Detection and Remediation of Dibutyl Phthalate in Plastic Bottle-Packaged Drinking Water

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DOI:10.37648/ijrst.v14i02.004

[1]*Received: 20 March 2024; Accepted: 15 June 2024; Published: 20 June 2024*

ABSTRACT

In the present study, we have reported the detection of Dibutyl Phthalate (DBP), a plasticizer used to make plastic material processable but is harmful to human health. Plastic water storage bottles available in the local market were used for sampling. The samples were divided into two groups based on different localities which included local city market and the markets on the outskirt of the city. The amount of DBP in the drinking water was detected and a simple water purification method was developed based on passing the contaminated water through a pre-treated sawdust glass column. This study will be useful for constructing a drinking water treatment plant on an economical basis.

Keywords: *Dibutyl Phthalate; Plasticizers; Leaching; Sawdust*

INTRODUCTION

Phthalate esters are chemical compounds that are added to various materials to improve their flexibility, durability and transparency [1, 2]. They are available in a wide variety of forms, and humans are highly susceptible to exposure. They are abundantly produced plasticizers, despite their established action as endocrine-disrupting chemicals and their severe impact on human health [3,4]. The most commonly used phthalates include bis(2-ethylhexyl) phthalate (DEHP), diisodecyl phthalate (DiDP), diisononyl phthalate (DiNP), Diethyl phthalate (DEP), Dibutyl phthalate (DBP), and benzyl butyl phthalate (BBP) [11]. Out of these, dibutyl phthalate (DBP) is the most widely used derivative in various consumer products and medical devices (Fig. 1). DBP, a popular plasticizer is used in the manufacturing of flexible polyvinyl chloride (PVC) goods, is also known as an endocrine disruptor. Since phthalate esters are attached to plastic polymers by weak van der Waals or hydrogen bonds, therefore they can leach from plastic goods easily and enter into the environment, water, or sediment easily. DBP along with its endocrine disruptor activity can also cause birth defects and developmental disorders [5-10].

[1] How to cite the article: Tomer S., Soni H.P..; June 2024; Detection and Remediation of Dibutyl Phthalate in Plastic Bottle-Packaged Drinking Water; *International Journal of Research in Science and Technology*, Vol 14, Issue 2, 35-41, DOI: http://doi.org/10.37648/ijrst.v14i02.004

