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ORIGINAL ARTICLE

Determination of Alkylphenols and Alkylphenol Ethoxylates in Some of the Textile Wastewater Samples in Dhaka Division, Bangladesh

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KEYWORDS

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LC-MS

ABSTRACT: Textile is one of the biggest industries and it has an enormous impact on the global economy. However, the textile industry is labelled as the most polluting of all the industries and this is due to its contaminated wastewater. Textile wastewater contains organic hazardous compounds like alkylphenols (APs) such as nonylphenols (NPs), and alkylphenol ethoxylates (APEOs) for example nonylphenol ethoxylates (NPEOs), which may come from various detergents, wetting agents, emulsifying agents, etc. used in textile industries. Literature review revealed that no work was reported on the APs and APEOs in the textile wastewater of Bangladesh. This study reports the status of some APs and some APEOs after assessing wastewater of some textile industries in Dhaka, Bangladesh. Investigations were carried out with the wastewater of seven textile industries located in the Dhaka Division, Bangladesh. Tests were carried out by an Agilent Liquid Chromatography-Mass Spectrometer (LC-MS). The results revealed that none of the wastewater samples contained APs, and APEOs other than nonylphenol ethoxylates (NPEOs) a form of APEOs. And it might have released from the textile products treating stuff through dissolution process. Among all the seven industries, two industries (28%) contained nonylphenol ethoxylates (NPEOs). The mean concentrations of the detected NPEOs were determined as 11.27 ± 0.24 µg L^{-1} and 14.01 ± 0.09 µg L^{-1} in the wastewater of the mentioned two industries. The levels of the observed concentrations of NPEOs were much higher than the specified limits for textile wastewater. Findings of the present work will create pressure on the textile industries of home and abroad for treating textile wastewater effectively and not letting APEOs cum NPEOs in the wastewater. And such activities all over will pave the way to save the ecological system.

INTRODUCTION

Bangladesh is heading towards the goal of becoming a middle-income country by 2021 [1]. The textile industry is a driving force towards this economic development. With all the pros of the textile industry, there are some serious cons of concern as it is causing environmental pollution indiscriminately. Wastewater is the main bane for damaging the environment and thus effluents from textile industries are declared as the most polluting of all industrial

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sectors [2-3]. Wastewater is being discharged into water bodies nearby the factories and polluting the water, aquatic life, soil, and even the groundwater by leaching [4-7]. Wastewater treatment is critical because of the presence of numerous hazardous organic and inorganic materials [8-9]. From environmental and social perspectives, organic materials like APs, APEOs, etc. are now the biggest environmental and health concern. Organic materials are being discussed much for their hazardous effects, such as alkylphenol ethoxylates (APEOs) are said to be endocrine disrupters in wildlife and human being [10-11] and they are emerging as a prominent pollutant [12]. The APs and APEOs (Figure 1) may contain alkyl groups (R-) of various lengths, may be linear or branched and may bind at various locations around the phenol ring (ortho, meta, and para positions). When R = C_9H_{19}-, on the left-hand side structure (Figure 1) then it is known as nonylphenols (NPs) while if R = C_9H_{19}- on the right-hand side structure (Figure 1) then that one is known as nonylphenol ethoxylates (NPEOs).

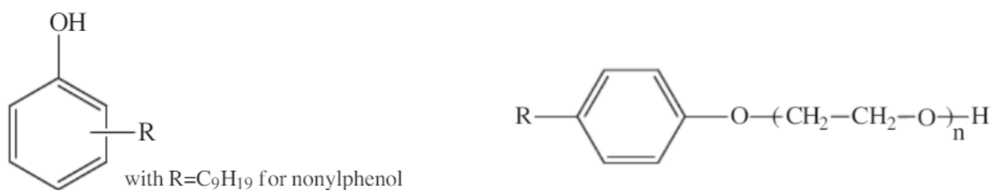

Figure 1. General molecular structure for alkylphenols (APs) on the left and alkylphenol ethoxylates (APEOs) on the right, where 'n' is the average number of moles of ethylene oxide per mole of alkylphenol.

Literature review in local context showed that a considerable number of works were done to detect and estimate any or some of the following physicochemical parameter TDS, TSS, DO, BOD, COD, EC, and pH [13] and some heavy metals [14] pertaining to wastewater of textile Industries of Bangladesh. Loos et al., (2007) [15] found NPEOs (4.5 μg L^{-1}) in the effluent of a textile industry in Italy but it is evident that no work was reported for the detection and quantification of the harmful organic pollutant like APs, and banned APEOs [12, 16, 17, 18] in the textile wastewater of Bangladesh. Therefore, the present study was aimed to identify as well as quantify some of the unexplored hazardous APs viz. NPs, and APEOs e.g., NPEOs in the textile wastewater of Dhaka division, Bangladesh.

