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Phthalate esters as emerging organic contaminants from common effluent treatment plants treating heterogeneous industrial wastewaters, Indian scenario

Kishore Malviya, M Suresh Kumar

Kishore Malviya
Butibori CETP Pvt. Ltd., MIDC Industrial Area, Nagpur (India)

M Suresh Kumar
Solid and Hazardous Waste Management Division, CSIR-National Environmental Engineering Research Institute, Nehru Marg, Nagpur (India)

Correspondence
M Suresh Kumar
Solid and Hazardous Waste Management Division, CSIR-National Environmental Engineering Research Institute, Nehru Marg, Nagpur-440020, India

Abstract
Phthalate Esters (PAEs) are widely used as non-reactive additives in plastics, particularly polyvinyl chloride, but also in rubber, cellulose and styrene production, to improve their softness and flexibility. As PAEs do not chemically bind in the polymeric matrix, they can enter the environment directly or indirectly, during the production of plastic and plastic material. However, in India, where industrialization and urbanization have proceeded rapidly during the past decades and the potential associated increase in PAEs input is of concern, no information on the environmental distribution of PAEs is available and there are no regulations exists in India. Hence, in the present study, phthalate esters were monitored in the CETP treating the wastewaters generated from heterogeneous cluster of 175 industries. The results indicated that the CETP is performing well as per the prescribed norms set by the regulator authority. But the treated wastewater shows the presence of phthalate esters in micro-quantity. There are total five different phthalate esters were detected in the inlet and outlet of the CETP treating the wastewaters receiving from heterogeneous industries. After treatment the wastewater are applied to the soils to grow the plants for High Rate Transpiration system. There is an increasing trend of accumulation of these PAEs in the soils are observed. However, the monitoring parameter for the trace elements and compounds needs to be revised by the regulatory authorities. More emphasis should be given to the PAEs which are persistent and endocrine disrupters as well as carcinogenic.

Keywords: CETP, wastewater, biological treatment, activated carbon filter, primary treatment, heterogeneous wastewater.

1. Introduction

Small and medium scale industries play an important role in Indian economy for their contribution to total industrial production, exports and employment. These industrial units contribute about 40% of the total industrial production of the country, while at the same time generate over 44% of the total industrial waste and are considered to be highly polluting industries. To address this problem the concept of Common Effluent Treatment Plant (CETP) was introduced and was widely believed as an ultimate solution to the wastewater treatment problem (Pathe *et al*., 2004; Cheda *et al*., 1984) [5, 2]. But the CETPs treating the wastewater coming form different types of industries are often consist of many plastic and polymer industries. These industries widely use phthalate esters as plasticizers in polyvinyl chloride, polyvinyl acetates, polyurethanes, and cellulosics. The global production of these phthalates is estimated to be several million tons and will continue to increase. As a result, phthalate esters have become ubiquitous contaminants in the environment. Elevated levels of phthalate esters are detected in different environmental matrices. Due to the teratogenicity, carcinogenicity, and mutagenicity, (Liao, *et al*. 2010) [4] Environmental Protection Agency (EPA) of the USA have listed phthalate esters as environmental priority pollutants.

It is therefore necessary to evaluate the current residues of phthalate esters in the wastewaters generated from plastics, polymers, cosmetics and other allied industries. The major purposes of this study were to investigate the concentrations, compositions, and distributions of phthalate esters in the wastewaters received at CETP. A review of the literature and the studies pertaining to the CETPs, indicate clearly that the most of the studies were carried out with respect to the compliance of only prescribed discharge norms. However, toxic compounds, which do not have prescribed norms, but are present in the influents, are the main environmental concern. Secondly studies were restricted to the CETP outlets and concentrating on compliance with the prescribed norms. But the norms set by the regulatory bodies were not reflecting the presence of phthalate esters like compounds which are present in micro-quantities still causes severe impact on human health. The present study aims at to study in detail for the presence of phthalate esters and to highlight the importance for the setting of permissible limits and parameters for these compounds.