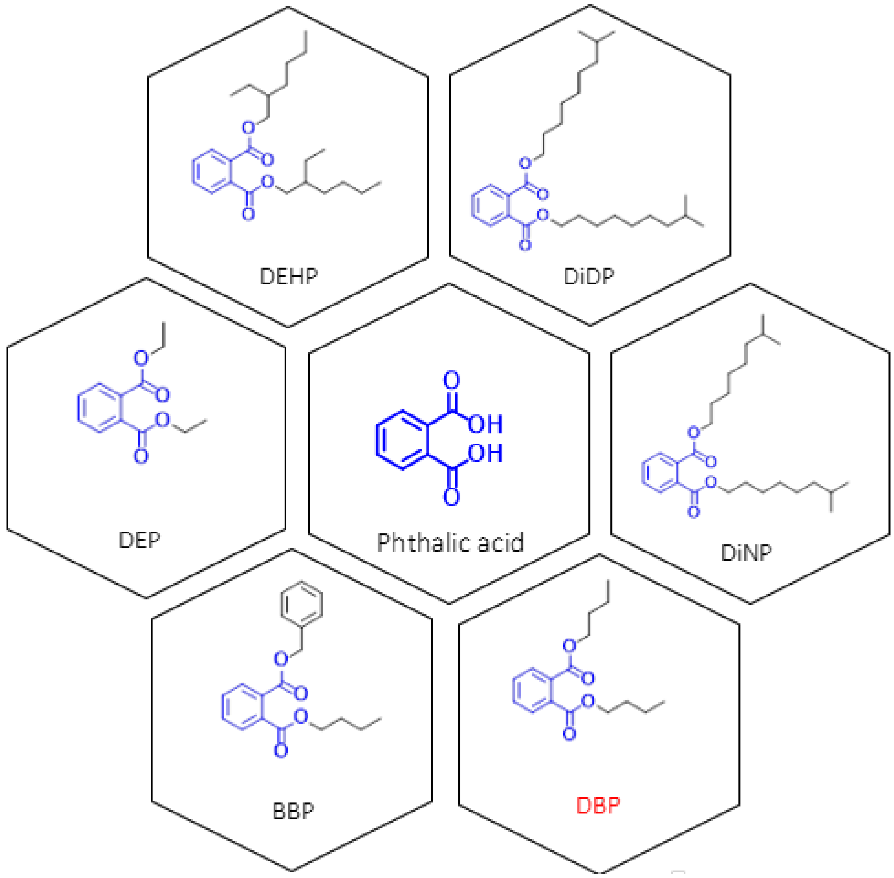

Figure 1: Chemical structures of common phthalates.

Dietary supplements, medical equipment, kids' toys, and other packaging materials commonly use DBP as a plasticizer [12]. On the European Union's list of possible endocrine disruptors, it is, nevertheless, classified as a category-1 endocrine disruptive chemical [13]. The European Union has classified DBP as a substance of very high concern because of its endocrine disruptive and reproductively harmful qualities. Women who are exposed to phthalates may experience infertility, endometriosis, breast cancer, early menarche, breast development, and pregnancy difficulties, as per research [14, 15, 16, 17]. Their urine and secretions contain mono-ester mono-butyl phthalate (MBP), which is the product of DBP hydrolysis. Compared to other environmental pollutants, phthalates are metabolized more quickly [18, 19]. If human neonates are exposed to phthalates during a critical stage of perinatal development, it could have negative developmental effects [20, 21]. Additionally, it has been observed that baby boys whose mothers had greater urine levels of phthalate metabolites had shorter anogenital distances (AGD). Short-branched phthalates are primarily eliminated in urine as its monoester phthalates. The more long-branched phthalates undergo multiple biotransformations, before they are expelled in urine and faeces, frequently as conjugated compounds, as shown in Fig. 2. [22-32].

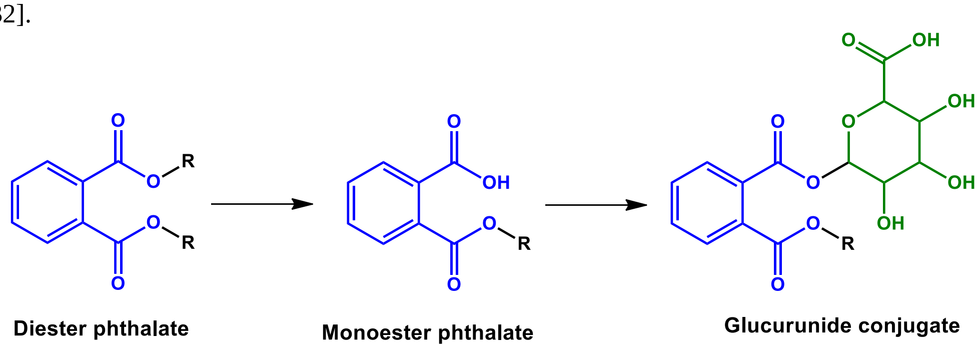

Figure 2. Metabolic pathway for phthalates

The use of phthalate esters in a range of industrial goods has been controlled and limited by several nations, including the US, China, Japan, and the European Union. For example, the Environmental Quality Standards for Surface Water [33] and Drinking Water Quality Standard [34] in China specify the DBP and DEHP limitations as 3.00 and 8.00 μg L^{-1}, respectively. According to the Environmental Quality Standards for Surface Water and Drinking Water Quality Standard, the US EPA established the concentration limits for DEHP and DBP at 2.00 μg L^{-1} and 2.00 mg L^{-1}, respectively. Restrictions on phthalates have been suggested in numerous Asian and Western countries since the year 2000. Japan outlawed DINP and DEHP in toys as well as DEHP in gloves used to handle food in 2001. Europe has prohibited the use of DEHP, DBP, and BBP in toys and childcare goods made of PVC and other plasticized materials since 2007. Additionally, products that can come into contact with children's mouths are prohibited from containing DINP, DIDP, or di-n-octyl phthalate (DnOP) [35, 36]. Recently, di-isobutyl phthalate (DiBP) was added to the restrictions in 2018 in 28 EU countries [37].

