



Development of natural sorbent based micro-solid-phase extraction for determination of phthalate esters in milk samples



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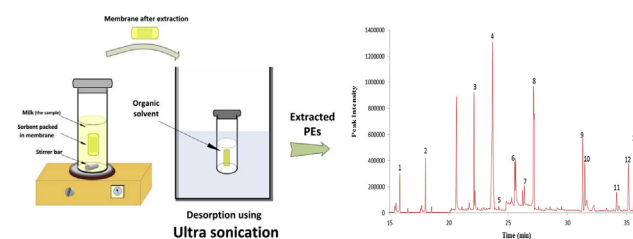
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HIGHLIGHTS

- For the first time, seed powder of *Moringa oleifera* was used as sorbent for micro-solid phase extraction.
- A simple and efficient analytical method for quantifying phthalates in milk samples was developed.
- This natural sorbent that is cheap and readily available and its performance was comparable with synthetic sorbents.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, a natural sorbent based micro-solid phase extraction (μ -SPE) was developed for determination of phthalate esters in milk samples. For the first time, an efficient and cost effective natural material (seed powder of *Moringa oleifera*) was employed as sorbent in μ -SPE. The sorbent was found to be naturally enriched with variety of functional groups and having a network of interconnected fibers. This method of extraction integrates different steps such as removal of proteins and fatty stuff, extraction and pre-concentration of target analytes into a single step. Thirteen phthalate esters were selected as target compounds for the development and evaluation of method. Some key parameters affecting the extraction efficiency were optimized, including selection of membrane, selection and amount of sorbent, extraction time, desorption solvent, volume of desorption solvent, desorption time and effect of salt addition. Under the optimum conditions, very good linearity was achieved for all the analytes with coefficient of determinations (R^2) ranging between 0.9768 and 0.9977. The limits of detection ranged from 0.01 to 1.2 $\mu\text{g L}^{-1}$. Proposed method showed satisfactory reproducibility with relative standard deviations ranging from 3.6% to 10.2% ($n = 7$). Finally, the developed method was applied to tetra pack and bottled milk samples for the determination of phthalate esters. The performance of natural sorbent based μ -SPE was better or comparable to the methods reported in the literature.

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1. Introduction

Phthalate esters (PEs) are famous class of polymer additives, which are used to introduce plasticity and durability to polyvinyl chloride (PVC) and other plastic materials. Since, they are not chemically bound to the structure of the polymer chains in plastics, they can migrate from plastics to the substances they are in contact with. The considerable environmental concern arises from their migration to food materials and water [1].

PEs have been specially considered from the perspective of their health implications on the human and wildlife. They are reported to induce reproductive, developmental and neurological disorders and thus considered as endocrine disrupters (EDCs) [2–4]. Due to their potential risks to human health and environment, PEs have been placed in priority pollutant list issued by United States Environmental Protection Agency (USEPA). Ingestion of contaminated food is major route of human exposure to PEs. Therefore, it is highly desired to develop sensitive analytical methods for trace level monitoring of PEs in food.

Due to its nutritional value and immunological benefits to infants and aged people, milk stands among imperious and highly consumed foods. Thus, monitoring of potential pollutants such as PEs in milk samples has great significance from human health perspective [5]. Milk can get contaminated with PEs through different sources including environmental diffusion, direct uptake by the animals through air or food, and processing by contact with different plastics, pipes, containers etc. [6]. In dairy forms and milk processing units, bulk transfer of milk between tankers and storage tanks is carried out through plastic pipes which can introduce PEs into milk [7]. Machine milking, where milk comes in contact with rubber parts of the machine, was also reported to enhance PE contents in milk [8].

Since milk represents a very complex matrix which is enriched with fats, lipids, carbohydrates, vitamins and minerals. Extraction of target compounds from milk samples is a rather challenging task. Conventional extraction methods such as liquid–liquid extraction and solid phase extraction require large amounts of solvents, samples and adsorbent materials. Furthermore, they are labor and time extensive and materials have lesser possibility to be reused. Thus, sample preparation scientists are nowadays dedicated to develop efficient, green, inexpensive and miniaturized extraction procedures in order to extract and pre-concentrate the analytes of interest prior to instrumental analysis [5]. Hence, over a period of time, number of microextraction methods have been developed for extraction of PEs in milk samples. In this regard, most commonly used methods are dispersive liquid–liquid extraction (DLLME) [5,9] and headspace solid phase microextraction (HS-SPME) [10]. For DLLME, clean samples are preferred for proper phase separation. Additionally, complex samples like milk cannot be used directly without pre-treatment. In order to remove proteins and fatty stuff from the samples, DLLME involves some additional steps such as use of number of organic solvents, which are not desired when analyzing PEs because PE residues can be found even in organic solvents and they are abundant in laboratory environment [11]. Moreover, pretreatment of proteins and fatty stuff using organic solvents such as methanol and acetonitrile may lead to loss or dilution of the target analytes. HS-SPME also has several limitations when dealing with PEs, particularly most of PEs show low volatility and reasonably high temperatures are required to vaporize PEs. In addition, SPME fibers are expensive and highly fragile [12].