2.0 Materials and methods

2.1 Wastewater characterization

The wastewater was characterized for the parameters such as pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), total nitrogen, ammoniacal nitrogen (NH_4-N), total kjeldahl nitrogen (TKN), phosphorous, mixed liquor suspended solids (MLSS), total dissolved solids (TDS), mixed liquor volatile suspended solids (MLVSS), dissolved oxygen (DO), sulfates (as SO_4), sulfides and metals. All the analyses were carried out as per the standard methods (APHA 2012) [1].

2.2 Sample extraction for Phthalate esters

Wastewater samples were extracted with dichloromethane (DCM) and the extracts were concentrated, solvent-exchanged to n-hexane, and further reduced to approximately 1.0 ml. Concentrated extracts were cleaned and fractionated on a 10-mm i.d. 1:2 alumina/silica gel glass column packed, with neutral silica gel (12 cm), neutral alumina (6 cm), and anhydrous sodium sulfate (1 cm). Then phthalate esters were eluted with 40 ml of a mixed solvent of acetone/n-hexane (2:8 v:v) as per the method suggested by Zeng and his coworkers (2005).

The extracted compounds were determined with QP 2010 gas chromatography and mass spectrometer (GC-MS Shimadzu, Japan), operating in electron impact and selective ion monitoring modes and a Resteck- 5 MS capillary column (30 m x 0.250 mm i.d, 0.25 µm film thickness). The transfer line and ion source temperature were maintained at 275 and 230^{o}C, respectively. The column temperature program was initiated at 65^{o}C for 1.0 min, increased to 220^o C at a rate of 25 ^{o}C min^{-}1, held for 1.0 min, and finally ramped at 5^{o}C min^{-}1 to 250 ^{o}C and held for 15 min. The flow rate of the carrier gas helium was kept constant at 1.0 ml, min 1. The injector temperature was kept at 250^0 and 1.0µL of extracted samples were injected in split less mode.

2.3 Details of the common effluent treatment plant under the study

The CETP under the study comprised of primary, secondary and tertiary treatment systems to treat the wastewater received from different types of industries. The schematic of the CETP is shown in Figure 1. The CETP under study was designed to treat 5 MLD combined wastewater from 175 small and medium scale heterogeneous industrial units. The treated wastewater from tertiary treatment units is supposed to meet the discharge standards set by the Maharashtra Pollution Control Board (MPCB), Mumbai, India.