Therefore, it was thought of interest to study the DBP contamination in food items including plastic water storage bottles and pouches which is essential to give a solid scientific foundation for setting food safety regulations. Hence, in the present short study, we have developed an HPLC method to detect the phthalates leached from the plastic articles into the water in contact. We have also developed a simple method which can be easily implemented to remove the phthalates from the contaminated water.

MATERIALS AND METHODS

Chemicals and standard

Methanol and acetonitrile of HPLC grade were obtained from Fisher Scientific. Dibutyl phthalate (DBP) was purchased from Sigma-Aldrich.

Sample collection

Six different brands of widely consumed bottled drinking water were purchased from the nearby market and five locally manufactured brands of bottled drinking water were purchased from the outskirts of the city.
All the samples were collected in newly purchased and thoroughly cleaned glass vials and were stored refrigerated until analysis.

Analytical methods

HPLC system equipped with UV-Visible detector, quaternary gradient pump and auto injector. The chromatographic parameters were X-Bridge C18 (250 mm x 4.6 mm), 5.0 µm, diluent Water: Methanol: 250:750 (V/V) and detector wavelength of 205 nm. The flow rate was 1.5 mL/min and the Injection volume of 75 µL. Total run time was 50 minutes and the Column oven temperature was 25ºC.

Mobile phase was prepared by adding 1000mL of Acetonitrile to 1000mL of 0.1% solution of orthophosphoric acid solution.

Standard solution was made by dissolving 70.0 mg of Dibutyl phthalate in 25mL diluent. One mL of this solution was further diluted to 25mL by using diluent. 1 mL of this solution was further diluted to 25mL by using diluent. 1 mL of this solution was further diluted to 10mL by using diluent.

Test sample was prepared by dissolving 300 mg of sample in 2mL diluent.

$$\text{Content of Dibutyl phthalate (ppm): } = \frac{\text{Area due to sample x Weight of standard x 2 x 1000000}}{\text{Area due to standard x 25 x 25 x 10 x weight of sample}}$$

RESULTS AND DISCUSSION

Two types of plastic water bottles, one from the local nearby market with six different brands and one from the outskirts of the city with five locally manufacturing brands were collected for the purpose. The bottles were used before the expiry date of the manufacturing.

Plastic pouches (generally made from LDPE) which are generally used to store little quantity of the water, cheap, and easily available were collected. The water sample collected from the glass storage bottle were used as a control. The results are reported in Table 1.

Table 1. Detection of DBP content in the water samples collected from the different commercial brands and types of plastic storage bottles through the HPLC analyses.

Sample	Description	Brand	Storage temperature while sampling	Dibutyl phthalate (DBP), ppm
1	Plastic bottle 1	Brand 1	Refrigeration	0
2	Plastic bottle 2	Brand 2	Refrigeration	0
3	Plastic bottle 3	Brand 3	Refrigeration	0
4	Plastic bottle 4	Brand 4	Refrigeration	0
5	Glass bottle	Brand 5	Refrigeration	0
6	Glass bottle	Brand 6	Refrigeration	0
7	Plastic bottle 5	Brand 1*	Refrigeration	188
8	Plastic bottle 6	Brand 2*	Refrigeration	364
9	Plastic bottle 7	Brand 3*	Refrigeration	230
10	Plastic bottle 7	Brand 3*	Room temperature	220
11	Plastic bottle 8	Brand 4*	Refrigeration	532
12	Plastic bottle 8	Brand 4*	Room temperature	464
13	Plastic bottle 9	Brand 5*	Refrigeration	524
14	Plastic bottle 9	Brand 5	Room temperature	442
15	Plastic pouch	-	Refrigeration	886

*Locally manufactured brands

It can be observed from Table 1 that the water sample collected from the bottles of locally manufactured 5 brands contain DBP level ranging from 188 to 450 ppm and the pouches made of LDPE sheet possess maximum amount of DBP i.e., 886 ppm while the water collected from the bottles of standard brands do not contains DBP.

