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Quantification and Human Health Risk Assessment of by-products of Photo Catalytic Oxidation of Ethylbenzene, Xylene and Toluene in Indoor Air of Analytical Laboratories

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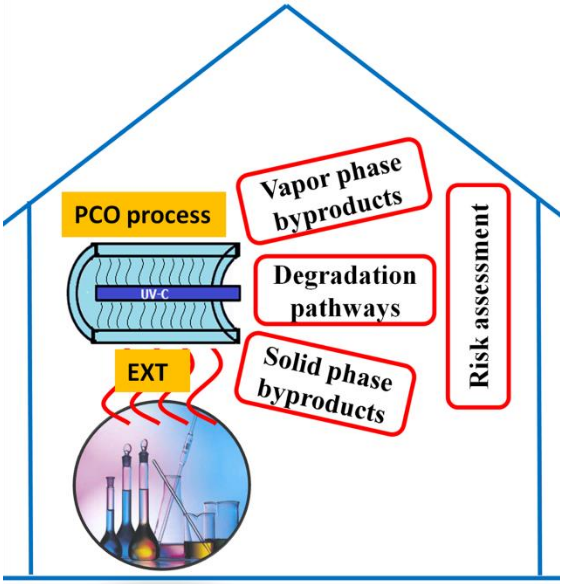
Graphical Abstract



Highlights

- TiO_2 based photo degradation of ethylbenzene, toluene, p,m-xylene and o-xylene (EXT)
- By-products of EXT degradation are identified and quantified on GC –MS/GC
- Cancer Risk and hazard index of by-products of EXT were assessed
- Degradation pathways for EXT were proposed based on identified by-products

ABSTRACT

The by-products of TiO_2-based photocatalytic oxidation (PCO) of ethylbenze, p,m-xylene,o-xylene and toluene (EXT) in vapour phase and those adsorbed on the catalyst surface (solid phase) were identified and quantified on GC/GC-MS. A factor was developed in terms of µg of by-product produced per mg of EXT removed per sq-meter surface area of catalyst for estimating the mass of by-products produced. The by-products quantified were: acetone, hexane, cyclohexane, benzene, crotonaldehyde, toulene, 1,4-benzoquinone, benzaldehyde, phenol, benzylalcohol, cresol, hydroquinone and benzoic acid. The by-products accounted for 2.3-4.2% of the total mass of EXT treated.

For treating concentrations of 220 µg/m^3 (ethylbenzene), 260 µg/m^3 (p,m-xylene), 260 µg/m^3 (o-xylene) and 320 µg/m^3 (toluene), at a flow rate of 7 L/min for 12 hours in a laboratory of volume 195 m^3, the estimated cancer risks of by-products to the occupants were 1.51×10^{-6}, 1.06×10^{-6}, 4.69×10^{-7}, and 1.58×10^{-9} respectively. The overall hazard index (HI) of the by-products for EXT was of the order 10^{-4}; which is much less than desired level of 1.0. The estimated risks were within the acceptable level. This study has also suggested the photocatalytic degradation pathways for EX which are through formation of toluene.

Keywords: Indoor air, photo catalytic oxidation, by-products, TiO_2, hazard index

1. Introduction

Volatile organic compounds (VOCs) are important air pollutants which are present in ambient air, households, industrial areas, laboratories and inside office buildings [1–4]. In the buildings, VOCs can accumulate and result in high concentrations harmful for occupants. Many VOCs have carcinogenic, mutagenic or teratogenic effects [5–7].

To improve the indoor air quality, often quantity of ventilation air is increased to dilute indoor VOC concentrations. This practice has limitations due to associated significant energy costs and it is not of much use when ambient air (as in industrial area or at traffic intersections) itself is highly polluted. The conventional VOC control technologies, condensation, incineration, and adsorption are not suitable for small rooms. Photo catalytic oxidation (PCO) with titanium and other semi-conductor based catalysts in the presence of external UV light has been extensively studied for VOC control in the indoor environment [8–12]. The PCO technology has several advantages as it is energy efficient, inexpensive and safe [13]. In a semiconductor material, an e^- of valence band (VB) is excited by photo-irradiation to a vacant conduction band (CB) creating an h^+ in VB. The excited e^- and h^+ lead to the formation of strong oxidizing hydroxyl radical (•OH) in the presence of humidity which can oxidize VOCs into water vapour and carbon dioxide [11,14].

The complete oxidation of VOCs does not happen instantly. Some by-products are formed due to partial oxidation [15] and can get released in the indoor air. These by-products may be harmful to the building occupants, sometimes even more than the parent VOC, which is being treated [16]. Harmful by-products could be a major limitation for field application of PCO technology. In addition to vapour phase by-products, some partially oxidised semi-volatiles can deposit on the catalyst surface and may be released when catalyst is regenerated.

Ethylbenzene, xylene (p,m-xylene, o-xylene) and toluene (EXT) are common VOCs found in ambient and indoor air. Mo et al [17] and Zhao et al [18] have identified and quantified some by-products (e.g. formaldehyde, methanol, propylene, acetaldehyde, formic acid, benzene, benzyldehyde, pentanal, benzoic acid etc) of toluene degradation using proton transfer reaction-mass spectroscopy. The identification and quantification of by-products using traditional GC/GC-MS is challenging because of extremely low concentration of by-products. In literature, there are limited studies [17,19–21]on formation of by-products of EXT. The impediments for adoption of PCO technology like TiO_2 coating, reaction kinetics, and catalyst deactivation/regeneration are duly addressed by Dhada et al. (2015) [9]. However, the issue of risk associated with by-products remains unanswered. Identification and quantification of by-products, formed in few minutes to few hours is essential. The risk assessment of exposure of by-products is challenging as by-products will not only be in vapour phase but partly also adsorbed on the catalyst surface (solid phase). On regeneration of catalyst by heating it at 450^{o}C, the solid phase adsorbed by-products will also be released. There is a need to characterize the risk in a comprehensive manner that accounts for by-products in vapour phase and those adsorbed on the catalyst.