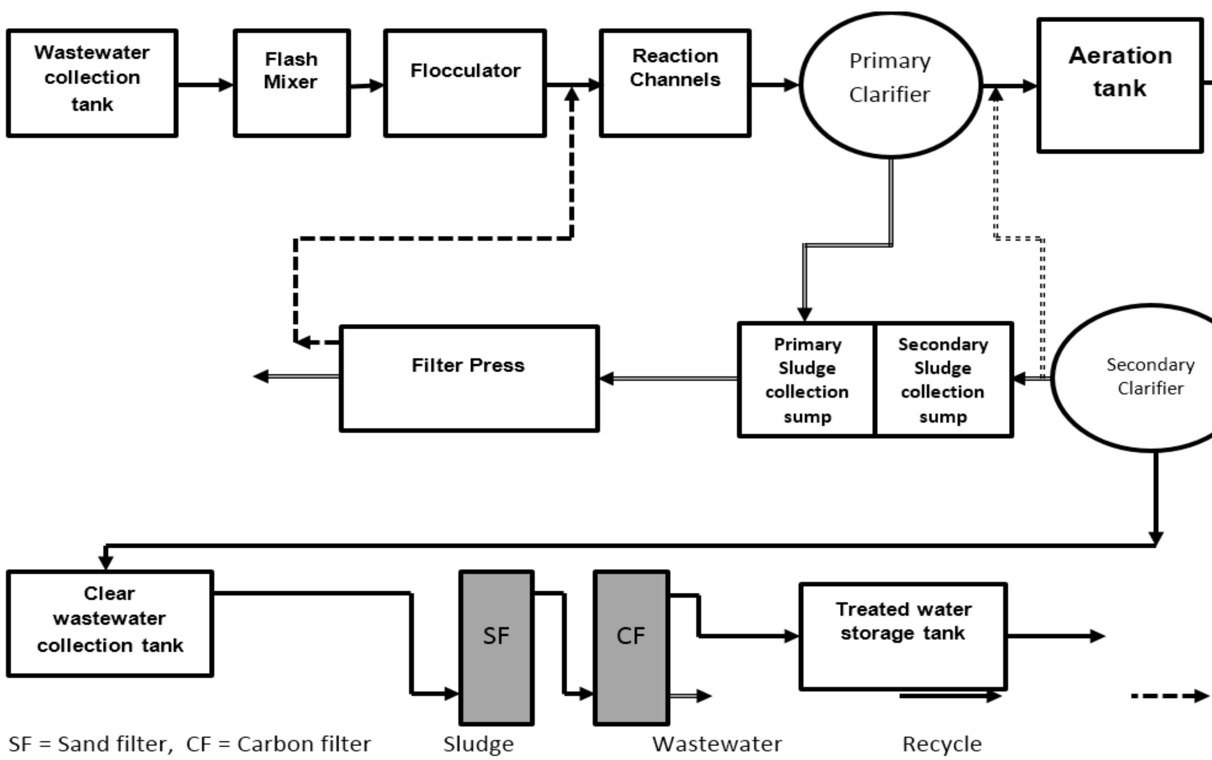

Fig. 1: Schematic of the Common Effluent Treatment Plant (CETP) for heterogeneous industrial cluster

2.4 Performance evaluation

The performance of CETP was monitored continuously for a period of 2 days in three seasons. During this period wastewater samples were collected from different stages of CETP at four hours' time interval. These samples were also composited for 48 hours and then analyzed for various physico-chemical parameters as mentioned earlier.

3.0 Results and discussions

3.1 Characteristics of combined wastewater

The characteristics of the wastewater received at CETP were analyzed for three seasons and the average values are presented in Table 1. The combined wastewater had pH in the range of 8.23 to 7.21, COD of 1160 mg/L, BOD of 480 mg/L, with nitrogen 46 mg/L, total suspended solids of 498 mg/L and total dissolved solids of 2980 mg/L, respectively (all values except pH are reported as average values).

Table 1: Characteristics of combined wastewater at various stages of treatment

Parameters	Combined Wastewater	Before Primary Clarifier	After Primary Clarifier	Aeration Tank Outlet	After Sec. Clarifier	After Tert. Treatment	Prescribed standards*
pH	8.02 (±0.01)	8.00 (±0.0)	7.68 (±0.03)	7.26 (±0.05)	7.21 (±0.04)	7.20 (±0.08)	5.5-9.0
TDS	2804 (±7.1)	2800 (±19.0)	2180 (±8.5)	2000 (±11.9)	2000 (±11.0)	2000 (±17.0)	2100
TSS	429 (±1.1)	418 (±8.0)	85 (±3.5)	2500 (±100)	108 (±2.0)	80 (±2.0)	100
COD	1040 (±2.0)	1000 (±10.0)	780 (±3.5)	240 (±8.0)	200 (±2.0)	184 (±2.0)	250
BOD	504 (±4.0)	500 (±13.0)	486 (±5.2)	100 (±5.0)	86 (±2.0)	28 (±1.0)	30
Oil & grease	20 (±1.5)	20 (±2.0)	10 (±2.0)	4 (±0.01)	ND	ND	10
Chloride	1240 (±2.0)	1210 (±10.0)	898 (±8.0)	807 (±6.6)	620 (±2.0)	536 (±4.0)	1000
Phosphate (PO_4)	0.8 (±0.0)	0.6 (±0.01)	0.6 (±0.01)	0.8 (±1.3)	0.8 (±1.3)	0.8 (±0.01)	-
Sulphate (SO_4)	862 (±2.0)	860 (±10.0)	649 (±9.5)	600 (±5.3)	600 (±12.0)	502 (±6.0)	1000
Sulphide (S)	0.95 (±0.01)	0.95 (±0.04)	0.63 (±0.01)	0.42 (±0.01)	0.46 (±0.01)	0.46 (±0.01)	2.8
Ammonical nitrogen	38 (±1.5)	38 (±2.0)	38 (±0.01)	30 (±0.01)	30 (±0.01)	28 (±1.0)	50
Kjeldahl nitrogen	40.6 (±0.02)	40.1 (±2.0)	38.82 (±0.01)	33.5 (±0.04)	32.6 (±0.01)	31.8 (±0.06)	100