In the current study, we applied porous membrane protected micro-solid phase extraction (μ -SPE) for extraction of PEs in milk samples. This technique was first introduced in 2006 [13] and is increasingly popular sample preparation method for different classes of organic compounds [14–16] present in food [17–19],

environmental [20,21], and biological [22,23] matrices. Technique continued to evolve over the period of time and it was assisted by vortex [21], microwave [24], and by combining with other extraction approaches [17,25].

In most of the previous studies, synthetic sorbents were used in μ -SPE. Although these sorbents offer unique advantages such as high affinity and selectivity toward target compounds but their preparation is labor and time extensive due to extended synthesis procedures. Any small variations in synthesis conditions may affect the activity of sorbent to a large extent. Likewise, the consumption of large amount of chemicals for synthesis of selective sorbents is hazardous both for workers and environment and contradicts basic rules of green chemistry approaches. Hence, there is a pressing need to explore green and readily available sorbent materials for extraction applications. Thus, low cost, easily assessable and disposable natural sorbents derived from plants can be an alternative.

We tested different natural sorbents for extraction of PEs in milk samples. Inspired from its better extraction efficiency and highly fibrous, heterogeneous and naturally functionalized surface, seed powder of *Moringa oleifera* (*M. oleifera*) was selected as sorbent. *M. oleifera* belongs Moringaceae family and it grows in many countries. It is an environment friendly, non-toxic and biodegradable sorbent [26]. A recent review article describes potential of *M. oleifera* for treatment of water and wastewater [27]. In addition, it has been widely used for removal of metals [28] [29] and dyes [30] in aqueous solutions. However, in few studies, it has been employed for analytical extractions [31]. To best of our knowledge, this is the first report where seed powder of *M. oleifera* is used as sorbent for extraction of PEs.

2. Experimental

2.1. Chemicals and materials

The mixture of PE standards was purchased from Restek (Bellevue, PA, USA). Following 13 compounds were considered for analysis from the mixture: dimethylphthalate (DMP), diethylphthalate (DEP), diisobutyl phthalate (DIBP), di-n-butylphthalate (DNBP), bis(2-methoxyethyl)phthalate (BMEP), bis(4-methyl-2-pentyl)phthalate (BMPP), bis(2-ethoxyethyl)phthalate (BEEP), dipentylphthalate (DPP), di-n-hexyl phthalate (DNHP), benzyl butyl phthalate (BBP), bis(2-n-butoxyethyl) phthalate (BBEP), dicyclohexyl phthalate (DCHP), bis(2-ethylhexyl)phthalate (BEHP). HPLC-grade toluene, acetone, acetonitrile, carbon tetrachloride and n-hexane were purchased from Tedia Company (Fairfield, OH, USA). Ultrapure water was produced on a Siemens Ultra Clear water purification system. Q3/2 Accurel 2E HF (R/P) polypropylene (PP) membrane sheet (157 μ m thickness, 0.2 μ m pore size) was purchased from Membrana (Wuppertal, Germany) and used for fabricating envelopes for the μ -SPE device. Cellulose acetate (0.2 μ m pore size, 47 mm diameter), polytetrafluoroethylene (PTFE) (0.2 μ m pore size, 47 mm diameter) and polycarbonate (0.2 μ m pore size, 47 mm diameter) were purchased from Advantec (Toyo Roshi Kaisha, Japan). C₁₈ was obtained from Alltech (Deerfield, USA). Dried *M. oleifera* seeds were purchased from local market (Alkhubar, Saudi Arabia) and ground to powder before using as sorbent. Banana peels were properly dried and powdered to use as sorbent and rice husk was obtained by a rice mill in India.

2.2. GC–MS analysis

Analysis was carried out using Shimadzu QP2010 GC–MS system equipped with a Shimadzu AOC-20i autosampler and Rxi -5 Sil MS (Restek) fused silica capillary column (30 mm \times 0.25 mm

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