The objective of this study is three fold: (i) identify and quantify the by-products of degradation of EXT, (ii) characterize the comprehensive risk of exposure of by-products through estimation of hazard index (HI) and carcinogenic risk and (iii) propose probable degradation pathways of EXT. Specifically, the risk was assessed for occupants serving the analytical laboratories for more than 30 years.

2. Materials and methods

2.1 Photo-oxidation reactor

A reactor made of borosilicate glass tube; 60 mm inner diameter and 270 mm length; effective volume = 700 cm^3 and inner surface area = 524 cm^2) was fabricated and coated with TiO_2 using sol gel method [9]. Two sols (Sol A and Sol B) were prepared from a mixture of titanium tetra-isopropoxide (TTIP; 98%; Spectrochem, Mumbai), di-ethanolamine (DEA; 99.5%; Merck, Mumbai), acetylacetone (AcAc; 99.55%; Loba Chemicals), deionized water (H_2O) and ethanol (C_2H_5OH) at a molar ratio of 1:1:0:0:34 (Sol A) and 1:0:1:3:20 (Sol B) respectively. For getting final sol gel, the above two sols were mixed and ultrasonicated (Ultrasonicator; Enertech, Mumbai) for 30 minutes. Following procedure was followed for coating the reactors; filling of the reactor with the sol-gel, emptying it gradually (after 2-3 minutes), drying slowly at room temperature (for 10 minutes), heating in a hot air oven at 120 °C (for 10 minutes), heating in a muffle furnace at 500 °C (for 15 minutes) followed by cooling at room temperature (for 10 minutes). The entire process was repeated 15 times to obtain the optimal catalyst film of TiO_2 [9]. The reactor was equipped with temperature and relative humidity (RH) sensors with the facility for holding a UV-C transparent germicidal lamps of 16 W (15 mm outside diameter, 300 mm length, and $\lambda = 254$ nm; Sankyo Denki, Japan) inside the reactor. The temperature and RH during the experiments were 22.4±2.3ºC and 57 ± 3%. Fig. 1 shows field-ready VOC control equipment having seven reactors in series which can operate at a flow rate of 7 L/min for 12 hours before the catalyst is regenerated.

The reactor was filled separately with EXT and it was operated as a batch reactor. The initial concentration of EXT taken in the batch reactor for identification and quantification of by-products were high (Table 1; column 2) compared to the levels observed in indoor air so that measurable amounts of by-products are obtained. The quantified amounts of by-products can be translated into emission factor like µg of byproduct produced per mg of EXT treated and these factors can be used for estimating emissions of by-products under varying situations.

2.2 Sampling and analysis

Samples were drawn at 40, 80, 120, 160, 200 minutes so that the majority of by-products are formed and quantified as a function of time. The experiment was repeated three times. The by-products of EXT in vapour and solid phase were identified on GCMS and quantified on GC (as per the extraction procedure described later in the text).

For vapour phase by-products, the gas samples (1 mL for each analysis) were drawn using a 5 mL gas tight syringe (SGE, Restek) and injected into GC-FID (Clarus 500, Perkin Elmer) which was equipped with fused silica capillary column SPB-624 (60m x 0.25 µm x 0.4 µm; Supelco make). The EXT degrade through formation of benzene or toluene [13,17] and therefore the GC was calibrated for previously reported by-products of benzene and toluene [i.e. n-hexane, benzaldehyde, phenol, pentane, crotonaldehyde, benzylalcohol, cyclohexane, cresol, benzoic acid, hydroquinone, benzene, toluene, xylenes, ethylbenzene, methanol [17, 22–27]] at four levels (5, 50,100,500 ppm). The temperature programming for GC was: 40^{o} C, 5 min hold-ramp@10^{o}C/min up to 200^{o}C, 5min hold -ramp@10^{o}C/min up to 240^{o}C, 1 min hold.

For quantification of by-products from catalyst regeneration, identically coated glass chips (same as coating of inside surface of reactor) of total area 3 cm^2 were kept inside the reactor and it was continuously operated. The coated chips act identical to the catalyst surface inside the reactor and represent the exhausted catalyst after full cycle of EXT degradation. Our study suggests that catalyst need to be regenerated after 12 hours of continuous operation [9]. The chips (after 12 hours of operation of reactor) were taken out and extracted with methanol for identifying and quantifying the by-products adsorbed on the catalyst (chips were immersed in 15 mL methanol and ultrasonicated (Fast Clean, India) for 30 minutes). Extracted methanol was filtered through 0.45 μm syringe filter (Millex-HV, PVDF) and concentrated to 1.5 mL with the help of Turbo Vap (Turbo Vap-II, Caliper Life Science) by purging N_2 gas at 23°C. Then 0.4 μL of extracted concentrated liquid sample was injected into the GC through 1μL syringe (Hamilton Bonaduz) for quantification of solid phase by-products.

The realistic concentration of EXT in indoor air (Table 1; column 3) is much less than the initial concentration used in the batch reactor. For demonstrating the risk assessment, it is assumed that a device consisting of seven reactors in series treats the initial concentration of EXT at a flow rate of 7 L/min for a laboratory of volume 195 m^3.