All the values are expressed in mg/L, except pH. ND=not detected, * In to inland surface waters, values in brackets are standard deviation

3.2 Performance evaluation of the CETP

The average pH of combined wastewater received at CETP was 8.02 (± 0.01), after primary treatment the pH was reduced to 7.68 (± 0.03), further there is no much change in the pH up to the tertiary treatment and finally the treated wastewater pH was 7.2 (± 0.08), which is very much in the range of prescribed standards. Total dissolved solids at primary treatment inlet were 2804 mg/l and reduced marginally at final discharge to 2000 mg/l as against 2100 mg/l prescribed standard. The suspended solids at the equalization tank were 429 mg/l and it was further reduced to 85 mg/l after primary clarifier outlet.

COD was initially 1040 mg/l, after primary treatment reduced to 780 mg/l and in the biological treatment it further reduced to 240 mg/l. Finally, after tertiary treatment the COD concentration was reduced to 184 mg/l and this was much more below the MPCB prescribed (CPCB, 2005) concentration of 250 mg/l. BOD was recorded in the combined wastewater was 504 mg/l and it was further reduced in the biological treatment unit upto 100 mg/l, and final treated wastewater contains only 28 mg/l of BOD. Average chlorides in the inlet of the CETP was found to be 1240 mg/l and at the final discharge it was 536 mg/l as against MPCB prescribed concentration 1000 mg/l. Sulfates, Phosphates, Sulfide and Ammonia concentrations were found to be within the prescribed values.

The average heavy metals content in the wastewater samples collected from six different locations are presented in Table 2. Cadmium, total chromium, hexavalent chromium, copper, zinc and nickel concentrations in the final treated wastewater was recorded as 0.1, 0.4, 0.09, 0.9, 2.1 and 2.0 mg/l respectively. It is clearly indicating that the combined treated wastewater showing the metals concentrations within the MPCB prescribed standard. Lead, Iron and manganese was detected 0.08 mg/l, 10 mg/l and 0.9 mg/l respectively in the final treated wastewater. The overall removal of suspended solids was observed nearly 81.35 %, COD removal was 82.30 %, BOD removal was 94.4 %, oil & grease removal was 100%, chlorides removal was 56.77% and the total metals removal was observed to be 99.52 % respectively. As far as the total dissolved solids are concerned there was only 28.6% reduction observed in overall treatment. Pathe and his co-workers (2004) was evaluated performance of an existing CETP serving a cluster of small scale tanneries and suggested measures and modifications for improving the performance. Safia and Madamwar, (2007) [6] has suggested cleaner production (CP) approach for tackling the TDS and colour problems in the CETP for tannery industry wastewaters (homogeneous clusters of Industries). But for CETPs treating wastewaters from heterogeneous industrial clusters, this approach is not suitable.

