

A NOVEL PROCESS AGAINST CORK TAIN

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Abstract

The latter-day development of nanotechnology has brought revolution in many scientific areas, such as material and biomedical engineering. The carbon nanostructures perform extraordinary properties making them potential useful in a great number of applications, such as energy storage, electrical circuits and as vessel for drug delivery. According to the current work, the use of Carbon NanoTubes (CNTs) in cork stopper processing is first suggested in order to improve final cork quality. The proposed treatment is based on the colmation technique, which is often applied by many cork industries for the superficial refinement of cork closures. The insertion of CNTs in the external porous surface of cork during colmation, combined with their high adsorption tendency against a variety of organic molecules can probably lead to better quality stoppers. The randomly sparse nanoparticles into the external cork structure is expected to act as a 'barrier' for odorous compounds, like 2,4,6-trichloroanisole (TCA), between cork and bottled wine, shielding the wine from the undesirable phenomenon of cork taint. The design of the suggested process with its technical advantages and disadvantages are cited in this paper, opening the route for its laboratory, pilot and industrial scale implementation.

keywords: *cork taint, cork stoppers, 2,4,6-trichloroanisole, process, colmation, carbon nanotubes*

Introduction

The undesirable alteration of wine taste and aroma, caused by the migration of odorous organic compounds from cork stoppers to bottled wine, is mainly known as 'cork taint' (Buser & others 1982). The organic molecule of 2,4,6-trichloroanisole (TCA) is largely involved to the majority (>80 %) of corking incidents (Buser & others 1982, Quercus Project 1996). As a consequence, cork industry has been accused of its followed manufacturing practices, included the chlorine bleaching treatment, which was gradually relinquished during the 90s (International Code of Cork Stopper Manufacturing Practices 2006). However, the phenomenon of cork taint is still appeared, inflicting sufferings on the economic status of relative industries and affecting their brand name reputation (Fuller 1995). Numerous attempts were conducted the last decade, i.e. research papers, patents and industrial innovations, targeting to a definitive solution of the discussed problem (Sefton & Simpson 2005). A significant number of these proposed processes is currently applied in pilot or/and industrial scale and the scientific community is awaiting the obtained results with excess interest. The evolution of nanotechnology offered a wide series of

technological solutions for many problems originated in various fields (Wikipedia 2008), demonstrating its usefulness and adaptability. The nanotechnology achievements and perspectives could be also proved as a valuable tool for the scientific efforts against cork taint. Carbon NanoTubes (CNTs) can be described as the material lying between fullerenes and graphite as a new member of Carbon allotropes and they have drawn a lot of attention because of their unusual physical properties (Anderson 2003). Future applications of CNTs include but are not limited to the nanowires, drug delivery, composite materials solar sails, hydrogen storage, micro machines and micro batteries (Anderson 2003). The extremely low size of CNTs (the diameter of a nanotube is in the order of a few nanometers (Wikipedia 2008)), their high tendency to adsorb organic molecules (Chen & others 2007) and their lacking of odor (Claveria 2008) constitute the major advantages of using CNTs in cork stoppers. According to previous studies, it was demonstrated that non polar aromatic compounds (i.e. 1,2,4,5 tetrachlorobenzene) were more strongly adsorbed on CNTs than non polar aliphatic compounds (Chen & others 2007). In addition it was investigated the adsorption of phenanthrene, naphthalene and 1-naphthol on multi-walled CNTs (Wang & others 2008), the adsorption of naphthalene, phenanthrene and pyrene onto six CNTs (Yang & others 2006) and finally the adsorption of n-hexane, benzene, trichloroethylene and acetone on two multi-walled CNTs (Shih & Li 2008). Furthermore, a polymeric filter containing CNTs wherein different types of metal are deposited was constructed and used in air conditioning systems for air sterilization and deodorization (Lee & others 2006). Notwithstanding that the aforementioned information and data enhance the aspect of CNTs usage in cork stoppers and other food applications, a detailed insight study on their toxic behavior must be implemented. Determining the toxicity of CNTs has been one of the most pressing questions in nanotechnology. Results from various scientific tests on cells have so far proven confusing, with some results indicating it to be highly toxic and others showing no signs of toxicity (Nano World 2006). Researchers at Rice University's Center for Biological and Environmental Nanotechnology (CBEN) have found that water-soluble carbon nanotubes can be made less cytotoxic to human skin cells as the functionalization of their sidewalls by chemical modification is increased (Sayes & others 2006).

According to this study, the novel approach of nanostructures use in cork material during its manufacturing process is suggested. Further experimental confirmation of the proposed process in lab and pilot scale is required in order to be successfully implemented in industrial scale in future.