2.3 Risk Assessment of Released By-products

This may be noted that most of the by-products have non-cancer risk and can be assessed through hazard index (HI) [32] and a few by-products have cancer risk. The total chronic hazard index can be calculated as

$$\mathrm{HI} = \sum_{i=1}^{n} \frac{\mathrm{CDI_i}}{\mathrm{RfD_i}} \tag{1}$$

Where CDI_i is chronic daily intake and RfD_i is the reference dose (mg/kg-day) for the i-th VOC

The CDI is calculated as per the following formulation

$$\mathrm{CDI} = \frac{(\mathrm{CA}\times\mathrm{IR}\times\mathrm{ABS_S}\times\mathrm{ET}\times\mathrm{EF}\times\mathrm{ED})}{(\mathrm{BW}\times\mathrm{AT})} \qquad (2)$$

Where CA: VOC concentration in air (mg/m^3); IR: Inhalation rate (0.83m^3/h for adult); ABSs: % VOCs absorbed into the blood stream; taken as 100%; ET: Exposure time (8h/day); EF: Exposure frequency (261days/year; 5 working days a week); ED: Exposure duration (35 years for occupancy); BW: Body weight (70kg); AT: Averaging time (period over which exposure is averaged: 70 years× 365days/year)

3. Results and discussion

3.1 Photo oxidation

The concentration of the by-products will depend on the surface area of the catalyst coating and amount of parent VOC removed. Table 2 presents mass of vapour phase by-products produced from batch operation of the reactor for PCO of one mg of ethylbenzene for an operation of 200 minutes. For a realistic 12hour of continuous operation of the reactor, it was assumed that after 200 minutes, there was no reduction in mass of by-products and at every 40 minute, same mass of ethylbenzene (i.e. 142.40 mg) enters the reactor for treatment; this is done to mimic the continuous operation of reactor. As an example, calculation of mass of toluene (one of the by-products) estimated at the end of 12 hour operation is shown (here each term shows the amount estimated at every 40 minutes for 12 hours of operation): [(11.23+20.1+11.17………till 18th term)/18]/Reactor Surface area=10.17 µg per mg of ethylbenzene removed per sq-meter of surface area of catalyst.

Similar to estimates of by-products produced from PCO of ethylbenzene, the by-products of PCO of xylene and toluene in the vapour phase for 12h operation of device were identified and presented in Table 3. It can be seen that among the by-products of ethylbenzene, hexane is the major intermediate followed by toluene and benzoic acid. Among the by-products of p,m-xylene, benzoic acid is the major intermediate followed by hydroquinone and benzyl alcohol. Similarly hexane is the major intermediate followed by benzoic acid and hydroquinone among the by-products of o-xylene and benzoic acid is the major intermediate followed by hydroquinone and benzene among the by-products of toluene.

The by-products (of EXT) adsorbed on the surface of the reactors in continuous 12 hour operation and likely to be released on regenerating the catalyst are presented in Figs. 2 - 5 and Table 4. The major by-products of ethylbenzene are (Fig. 2) benzoic acid followed by cresol, hexane and acetone and these account for 3.30% of mass of the ethylbenzene removed. The major by-products of p,m-xylene (Fig. 3) are hexane followed by benzoic acid, acetone and crotonaldehyde and these account for 2.27% of mass of the p,m-xylene removed. The major by-products of o-xylene (Fig. 4) are acetone followed by hexane and benzoic acid and account for 4.14% of mass of the o-xylene removed. The major by-products of toluene (Fig. 5) are acetone followed by benzoic acid and hydroquinone and account for 2.96% of mass of the toluene removed.

The by-products adsorbed on the surface of the reactors (solid phase) and likely to be released on regenerating the catalyst are presented in Table 4. The major by-products of ethylbenzene are benzoic acid followed by cresol, hexane and acetone and accounts for 3.3% of mass of the ethylbenzene treated. The major by-products of p,m-xylene are hexane followed by benzoic acid, acetone and crotonaldehyde and accounts for 2.4% of mass of the p,m-xylene treated. The major by-products of o-xylene are acetone followed by hexane and benzoic acid and account for 4.14% of mass of the o-xylene treated (Table 4). The major by-products of toluene are acetone followed by benzoic acid and hydroquinone and accounts for 3.0% of mass of the toluene treated.

The probable by-products of PCO of EXT with their retention time (RT) in GC-MS are presented in Table S1.

3.2 Risk Assessment

For demonstrating the risk assessment, it is assumed that a device consisting of seven reactors in series treats the initial concentration of EXT (ethylbenzene: 220 μg/m^3; p,m-xylene μg/m^3: 260 μg/m^3; o-xylene: 260 μg/m^3; toluene : 320.5 μg/m^3) at a flow rate of 7 L/min for a laboratory of volume 195 m^3 for 12 hours. The estimated CA, HI and carcinogenic risk for ethylbenzene are given in Table 5. It can be seen from the Table 5 that the cancerous risk is in the order of 10^{-6} and overall HI (3.28×10^{-4}) is well below the permissible limit of 1.0.

Likewise risk assessment of by-products of ethylbenzene, the risk of by-products of p,m-xylene (see Table S2), o-xylene (see Table S3) and toluene (see Table S4) has been assessed. The overall risk of by-products of EXT is presented in Fig. 6 (Carcinogenic risk) and Fig. 7 (HI). It can be seen from Table 5 that the cancerous risk is in the order of 10^{-6} and overall HI is well below 1.0.

It is concluded that the risk associated with the by-products of photo-degradation of EXT is well within acceptable limits and the technology can be adopted with confidence. It is to be noted that carcinogenic risk and HI are higher from by-products adsorbed on the catalyst surface (solid phase) than vapour phase by-products. The users of technology are well advised to release the vapours from catalyst regeneration process outside the room and away from the inlet of fresh air for air conditioning. This will ensure dilution of harmful by-products.