In the next experiment, as can be seen in the Fig. 3, from nearby saw mill, saw dust was collected from pine tree wood and treated to make it clean and impurities free. Then the treated saw dust was filled and packed in a glass column and the above collected water sample was passed through the same. The eluted water from the saw dust column was again analyzed for DBP content.

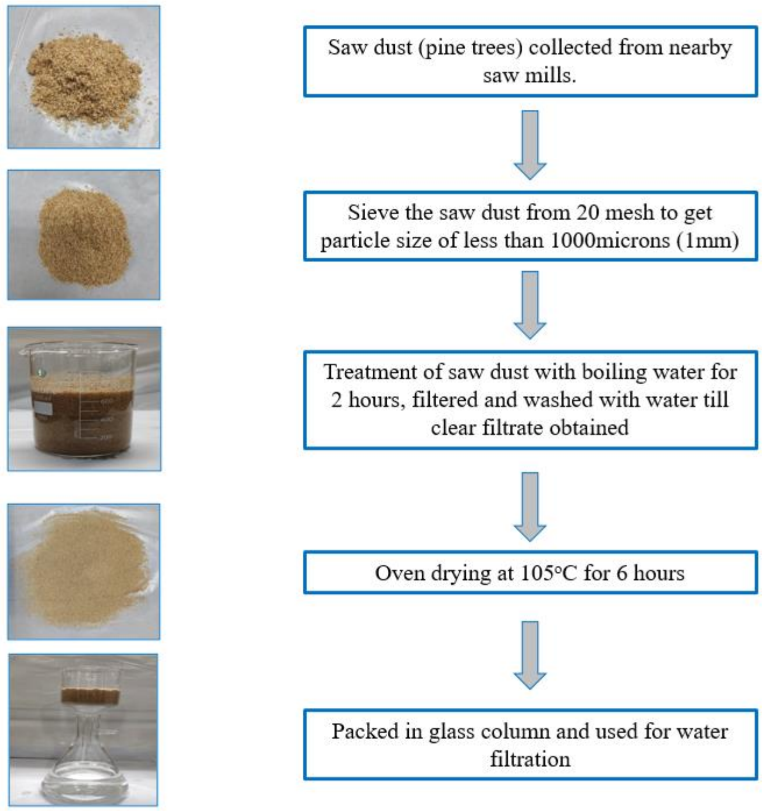

Figure 3. Treatment procedure for sawdust to make water sample DBP free.

Table 2. Detection of DBP in saw dust treated water. *

Sample	**Saw dust quantity (g)**	**Quantity (liters)**	**Dibutyl phthalate content (ppm)**
1		20	0
2		30	0
3	50	40	6

Water having DBP (sample of brand 4, 5*, and plastic pouch) passed through saw dust column.

It can be seen from Table 2 that the processed saw dust about 50g can completely remove dibutyl phthalate from the water sample up to 30 liters which has a dibutyl phthalate of about 500 ppm.

CONCLUSION

The DBP content in the water samples collected from the different brands of plastic bottle was analyzed and it can be concluded from this study that the DBP plasticizer can leach to drinking water if the plastic bottle used for its storage is not properly processed during the addition of plasticizers may be due to economic or other reasons. When the DBP-contaminated water was passed through the pretreated sawdust-packed glass column, it could be effectively made DBP-free. This small study may be useful for the economical set-up of a water purification plant.

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