Table 2: Metals concentration in the combined wastewater at various stages of treatment after implementing corrective measures

Parameters	Combined Wastewater	Before Primary Clarifier	After Primary Clarifier	Aeration Tank Outlet	After Sec. Clarifier	After Tert. Treatment	Prescribed standards*
Cadmium	3.1 (±0.0)	3.0 (±0.19)	0.8 (±0.02)	0.6 (±0.01)	0.4 (±0.004)	0.1 (±0.008)	1.0
Total Chromium	4.2 (±0.1)	4.2 (±0.07)	0.9 (±0.01)	0.8 (±0.01)	0.8 (±0.01)	0.4 (±0.02)	2.0
Hexavalent chromium	2.1 (±0.1)	2.0 (±0.18)	0.2 (±0.004)	0.18 (±0.002)	0.11 (±0.005)	0.09 (±0.01)	0.1
Copper	5.1 (±0.1)	5.0 (±0.06)	1.5 (±0.02)	1.0 (±0.005)	1.0 (±0.05)	0.9 (±0.03)	3.0
Zinc	10.0 (±2.0)	10.0 (±0.3)	4.4 (±0.1)	3.1 (±0.03)	3.1 (±0.03)	2.1 (±0.005)	5.0
Nickel	12.0 (±0.1)	12.0 (±0.11)	4.8 (±0.01)	4.7 (±0.03)	2.2 (±0.009)	2.0 (±0.002)	3.0
Arsenic	ND	ND	ND	ND	ND	ND	0.2
Mercury	ND	ND	ND	ND	ND	ND	0.01
Lead	8.1 (±0.4)	7.0 (±0.02)	0.12 (±0.01)	0.1 (±0.002)	0.1 (±1.6)	0.08 (±0.003)	0.1
Iron	3406 (±3.2)	3400 (±30.0)	106 (±11.0)	106 (±7.2)	100 (±2.0)	10 (±0.9)	-
Manganese	6.0 (±0.0)	6.0 (±0.10)	1.8 (±0.02)	1.0 (±0.0)	1.0 (±0.01)	0.9 (±1.3)	-

All the values are expressed in mg/L, except pH. ND=not detected, * In to inland surface waters, values in brackets are standard deviation

The phthalate ester compounds detected in the CETP treated wastewater samples are presented in the Table 3. There are total five different phthalate esters were detected in the inlet and outlet of the CETP treating the wastewaters receiving from heterogeneous industries. However, in India, where industrialization and urbanization have proceeded rapidly during the past decades and the potential associated increase in PAEs input is of concern, no information on the environmental distribution of PAEs is available and there are no regulations exists in India.

Table 3: Organic compounds detected in the wastewater at CETP inlet and outlet

		Compound	Concentration (μg/l)
During Monsoon	Combined wastewater at CETP inlet	Di-n-hexyl phthalate	4.842
		Diethyl Phthalate	6.624
		Dibutyl phthalate	4.095
		Octasiloxane	1.892
		Benzyl butyl phthalate	6.681
	Combined treated wastewater at CETP outlet	Di-n-hexyl phthalate	0.568
		Diethyl Phthalate	0.794
		Dibutyl phthalate	0.968
		Octasiloxane	0.642
		Benzyl butyl phthalate	0.564
During Winter	Combined wastewater at CETP inlet	Di-n-hexyl phthalate	4.211
		Diethyl Phthalate	5.834
		Dibutyl phthalate	5.016
		Octasiloxane	1.798
		Benzyl butyl phthalate	5.845
	Combined treated wastewater at CETP outlet	Di-n-hexyl phthalate	1.064
		Diethyl Phthalate	1.094
		Dibutyl phthalate	0.849
		Octasiloxane	0.736
		Benzyl butyl phthalate	0.816
During Summer	Combined wastewater at CETP inlet	Di-n-hexyl phthalate	3.981
		Diethyl Phthalate	5.364
		Dibutyl phthalate	4.872
		Octasiloxane	1.906
		Benzyl butyl phthalate	5.628
	Combined treated wastewater at CETP outlet	Di-n-hexyl phthalate	0.902
		Diethyl Phthalate	0.864
		Dibutyl phthalate	0.827
		Octasiloxane	0.841
		Benzyl butyl phthalate	0.584