3.3 Proposed Degradation Pathways

The •OH radical produced from photo irradiation will degrade adsorbed VOCs on the TiO_2 surface. There are three possible pathways for degradation of toluene (Fig. 8): (i) through benzene (Pathway-I; He et al. (2014)[35]), (ii) through phenol-hydroquinone-benzoquinone (Pathway-II; Zhong et al., 2007[36]) and (iii) benzaldehyde/benzylalcohol/benzoic acid (Pathway-III). For the pathway through benzaldehyde/benzyl alcohol/benzoic acid, the pathway given by Mo et al. (2009) [17] has been modified to include pentane cyclohexane, hexane and 2-methyl crotonaldehyde, which were identified in this study and the modified pathway is referred to as Pathway-III.

The literature does not suggest the pathway for the degradation of EX. Based on the by-products identified and quantified, possible pathways have been suggested for EX (Figs. 9-10). It was seen that for the degradation of EX, toluene is the first compound that was observed and quantified. The possible pathway for the formation of toluene is through addition of •OH radical followed by abstraction •H radical from E and X. The toluene is expected to follow the pathways suggested in the above paragraph (Fig. 8). It was observed that the by-products belonging to Pathways –I to III, were present at the same time, which suggests that different pathways can coexist and occur concurrently.

4. Conclusions

In summary, this study has identified and quantified the by-products of photo catalytic degradation of EXT (both in vapour phase and those from catalyst regeneration). A factor was developed in terms of µg of by-product produced per mg of EXT removed per sq-meter surface area of catalyst for estimating the mass of by-products produced under varying conditions. Human health risk of exposure of by-products was estimated for long-term laboratory occupants. The carcinogenic risk ($\sim 10^{-6}$) and HI ($\sim 10^{-4}$) both are within acceptable level and technology can be adopted in field. Based on the identified by-products, the study has suggested the pathways for PCO of EXT.

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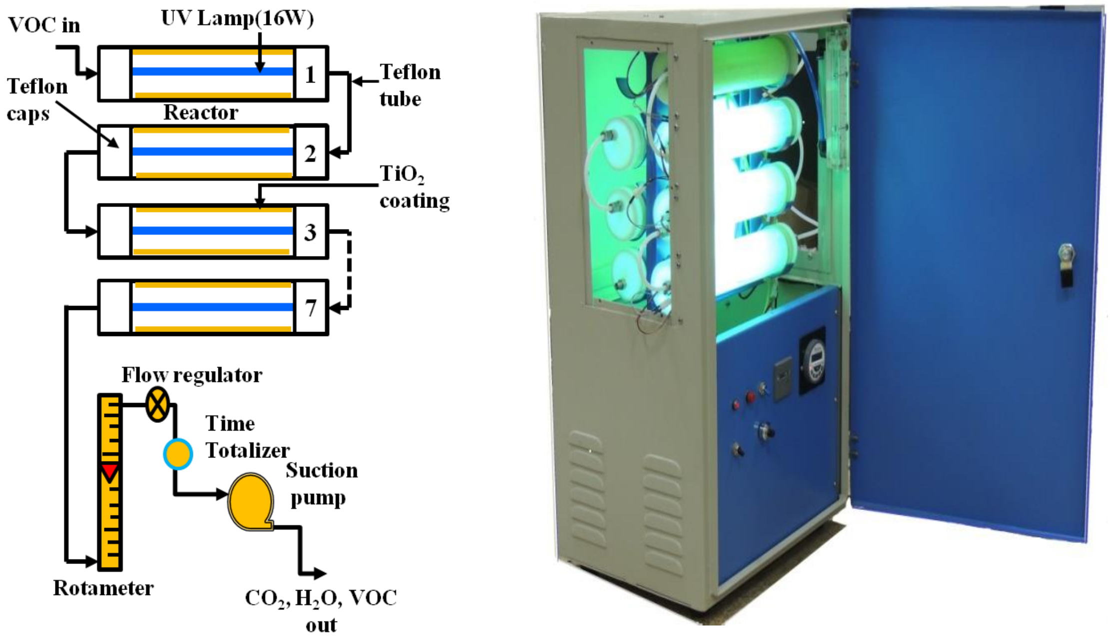

Fig. 1. VOC control device consisting of TiO_2 coated reactors (7 numbers) with Teflon caps.

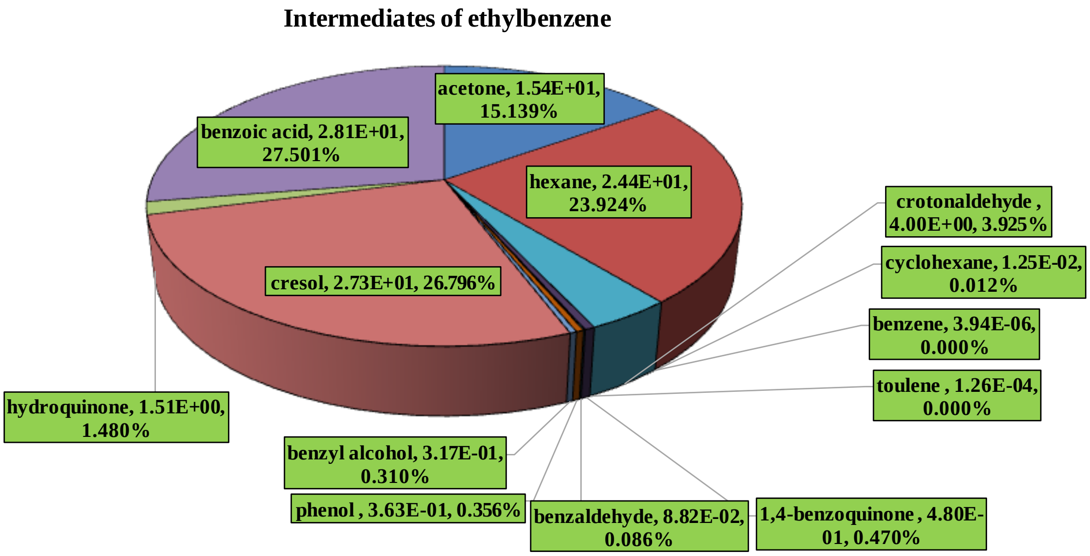

Fig. 2. Mass of intermediates (μg) adsorbed on the catalyst for each mg of ethylbenzene removed per sq-meter surface area of catalyst coating.