MATERIALS AND METHODS

Materials and reagents used

Nonylphenol ethoxylates, Octylphenol ethoxylates, Ammonium acetate, Acetic acid, Dichloromethane were of AR grade reagents while the solvent methanol and acetone were of chromatographic and or MS grade. These chemicals, and silica, borosilicate glass etc. materials were bought from local suppliers like Labtex Bangladesh.

Column specifications

The length of the column was 15 cm, the internal diameter was 5 mm, and the coating material was reversed-phase porous silica.

Sample (wastewater) collection

Seven textile industries located in Gazipur, Savar, Narayonganj, and Mirpur, Dhaka division were randomly selected and the wastewater samples from those industries were collected. The final outlets of each of the wastewater treatment plant were chosen for wastewater sample collection. The obtained samples were then coded as A, B, C, D, E, F and G for the sake of confidentiality and also from ethical consideration. Samples were kept in borosilicate glass containers having PTFE-lined lids. Collected samples were kept immediately in cool boxes to maintain a temperature of less than 4°C during transportation. The samples were finally preserved in a freezer in the laboratory at a temperature less than 4°C for further use.

Method of identification and quantification of APEOs

The present study was carried out by an Agilent (6460C model) LC-MS instrument using the LC-MS technique of Loos et al. (2007) [15] blending with ISO/DIS 18254-1: 2016 [19]. For APEOs analysis, 250 mL wastewater was taken from each sample and it was then pre-concentrated using SPE (Figure 2). According to the method of ISO/DIS 18254-1: 2016 [19] the final volume was made 5 mL after extraction. The extracted and pre-concentrated sample was introduced into the LC-MS system. The peak of the analyte was identified from the retention time of the standard of the respective APEOs. The area of the peak found for the sample was compared with the reference standard peak area and thus quantified the concentration of the respective APEOs present in the wastewater. The obtained results were presented in Tables 1 and 2 in the results and discussion section.

