NBt (**a**) with Boltron-type dendritic nanomolecules of second, third and fourth generations (**b**).

By treating white wine with hybrid organic–inorganic materials (bentonite–dendrimers), the effect of these nanomaterials on proteins and polyphenolic compounds in the wine was studied. This was performed by applying the thermal stability test, spectrophotometric analysis and making turbidity measurements. Another aspect monitored was the capture degree of DBP and DEHP phthalates from Aligoté white wine, identified with the help of gas chromatography coupled to mass spectrometry (GC–MS).

2. Materials and Methods

2.1. Materials

A white wine from the European Aligoté grape variety was selected for research. It was obtained in 2019, following a general technological process for white wines. The raw material was cultivated and processed at the Microvinification of the Department of Oenology, Technical University of Moldova, Republic of Moldova. The wine sample was filtered with a 0.45 µm microfilter and determined spectrophotometrically using the Analytik Jena Specord 250 Plus UV–Vis device. As polluting materials, two standard solutions of high-purity PAEs were chosen for this study, namely di-butyl phthalate (DBP, 99.8%) and dihexyl phthalate (DEHP 99.7%), both purchased from Sigma-Aldrich (Darmstadt, Germany).

The raw material used to obtain the adsorbent materials ($NBtH_{20}$, $NBtH_{30}$, and $NBtH_{40}$) was sodium bentonite Fluka (NBt) procured from Sigma-Aldrich, Germany. This was intercalated with Boltron dendrimers (second, third and fourth generation) purchased from Perstorpt Polyol (Toledo, OH, USA). Acetone and 70% ethyl alcohol were purchased from Sigma-Aldrich.

2.2. Modification of Clay-Based Material

Second-, third- and fourth-generation dendrimer solutions were obtained by dissolving 347 mg of the dendrimer of each generation in 10 mL of water/ethanol solution (in a 1:1 mass ratio) at room temperature and under constant stirring for 5 h. Then, 10 mL of the prepared dendrimer solution was added drop by drop over 1.5 g of NBt. After the intercalation of bentonite with each organic solution, they were placed in the thermostat at 308 K for 3 days, discontinuously, with resting periods of 7.5 h at 295 K. The nanomaterials obtained based on the clay chemically modified with dendrimers were further named $NBtH_{20}$, $NBtH_{30}$ and $NBtH_{40}$.

2.3. Preparation of Phthalic Solutions and Synthetic Solutions of Pollutants

Two synthetic phthalic solutions of di-butyl and di-ethylhexyl were prepared. From each phthalate solution (>99% concentration), 20 µL was taken. The sampled solution was placed in one Eppendorf tube, with each tube containing 1 mL of 70% ethanol solution. In the end, two different phthalic solutions of 2% concentration (DBP 2% and DEHP 2%) were obtained, which were immersed for 13–15 h at 276 K.

For the preparation of 17 wine samples, 10 mL of filtered Aligoté wine was used. The samples were prepared for synthetic contamination at room temperature (292–296 K). Then, 20 µL of 2% DBP solution and 20 µL of 2% DEHP solution were added to each white wine sample. After the addition of phthalates to the wine samples, the entire sample was shaken using a Hettich EBA200 centrifuge at 200 rpm for 5 min. After this time, the samples were left to rest for 15–20 min at room temperature. After resting, the samples were divided into four wine samples. These were put in contact with the sodium bentonite and with the three chemically modified nanomaterials via impregnation with Boltron dendrimers. For each clay adsorbent material, four white wine samples were allocated. The 17th wine sample was considered the control sample.

The first mini-sample was treated with the raw material (NBt), the second with $NBtH_{20}$, the third with $NBtH_{30}$ and the fourth with $NBtH_{40}$. The adsorbent materials used (5% concentration) were added to each wine sample in different volumes: 50, 100, 250 and 500 µL of adsorbent nanomaterial/10 mL wine. After adding the adsorbent materials, the 4 mini-samples of wine and the control sample were centrifuged (200 rpm, for 10–15 min), then immersed for 48 h in the cold (275–276 K).

2.4. Determination of the Degree of Protein Stability

After 48 h of cold immersion, the synthesized wine samples were left at room temperature for 35 min. Next, the control sample and the 4 series of wine treated with the four adsorbent nanomaterials (NBt, $NBtH_{20}$, $NBtH_{30}$, $NBtH_{40}$) were heated at 333 K for 60 min, then cooled at 295 K. To test the protein level in the treated wine, 5 mL of wine sample

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