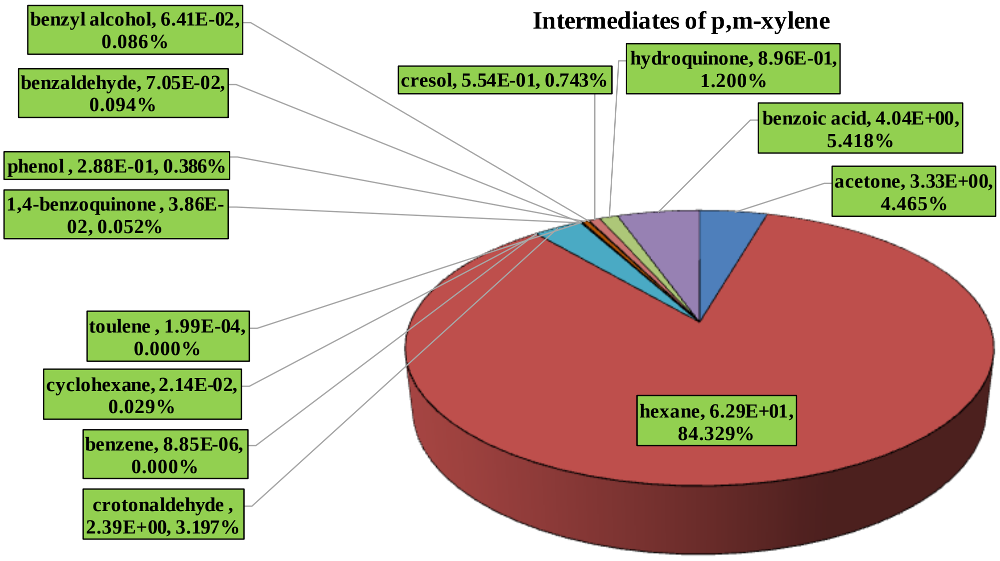

Fig.3. Mass of intermediates (μg) adsorbed on the catalyst for each mg of p,m-xylene removed per sq-meter surface area of catalyst coating.

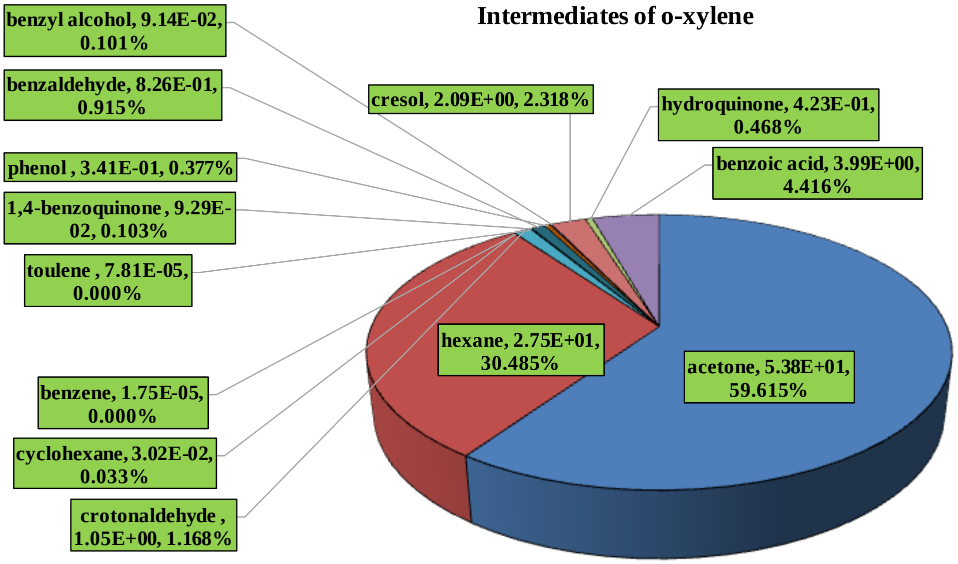

Fig. 4. Mass of intermediates (μg) adsorbed on the catalyst for each mg of o-xylene removed per sq-meter surface area of catalyst coating.

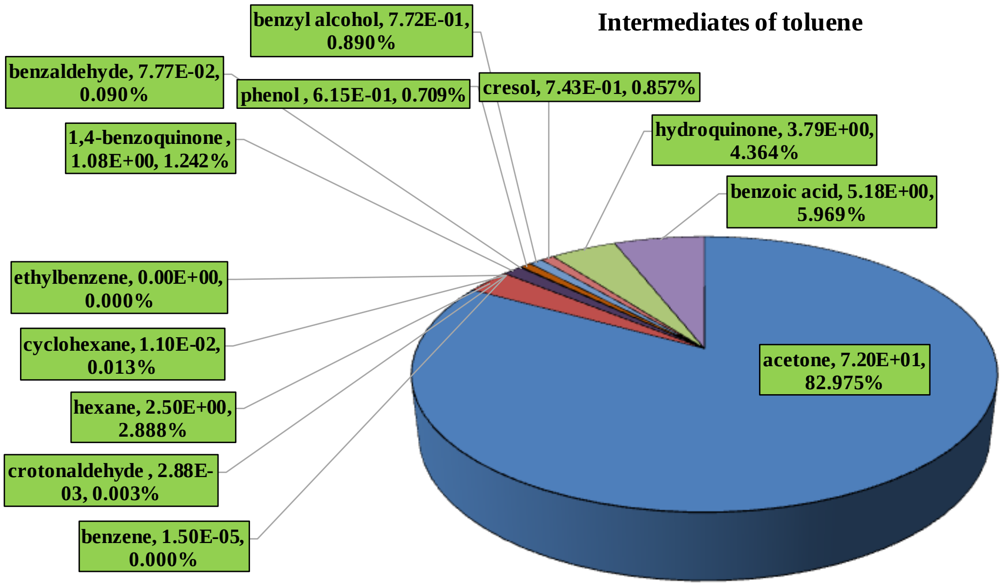

Fig. 5. Mass of intermediates (μg) adsorbed on the catalyst for each mg of toluene removed per sq-meter surface area of catalyst coating.