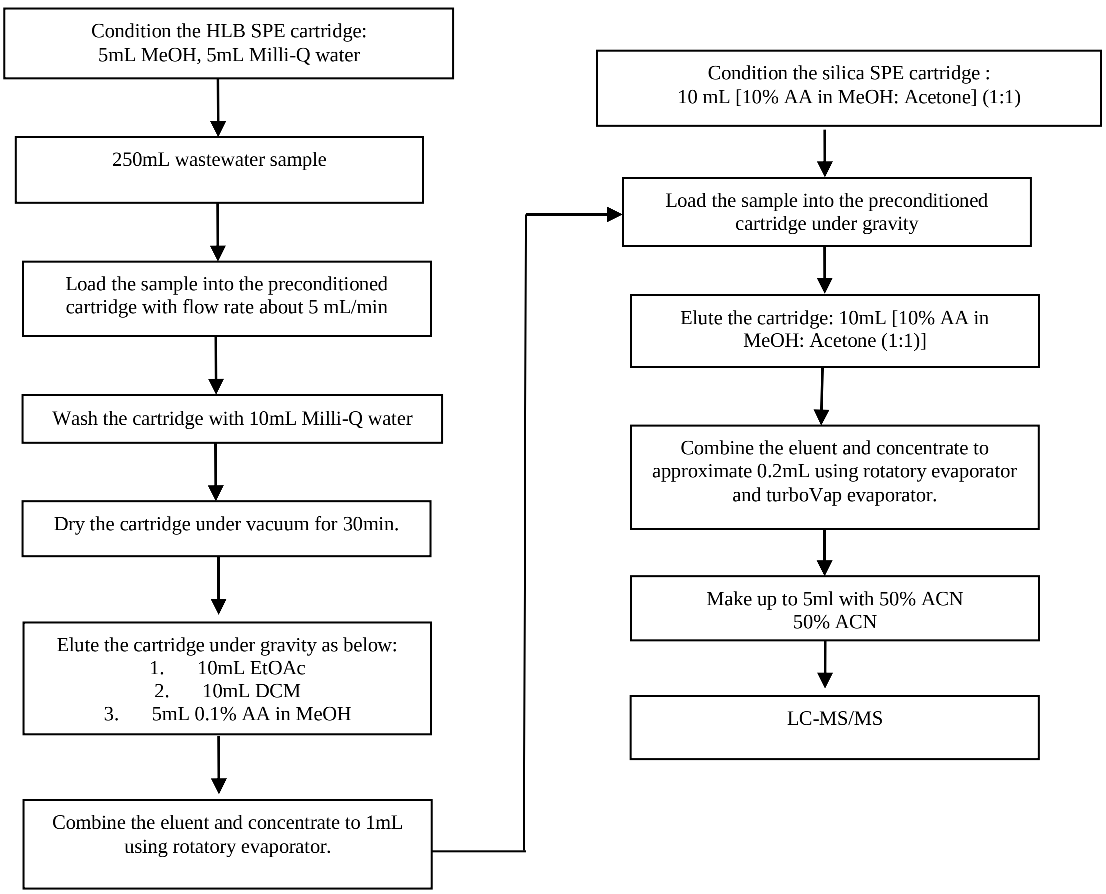

Figure 2. Steps of extraction and pre-concentration of the wastewater sample.

RESULTS AND DISCUSSIONS

Figure 3 shows the chromatogram of the standard NPEO and it is evident from the Figure that RT value for the NPEO is 11.892 min. Figure 4 shows the chromatogram of a representative sample (sample-A) having RT value 11.685 min, and Figure 5 shows the chromatogram of a representative sample (Sample-D) with RT value 11.933 min, which are similar and within ± 0.200 min to the RT value of that of the standard NPEO (11.892 min) and thus indicated that the sample-A and Sample-D contained NPEO. A calibration line was drawn by regression analysis with the standard NPEO (Figure 6), which shows an excellent fit and linearity (r^2 = 0.9995) of the straight line, which represents the equation y = 70628.48 x + 3311.76. The regression line was used to determine the content of NPEO in the studied wastewater samples (A to G).

The results obtained from the LC-MS analysis of the textile wastewater as described in the method part of the Materials and Methods of this paper were tabulated in the tables below here. Note that since APs and APEOs were not detected in the samples B, C, E, F, and G, therefore, the results of those samples were not shown here. It was done so for the space wasting consideration too. Tables 1 and 2 as shown below to show the wastewater analysis results for APs and APEOs of the samples A and D.

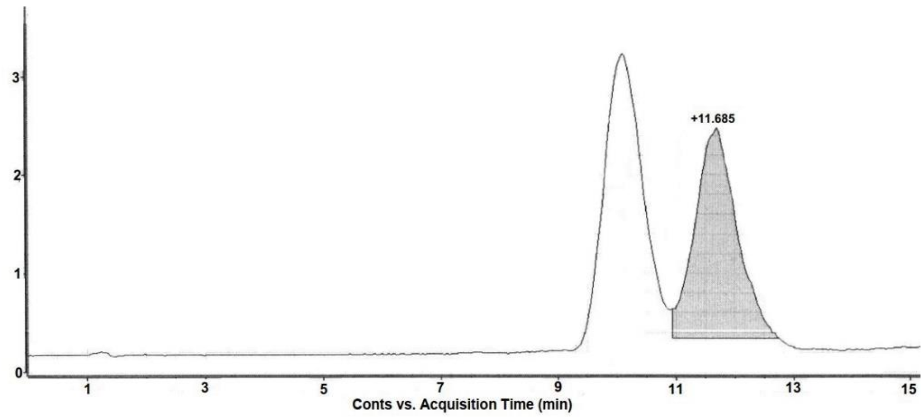

Figure 3. Chromatogram of the Standard NPEO; MP: Pure methanol (99.9%), RT = 11.685 min.

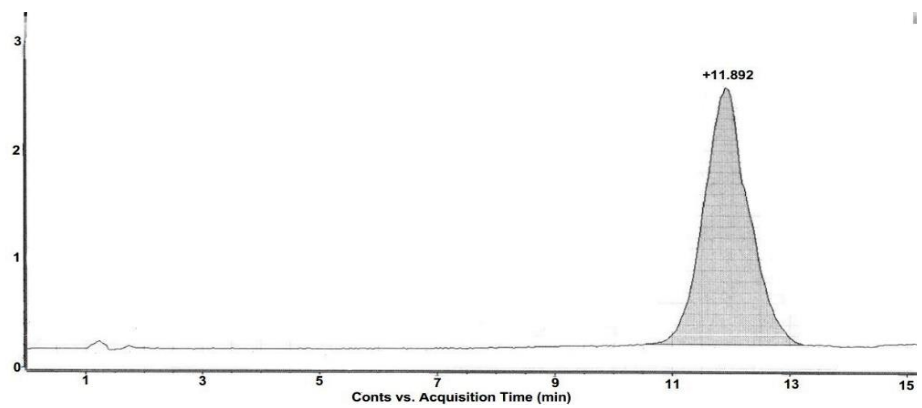

Figure 4. Chromatogram of the Sample A; MP: Pure methanol (99.9%), RT = 11.892 min.

