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# Removal of volatile organic compounds (VOCs) from water using mixtures of olive oil, lecithin, and vitamin E as phase transfer agents

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## ABSTRACT

Two methods to remove VOCs from water using the natural food additive, lecithin, assisted by olive oil or vitamin E were explored. Lecithin combined with olive oil was utilized in a phase exchange and solvent extraction process to remove VOCs from water into the olive oil layer. The addition of 0.5 ppm of lecithin together with the olive oil were found to be sufficient to remove halogenated and aromatic VOCs completely; however, the method was less efficient against ketones and esters due to their better water solubility and smaller molecular mass in comparison to other VOCs tested. The second method involved combining lecithin with vitamin E to produce an aqueous suspension of micelles that facilitated the removal of VOCs from water into the micelles, with the optimal ratio of lecithin to vitamin E found to be 82:18 w/w. The overall removal of VOCs from water using lecithin/vitamin E micelles was not as effective as lecithin/olive oil layers due to the problems faced when removing lecithin from the samples.

## 1. Introduction

Approximately 2.5% of the world's water supply is freshwater, but most of it is locked in ice caps, glaciers, permanent snow or stored underground [1]. Water purified from freshwater and alternate sources in areas lacking supplies are strictly regulated to safeguard the quality of drinking water. Although the amount of trihalomethanes (THMs), a type of disinfectant byproduct from the chlorination process, have to meet requirements set out by governing bodies [2,3], exceptions were found in preceding papers where several tap water samples exceeded the specified limit [4,5]. THMs that are known to be cytotoxic or carcinogenic include chloroform and bromodichloromethane [6]. They are part of a bigger group, volatile organic compounds (VOCs), characterized by their low boiling point and high mobility, increasing their potency and problems caused. The risk of VOCs present in water for consumption is not limited to ingestion alone as exposure through inhalation is very possible when participating in activities like showering [7–9]. One study demonstrated that the dosage of chloroform and the associated cancer risk from 10 min of showering can be greater than or equal to that from the daily water intake [9].

The amount of THMs in drinking water can be reduced by introducing coagulation [10] before chlorination to remove chlorine sensitive organic compounds and the usage of granular activated carbon (GAC) [11], air stripping [12] after chlorination for adsorption or purging . These methods have since been enhanced, and new approaches targeting THM removal which include membrane nanofiltration [13], carbon nanotubes [14], and combination techniques have been explored [15,16]. Systems such as GAC and nanofiltration though effective, have shortcomings associated with bacteria build up, fouling, the relative high cost of installation and operation [17,18]. Other than THMs, other VOCs with adverse effects when consumed such as styrene and formaldehyde have also been detected in drinking water due to migration from storage materials [19–21], while industrial chemicals like tetrachloroethylene can make their way into groundwater through improper waste disposal [22]. For these reasons, new methods for removing VOCs including THMs using natural and low-cost materials should be examined.

Lecithin, a natural emulsifier that can be obtained from soy and eggs, had been reported to form organogels and microemulsions with aid from co-surfactants under certain conditions and has been used as a form of drug delivery by encapsulating organic compounds [23–25]. The use of lecithin and *n*-butanol mixture microemulsions of ketoprofen with oleic acid as the oil phase resulted in enhanced permeation through human skin [24], and a similar safe carrier for tetracaine hydrochloride using microemulsions of lecithin, *n*-propanol, isopropyl myristate and water was also reported [25]. The encapsulation ability of lecithin requires the presence of additional compounds as it does not spontaneously form micelles in water but packs into a highly stable lamellar liquid crystalline phase [26]. Nevertheless, the formation of an emulsion with lecithin can be achieved in several different ways. In this

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research, the possibility of using lecithin assisted with non-toxic natural organic materials such as olive oil and vitamin E to remove different classes of VOCs including THMs from water was investigated.

## 2. Materials, sample preparation, and analysis

Two approaches for the removal of VOCs from water utilizing lecithin were examined. The first procedure involved the use of an organic phase (olive oil) in a phase transfer step originally proposed for the transfer of gold nanoparticles [27], while the second method involved the use of encapsulated vitamin E [28] as a foundation for emulsion formation. These methodologies were considered because the supporting materials involved are food or supplements that are safe for use, and relatively low in cost. The effectiveness of the purification processes was ascertained by comparing the amount of VOCs in a blank with the amount of VOCs in samples subjected to the water purification methods, with quantification carried out by purge and trap gas chromatography–mass spectrometry (PAT GC–MS).

### *2.1. Materials*

Lecithin (refined) and DL-α-tocopherol (vitamin E, 97%) used in the experiments were obtained from Alfa Aesar while olive oil (100%) was purchased from a local food supplier. Neat reference chemicals of internal/surrogate standards and VOCs used to test the efficiency of the purification processes were purchased from Alfa Aesar, Sigma-Aldrich, Merck, VWR, Fluka, Acros Organics, and TCI with purity greater than 95% [Table S1 in Supporting information]. Two stock solutions of the internal standards and VOCs tested (1 g $L^{-1}$) were made by diluting neat chemicals with Pestinorm PAT grade methanol from VWR. Calibration curves used to quantify the relative integrated areas were prepared by injecting 2–10 μL of diluted stock solutions into ultrapure water (Millipore Milli-Q Integral 5) to achieve an internal standard concentration of 5 μg $L^{-1}$ and calibration range of 0.25–100 μg $L^{-1}$. All samples tested contained 5 μg $L^{-1}$ of the internal standard for quantitative analysis.