Materials & Methods

The suggested system capable of treating the cork stoppers with nanoparticles (CNTs) is shown in the following figure.

The cylindrical vessel can be made of stainless steel 316 in order to increase its resistance during the operation and cleaning processes and avoid any potential adsorption of volatile compounds released by corks to its surrounding walls. In this point, it is worthy to mention that the proposed process could be combined to the colmation procedure, followed by many cork manufacturers for cork superficial refinement. The proposed process can be separately applied, in the case of a cork industry does not apply the colmation technique or it is difficult to adjust it to the suggested requirements. In the sequel, an appropriate motor must be installed for the vessel rotation and the rotation rate can be controlled via a fully programmable

inverter. The CNTs are contained in a separate sealed tank and they are automatically supplied into the cylindrical vessel via an appropriate spraying system. The CNTs can be used as a dry dust or after their dilution in an ethanol/water mixture (volume ratio: 1/9).

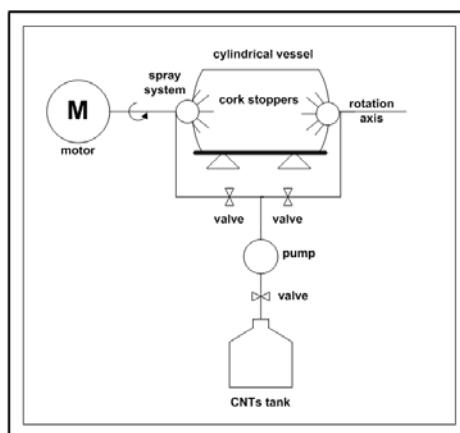


Figure 1. Schematic diagram of experimental configuration

The injection of CNTs spray into the rotated vessel must be taken place through its two opposite bases. Furthermore, an air tight vessel, hoods and mechanical ventilation systems must be used, in order to minimise any loss of CNTs at the surrounding environment and avoid any contact with the experienced staff. In the absence of engineering controls, personal protective equipment provides adequate safe handling protection (Safety data for carbon nanotubes, 2008). Finally, a specific number of cork closures can be placed in the vessel and treated according to the process operational conditions.

Discussion

The proposed process philosophy against cork taint is based on the cork closure treatment, during cork manufacturing and prior to bottling of wine. Especially, the cork stoppers during the application of colmation technique or not, must be sprayed with an appropriate amount of CNTs in powder form or in a liquid solution. The CNTs are probably distributed on the external porous surface of cork stoppers, providing a barrier to TCA migration between cork and wine phase, due to their high adsorption capability. As it has been demonstrated that TCA is slowly diffused in cork material and it is mainly located at the external layer of cork (Howland & others 1997, Capone & others 2002), there is no any further requirement for CNTs forced insertion in deeper layers of cork. In addition, the final step of cork manufacturing with the paraffin or silicone facing maybe reduces the CNTs losses from the stopper to the bottled wine. The last notification is crucial, as the scientific community still researches the CNTs impact on human and environment toxicology. So, the first prerequisite for commercial application of the process demands to secure that CNTs are massively remained on cork material and not dissolved in the wine at unallowable concentrations. Furthermore, during the process implementation, the following operational factors must be considered: 1) the filling percentage of the vessel determining by its operational volume and the number of treated cork stoppers, 2) the vessel rotation rate and 3) the amount and the type of CNTs. However the temperature and the relative humidity are not mentioned among the aforementioned parameters,

they must be controlled at accepted values for cork stoppers (i.e. T=25°C, RH=5-8%). The filling percentage and the rotation rate of the vessel must be determined after optimization, in order to avoid cork surface overlaps and increase the time contact between CNTs spray and cork stoppers. It is also very important to avoid any delignification of cork stoppers due to their each other collisions, which can be possibly happened at high rotation rates. The required amount of CNTs inserted into cork pores is highly depended on their toxicity, as it was previously mentioned, and the CNTs adsorption capacity against the TCA molecules. However, it can be easily concluded that the inserted amount of CNTs into cork body may be different between cork stoppers from different grades (different degree of morphological defects and porosity). The last observation reveals that in order to treat likely cork stoppers from various grades, different initial amounts of CNTs must be sprayed each time. Additionally, the type of CNTs seems to take a hand in the whole process. According to Chen & others (2007), the adsorption affinity of tetrachlorobenzene (on a unit surface area basis) to a single-walled CNT was much stronger than to multi-walled CNT, indicating a probable molecular sieving effect (Chen & others 2007). Single-walled CNTs and multi-walled CNTs differ in arrangement of graphene cylinders. Consequently, in the case of TCA molecule, due to its chemical similarity with the tetrachlorobenzene molecule, the use of single-walled CNTs seems to be preferable. Furthermore, it can be said that the proposed process is convenient. No complicated interventions in the cork manufacturing process are claimed. The cost of the process probably proved to be competitive, compared with other related processes (Sefton & Simpson 2005). New products of CNTs with improved quality and in lower prices are currently produced, making this process more feasible. The consumed CNTs amount per cork stopper in order to achieve the desirable result is a critical parameter for the process cost estimation. Finally, the process can be applied either in natural or in agglomerated cork stoppers before their agglomeration, in which cork taint is also observed.