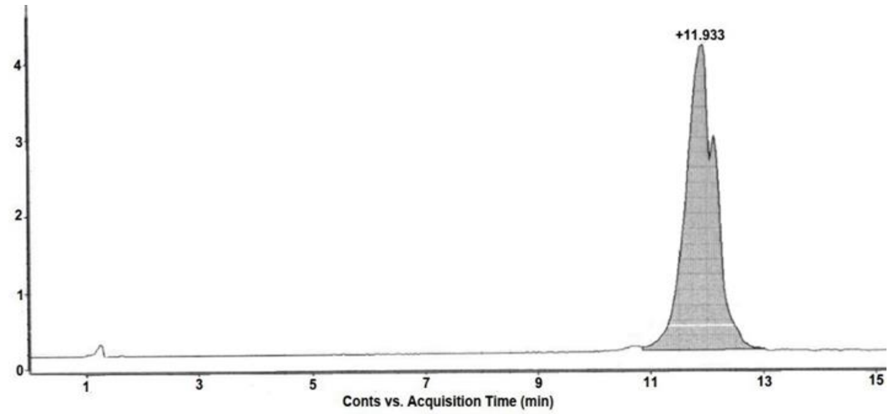

Figure 5. Chromatogram of the Sample D; MP: Pure methanol (99.9%), RT = 11.933 min.

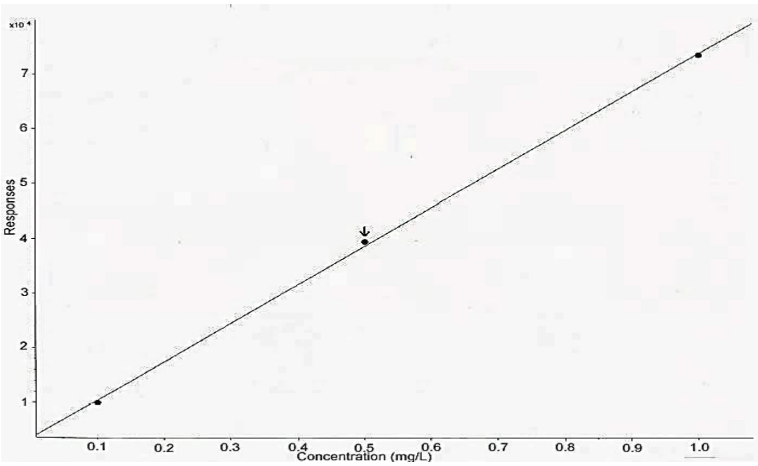

Figure 6. Calibration line with the standard NPEO (y = 70628.48 x + 3311.76, r^2 = 0.9995).

Table 1. Results of LC-MS Analysis of AP, and APEOs of the textile wastewater Sample-A

APs and APEOs	Cas No	Results				
		Test 1	Test 2	Test 3	Range	Mean ±SD**
		[μg L^{-1}]				
Nonylphenols (NPs)	Various 104-40-5 25154-52-3 11066-49-2 84852-15-3	ND*	ND*	ND*		
Octylphenols (OPs)	Various 140-66-9 27193-28-8 1806-26-4	ND*	ND*	ND*		
Nonylphenol Ethoxylates (NPEOs) (n=2-18)	Various 9016-45-9 26027-38-3	11.49	11.02	11.32	11.02 – 11.49	11.27± 0.24

	68412-54-4 127087-87-0 37205-87-1					
Octylphenol Ethoxylates (OPEOs) (n=2-16)	Various 9002-93-1 9036-19-5 68987-90-6	ND*	ND*	ND*		

*ND = Not Detected; **SD = Standard Deviation

Table 2. Results of LC-MS Analysis of AP, and APEOs of the textile wastewater Sample-B.