### *2.2. Sample preparation*

#### *2.2.1. Lecithin with olive oil*

Samples were prepared by weighing lecithin (0.01–100 mg) into a 40 mL amber glass vial with an open top cap sealed with septum before the addition of 20 mL of ultrapure water, 4 μL of diluted stock solution (200 mg $L^{-1}$), a stirrer bar and 5 mL of olive oil. The vial was stirred at room temperature for 30 min, and samples were further diluted to their final concentrations of 15 μg $L^{-1}$ for preliminary studies and 20 μg $L^{-1}$ for optimization studies after removal of the olive oil layer if present. A blank and a control sample were prepared in similar fashion with the absence of lecithin and lecithin/olive oil respectively, for comparison. Samples and blanks in the preliminary studies were centrifuged after the removal of the olive oil layer using a Sorvall Lynx 6000 centrifuge (Thermo Scientific) 2 times at 23,000 rpm, while no further treatment was performed with samples and blanks in the optimization studies. Analysis of the samples were performed by a PAT GC–MS system described in the sample analysis section.

#### *2.2.2. Lecithin with vitamin E*

Lecithin encapsulated vitamin E micelles were first prepared by slow rotatory evaporation of 2 mL chloroform containing weighed vitamin E (0.01–0.10 g) and lecithin (0.05–0.10 g) in a 50 mL round bottom flask prior to drying under vacuum overnight. Into the round bottom flask, 20 mL of ultrapure water spiked with 4 μL of diluted stock solution (200 mg $L^{-1}$) was stirred at 40 °C or sonicated for 1 h in the preliminary studies and only stirred at 40 °C for 1 h for optimization studies. Sonicating or stirring at 40 °C is required for the uniform encapsulation of vitamin E in lecithin. Water samples were centrifuged 2 times at 23,000 rpm for 20 min using a Sorvall Lynx 6000 centrifuge. Similar treatment was performed on the blank prepared without lecithin and vitamin E while the final dilution was performed on the samples and blank to achieve their final concentrations of 10 μg $L^{-1}$ for sonicated samples and 20 μg $L^{-1}$ for stirred samples. Analysis of the samples were also performed by a PAT GC–MS system described in the Sample analysis Section.

### *2.3. Sample analysis*

An Atomx PAT system from Teledyne Tekmar was equipped with a 5 mL nitrogen gas (99.999% from Air Products) sparger and a #9 analytical trap. The analysis method was optimized by purging at 50 mL $min^{-1}$ for 10.4 min followed by dry purging at 100 mL $min^{-1}$ (0.25 min) with samples kept at 40 °C. The trap was then preheated at 245 °C for 0.25 min before desorption at 250 °C for 1.5 min and baked for 15 min at 260 °C to reduce carryover for the next run. All VOCs tested with this method had relative standard deviations ≤ 20% and percentage recoveries within the range of 80–120% using toluene-$_{D8}$ and *p*-bromofluorobenzene as the internal standards. The PAT system was joined to a GC–MS system (7890A GC system and 5975C inert MSD with Triple-Axis Detector) from Agilent Technologies that was furnished with a 60 m DB-VRX column using helium gas (99.999%) from Air Products as the mobile phase. Scan mode using electron ionization (EI) with quadrupole mass separator was set to perform scans from 35 to 300 amu. Samples were introduced into the system with a 1:4 splitting ratio and separation through oven temperature programming was set to hold at 30 °C for 7 min before ramping at 40 °C $min^{-1}$–145 °C (3 min), 40 °C $min^{-1}$–150 °C (5.8 min) and 60 °C $min^{-1}$–200 °C (4 min). The solvent delay was set to 7 min for lecithin/olive oil samples and 11.5 min for lecithin/vitamin E samples. The data obtained were processed via the Environmental data analysis program.

## 3. Results and discussion

### *3.1. Lecithin with olive oil*

#### *3.1.1. Preliminary studies*

PAT GC–MS analysis of VOC residues remaining in the aqueous layer after treatment with lecithin and olive indicated a reduction of between 66 and 71% when compared with a control blank without olive oil and lecithin (Table 1). The bulk reduction in the VOC residues concentration below that of the blank was mainly attributed to the presence of olive oil, while a small further increment of 9–14% in the total residual VOCs reduction was caused by the addition of 250 ppm and 5000 ppm of lecithin. Olive oil alone was observed to be effective in lowering the concentration of all VOCs in the aqueous phase through solvent extraction with the exception of hexanal. Olive oil was used due to its availability, and as a representation of edible oil, however, hexanal is naturally present in olive oil [29], thus it was found to be added into the treated water instead of being removed from the water samples. The addition of hexanal can be avoided by using another edible oil that does not naturally contain VOCs. The proposed use of edible oil for the removal of VOCs, though uncommon, has been reported in the past where sunflower oil was used in a membrane assisted solvent extraction (MASX) system for VOCs removal from groundwater with a semi-permeable membrane that acted as a barrier between the contaminated water and oil [30].

The theoretical concentration of residual VOCs in the aqueous layer of the control blank without olive oil and lecithin should have been 15 μg $L^{-1}$ after dilution (Table 1). However, all compounds were detected at concentrations lower than this because of the natural ability of the VOCs to escape from the water during the sample preparation steps. The subjection of water samples to centrifugation for the removal of lecithin could also have encouraged the discharge of VOCs. The use of