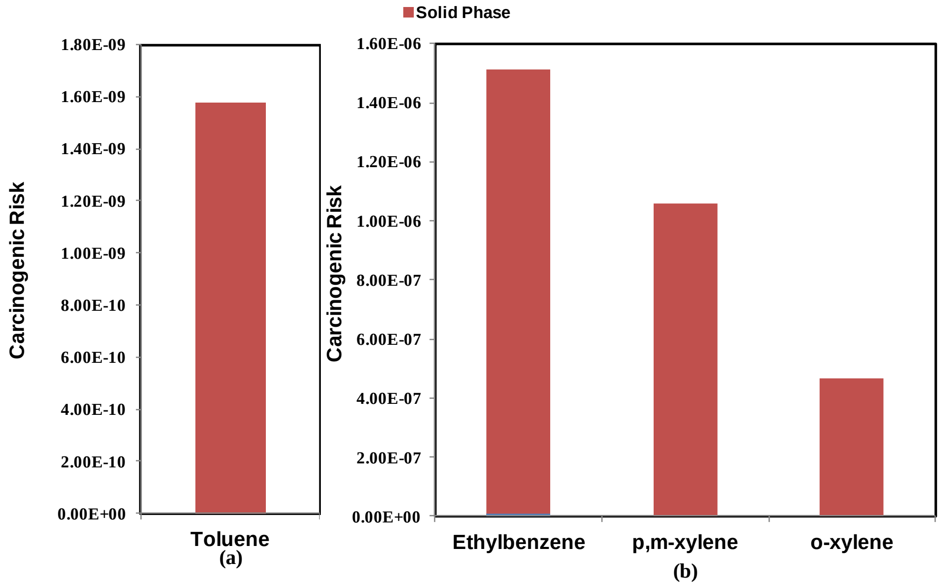

Fig. 6. Carcinogenic risk for solid phase by-products of EXT (vapour phase risk was negligible)

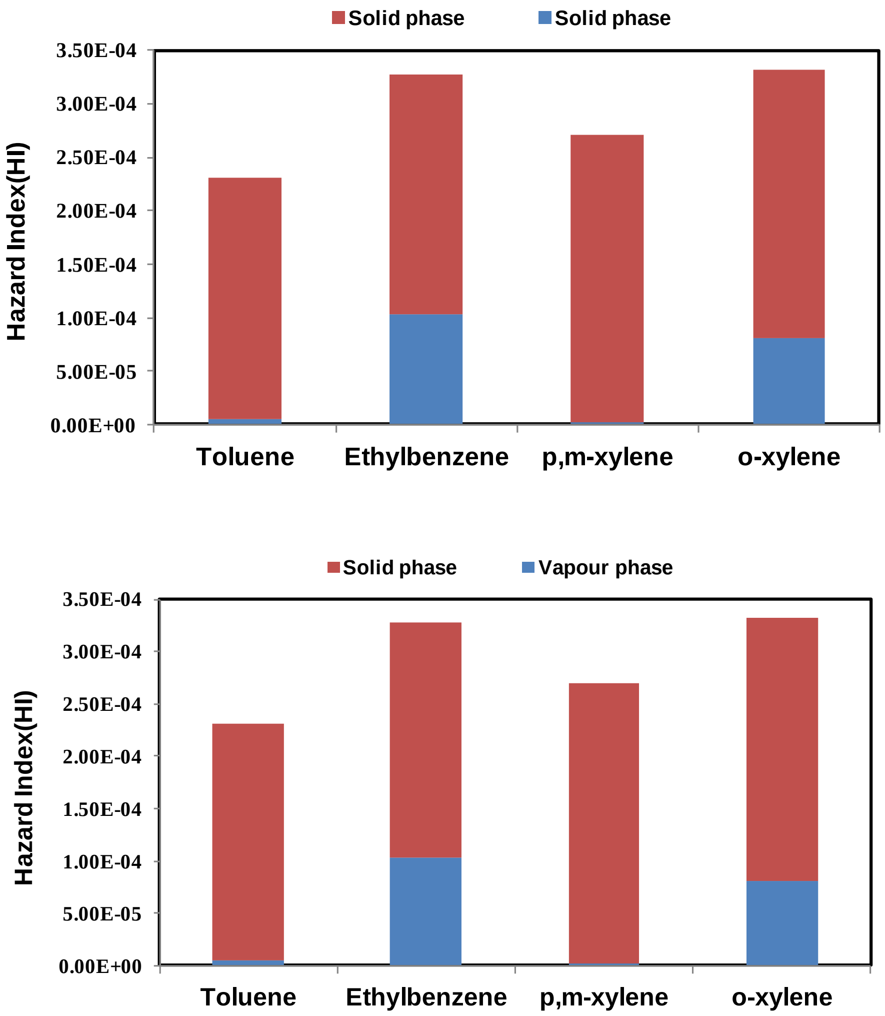

FIG. 7. HAZARD INDEX FOR VAPOUR AND SOLID PHASE BY-PRODUCTS OF EXT.