APs and APEOs	Cas No	Results				
		Test 1	Test 2	Test 3	Range	Mean ±SD**
		[μg L^{-1}]				
Nonylphenols (NPs)	Various 104-40-5 25154-52-3 11066-49-2 84852-15-3	ND*	ND*	ND*		
Octylphenols (OPs)	Various 140-66-9 27193-28-8 1806-26-4	ND*	ND*	ND*		
Nonylphenol Ethoxylates (NPEOs) (n=2-18)	Various 9016-45-9 26027-38-3 68412-54-4 127087-87-0 37205-87-1	14.01	13.92	14.10	13.92 – 14.10	14.01± 0.09
Octylphenol Ethoxylates (OPEOs) (n=2-16)	Various 9002-93-1 9036-19-5 68987-90-6	ND*	ND*	ND*		

*ND = Not Detected; **SD = Standard Deviation

It was evident from Table 1 and Table 2 that none of the textile wastewater Sample-A and Sample-D contained APs. However, out of the two APEOs viz. NPEOs and OPEOs were studied, only NPEO was found in the wastewater of the industries corresponding to Sample-A and Sample-D. The mean concentration of the NPEO in the wastewater of the factory corresponding to the wastewater Sample-A was 11.27 ± 0.24 μg L^{-1} (Table 1), and that of the factory corresponding to the wastewater Sample-D was 14.01 ± 0.09 μg L^{-1} (Table 2). APEOs, some sort of surfactants, are mostly used in washing, dyeing, and printing industries and these compounds are released with wastewater when the relevant textile products are washed [15, 20, and 21]. Moreover, toxic APEOs are unstable in the environment and their degradations lead to widespread release of more toxic and more stable NPs and OPs [12, 22, 23, 24, and 25]. However, since the samples were preserved properly and were analysed soon after their collection, that could be one of the reasons for not detecting the NPs and OPs in the present study.

Next, the present findings of NPEOs, a form of APEOs, were much higher (11-14 µg L^{-1}, Table-1 and 2) than the limits set for APEOs by US EPA (1.7 µgL^{-1}), Environment Canada (0.7 µg L^{-1}) and Detox to Zero by Oekotex (1.0 µg L^{-1}) [18, 26] as shown in the Table 3. The high content of NEPOs was also reported (4.5 µg L^{-1}) in the effluent of a textile industry in Italy [15], but in the present case it (NPEOs) is 2.5 to 3.11 folds higher (11 to 14 µg L^{-1}) than the content of NPEOs (4.5 µg L^{-1}) in the textile wastewater of Italy. This observation may conclude that harmful APEOs are being used in the textile industries of Bangladesh and may also raise the question about the efficacy of the textile wastewater treatment or whether wastewater is being treated or not in the textile industries of Bangladesh. Due consideration is needed from the textile industries as well as from the government of Bangladesh in this respect as NPEO is very toxic to aquatic life [11, 27]. They also cause endocrine disruption among fish, birds, wildlife, and human beings via their metabolites [11, 28].

Table 3. Limits of APs and APEOs in water or wastewater

APs and APEOs	Agencies in literatures		
	Water quality criteria		Wastewater quality criteria
	US EPA	Environmet Canada	Oekotex
	[µg L^{-1}]		
NPs	1.7 for chronic exposures	0.7 for chronic exposures	1
OPs	--	--	1
NPEOs	--	0.7	1
OPEOs	--	--	1

CONCLUSIONS

From the present study, NPEO was found in the wastewater of 28% textile industries (i.e., 2 out of the 7 studied industries) of Dhaka Division, Bangladesh. For the first time the banned nonylphenol ethoxylate (NPEOs) was found, through the present study, in the wastewater of some of the textile industries of Dhaka division, Bangladesh. Investigations revealed that concentrations of the banned nonylphenol ethoxylates were much higher than the specifications of the literature.

Recommendations

Enforcement of legislation, for example, pertaining to ETP is inevitable for controlling environmental pollution from wastewater of textile industries. DoE should go for strict and frequent monitoring of textile wastewater utilizing its 'Power of entry' as described in Environmental Conservation Act (ECA 1995) [29] to prevent environmental pollution. Amendment of ECA 1995 and Environmental Conservation Rules (ECR 1997) [30] is needed to allow other independent research organizations with permission but without specifying time and date for collecting wastewater from the textile industries. DoE should include specifications for the hazardous organic materials in the textile wastewater of Bangladesh.

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Conflict of interests

Authors of the article declare that they have no conflict of interest.

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