Conclusions

Cork taint constitutes a global phenomenon that affects a significant portion of the bottled wine. Many technological solutions targeting to TCA elimination from cork stoppers have been suggested so far, but the incoming results obtained by their application indicate that the definitive win against cork taint is not yet achieved. However, the persistent research progress has brought us closest to the final point. In this study, a novel process is proposed in order to aid these attempts. The nanotechnology can be applied in the food engineering field and the current work is a characteristic example. The application of the proposed process may supply the humans who fight against cork taint with valuable information.

References

1. Anderson, SL. 2003. Downloaded from http://eed.gsfc.nasa.gov/562/SA_CarbonNanotubes.htm on 15/8/2008.
2. Buser, HR, Zanier, C & Tanner, H. 1982. Identification of 2,4,6-Trichloroanisole as a Potent Compound Causing Cork Taint in Wine. *J. Agric. Food Chem.* 30:359-62.
3. Capone, DL, Skouroumounis, GK & Sefton, MA. 2002. Permeation of 2,4,6-trichloroanisole through cork closures in wine bottles. *Aust. J. Grape Wine Res.* 8:196-99.

4. Chen, W. Duan, L & Zhu, D. 2007. Adsorption of Polar and Non-polar Organic Chemicals to Carbon Nanotubes. *Environ. Sci. Technol.* 41: 8295–8300.
5. Claveria, J. 2008. Downloaded from <http://www.dropsens.com/en/productos.html> on 25/7/2008.
6. Fuller, P. 1995. Closing in on an Industry Problem. *Aust. N. Z. Wine Ind. J.* 10:58-60.
7. Howland, PR. Pollnitz, AP. Liacopoulos, D. Mclean, HJ & Sefton, MA. 1997. The location of 2,4,6-trichloroanisole in a batch of contaminated wine corks. *Aust. J. Grape Wine Res.* 3:141-45.
8. International Code of Cork Stopper Manufacturing Practices. 2006. CE Liège (eds). 5th edition-English Version. Paris.
9. Lee, JK. Kim, YS & Park, CH. 2006. Downloaded from <http://www.freepatentsonline.com/7074260.html> on 13/8/2008.
10. Nano World: Nanotube toxicity exams differ. 2006. Downloaded from <http://www.physorg.com/news68394917.html> on 25/9/2008.
11. QUERCUS PROJECT. 1996. Qualitative Experiments to Determine the Components Responsible and Eliminate the Causes of Undesirable Sensory Characteristics in Drinks Stopped With Cork. European Union and CE Lieges contract No. AIR1-CT92-0372.
12. Safety data for carbon nanotubes. 2008. Downloaded from http://msds.chem.ox.ac.uk/CA/carbon_nanotubes.html on 14/5/08.
13. Sayes, CM. Liang, F. Hudson, JL. Mendez, J. Guo, W. Beach, JM. Moore, VC. Doyle, CD. West, JL. Billups, WE. Ausman, KD & Colvin, VL. 2006. Functionalization density dependence of single-walled carbon nanotubes cytotoxicity in vitro. *Toxicol. Lett.* 161:135-42.
14. Sefton, MA & Simpson, RF. 2005. Compounds causing cork taint and the factors affecting their transfer from natural cork closures to wine_A review. *Aust. J. Grape Wine Res.* 11:226-40.
15. Shih, YH & Li, MS. 2008. Adsorption of selected volatile organic vapors on multiwall carbon nanotubes. *J Hazard Mater.* 154:1-3.
16. Wang, X. Lu, J & Xing, B. 2008. Sorption of pyrene by regular and nanoscaled metal oxide particles: Influence of adsorbed organic matter. *Environ. Sci. Technol.* 42:3207–12.
17. Wikipedia. Downloaded from http://en.wikipedia.org/wiki/Carbon_nanotube_Wikipedia on 1/10/2008.
18. Yang, K. Zhu, L & Xing, B. 2006. Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials. *Environ. Sci. Technol.* 40:1855–61.