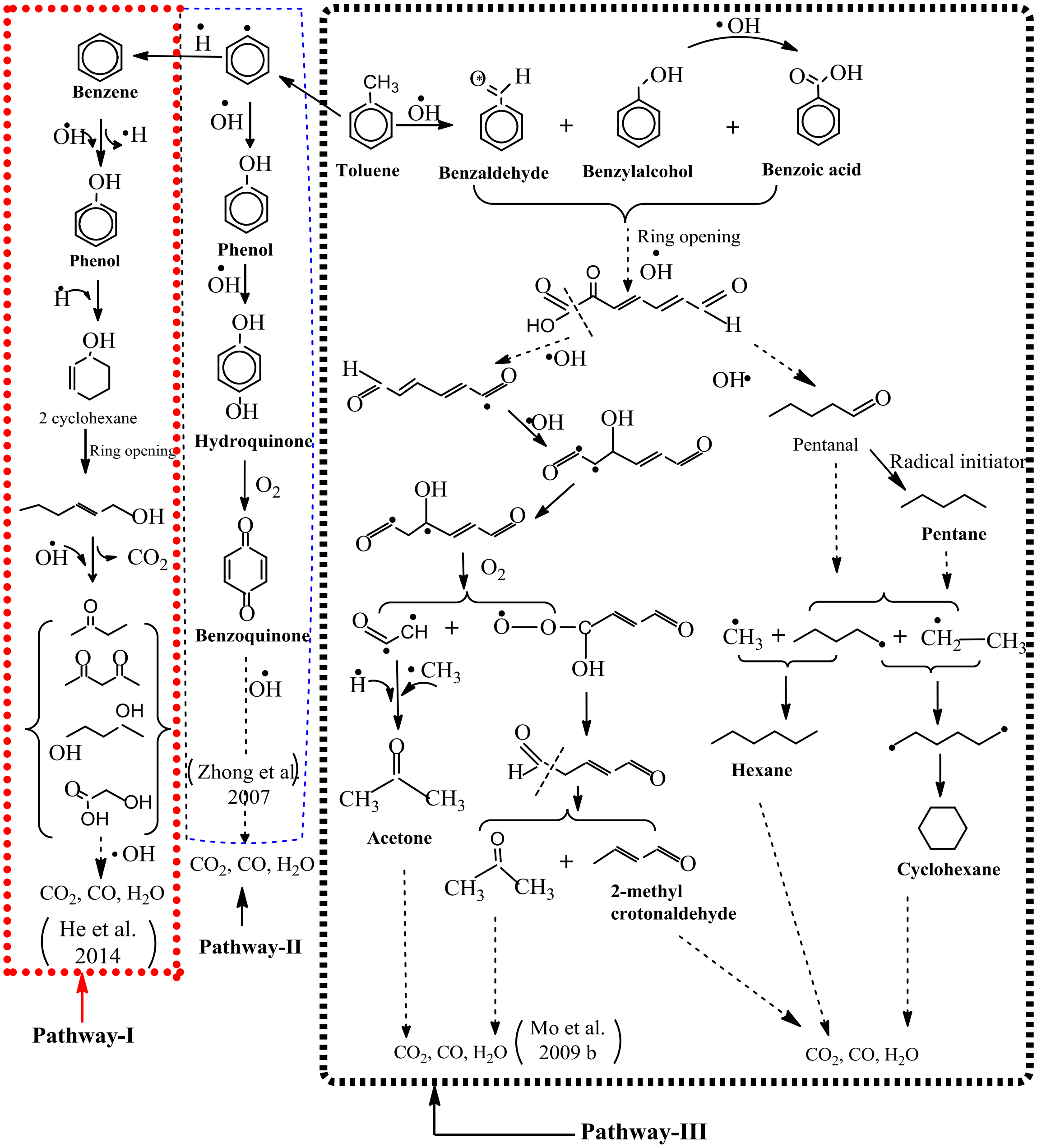

Fig. 8. Possible photocatalytic oxidation pathways of toluene.

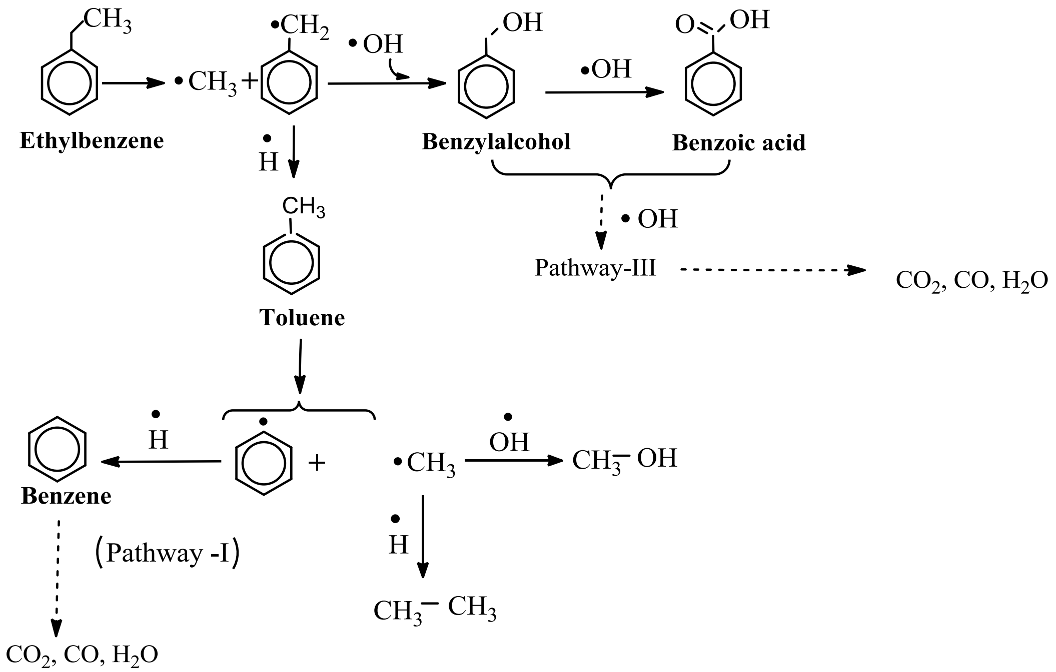

FIG.9. POSSIBLE PHOTOCATALYTIC OXIDATION PATHWAYS OF ETHYLBENZENE.