Normally these compounds are present in very minute concentrations and it would not reflect in the traditional analysis like COD. The regulatory authorities have set the discharge limits for the treated wastewater like COD especially for organics, however, the COD may be within the limit but the presence of PAEs in trace concentrations will not appear in the COD. These PAEs are well known endocrine disrupters and also carcinogenic compounds and even in micro level quantities may cause the health impacts. However, the monitoring parameter for the trace elements and compounds needs to be revised by the regulatory authorities. More emphasis should be given to the PAEs which are persistent and endocrine disrupters as well as carcinogenic. These micro level compounds do not reflect in the present existing standard parameters prescribed by the pollution control authorities.

4.0 Conclusions

The CETP situated at heterogeneous cluster of industrial area consists of different type of small, medium and large scale industries viz., textile, chemical, metallurgical, pharmaceuticals, cosmetics, petrochemicals, plastics and polymers, aluminum, dyes and pigments, wood, food and dairy industries etc. The CETP was evaluated for the performance during the three seasons (summer, monsoon and winter) by monitoring the individual unit's efficiency of treatment. The results indicated that the CETP is performing well as per the prescribed norms set by the regulator authority. But the treated wastewater shows the presence of phthalate esters in micro-quantity. There are total five different phthalate esters were detected in the inlet and outlet of the CETP treating the wastewaters receiving from heterogeneous industries. However, the monitoring parameter for the trace elements and compounds needs to be revised by the regulatory authorities. More emphasis should be given to the PAEs which are persistent and endocrine disrupters as well as carcinogenic. These micro level compounds do not reflect in the present existing standard parameters prescribed by the pollution control authorities.

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6.0 References

1. APHA-AWWA-WPCF, Standard methods for examination for water and wastewater, 22nd edition, American Public Health Association, Washington D.C, 2012.
2. Cheda, P. V.; Mandlekar, U. K.; Handa, B. K.; Khanna, P. Joint wastewater management for cluster of tanneries at Kanpur. Proc. 39 Industrial waste conference, Purdue University, W. Lafyetta, Indiana, May 9-10, 1984, 151-162.
3. CPCB. "Performance status of common effluent treatment plants in India". Central pollution control board, New Delhi, India, Report, 2005. www.cpcb.nic.in/ NewItem_19_ Pollution ControlLaw.pdf.
4. Liao, T. T., Shi, Y. L., Jia, J. W and Wang, L. (2010). Sensitivity of different cytotoxic responses of vero cells exposed to organic chemical pollutants and their reliability in the biotoxicity test of trace chemical pollutants. *Biomedical and Environmental Sciences*, 23(3): 219-229.

5. Pathe, P. P.; Suresh Kumar, M.; Kharwade, M. R.; Kaul. S. N.(2004). Common effluent treatment plant (CETP) for wastewater management from a cluster of small scale tanneries. Environ. Technol. 25*:* 555-563.
6. Safia Moosvi and Datta Madamwar, (2007). An integrated process for the treatment of CETP wastewater using coagulation, anaerobic and aerobic process. *Bioresource Technology*, 98: 3384-3392.
7. World Bank. (1991). "Industrial pollution control projects, India: Feasibility assessment of common treatment facilities in Gujarat, Maharashtra and Tamil Nadu". Prepared for the World Bank by Chemcontrol A/S, Denmark.
8. Zeng, F., Cehen, L.X., Cui, K.Y and Zhang, G. (2005). The determination of phthalateesters in sediment sample by silica gel-alumina column separation and gas chromatography. Chinese journal of Analytical Chemistry 33:1063-1067.