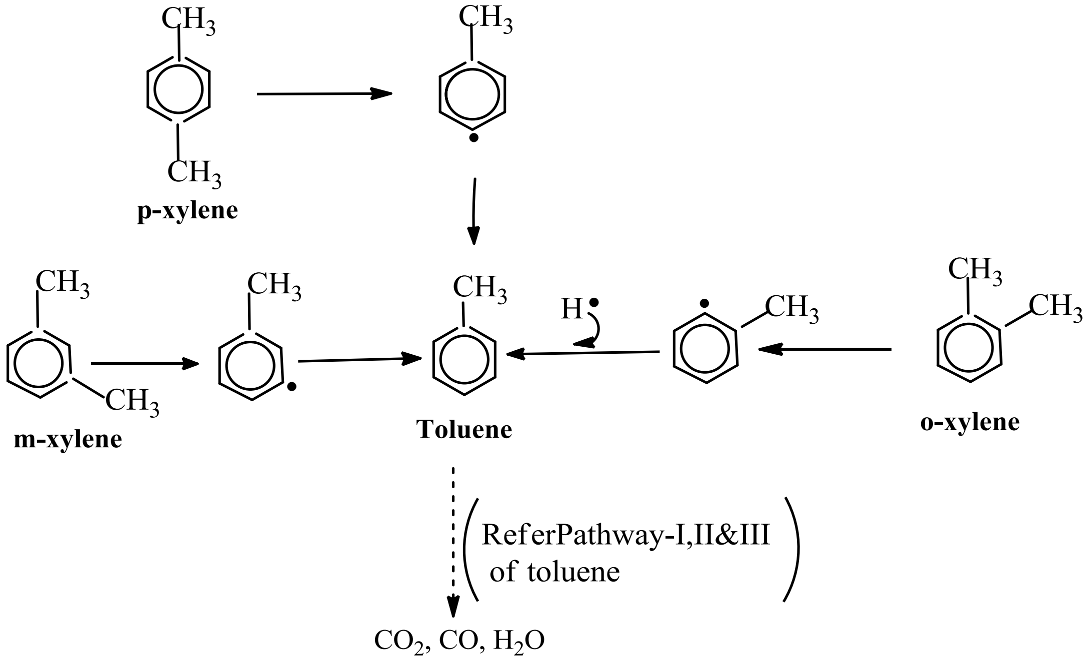

Fig. 10. Possible photocatalytic oxidation pathways of p-xylene, m-xylene and o-xylene.

TABLE 1 VOCS STUDIED FOR BY-PRODUCTS

VOC	Initial VOCs concentration (mg/m^3) for batch study to identify and quantify by-products	Realistic indoor VOCs concentration (µg/m^3) for treatment and risk assessment of by-products*
Ethylbenzene	180	220
p,m-xylene	190	260
o-xylene	130	260
Toluene	170	320

**Highest indoor air concentration reported earlier* [28–31]

Table 2 Mass of vapour phase by-products produced from PCO of ethylbenzene

Time of operation (minutes)	Ethyl benzene (mg)	Measured mass of by-products(μg) per mg of ethylbenzene removed per sq-meter surface area of catalyst coating					
		Hexane	Benzene	Toluene	Phenol	Benzoic acid	Hydro quinone
0	142.40	0.00	0.00	0.00	0.00	0.00	0.00
		(0.0)	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
40	4.73	0.00	0.00	11.23	0.00	0.00	0.00
		(0.0)	(0.0)	(1.12)	(0.0)	(0.0)	(0.0)
80	2.44	41.88	6.57	20.10	0.00	0.00	0.00
		(4.19)	(0.65)	(2.01)	(0.0)	(0.0)	(0.0)
120	0.93	20.19	8.36	11.17	0.00	0.00	0.00
		(2.02)	(0.84)	(1.12)	(0.0)	(0.0)	(0.0)
160	0.42	46.16	4.79	11.16	0.00	5.75	2.40
		(4.62)	(0.48)	(1.12)	(0.0)	(0.58)	(0.24)
200	0.34	29.88	0.00	9.24	0.98	5.56	2.10
		(2.99)	(0.0)	(0.92)	(0.10)	(0.56)	(0.21)
		Estimated total mass of by-products produced (µg per mg of ethylbenzene removed per sq-meter surface area of catalyst coating)					
720	-	29.25	1.10	10.17	0.76	4.64	1.76
		(2.92)	(0.11)	(1.02)	(0.08)	(0.46)	(0.18)

The number in parenthesis shows the percent mass fraction (round off to two decimal numbers) of the by-products with respect to the initial concentration of parent VOC.

Table 3 Mass of by-products produced from PCO of xylenes and toluene (Vapour phase)

By-products	Measured mass of by-products(μg) per mg of VOCs removed per sq-meter surface area of catalyst coating (12hour continuous operation)		
	p, m- xylene	o-xylene	Toluene
Acetone	-	0.04 (0.00)	0.45 (0.05)
Hexane	-	19.71 1.97)	0.94 (0.09)
Phenol	-	1.14 (0.11)	-
Benzoic acid	5.51 (0.55)	5.85 (0.58)	5.26 (0.53)
Hydroquinone	4.83 (0.48)	4.47 (0.45)	3.59 (0.36)
Pentane	0.39 (0.04)	-	-
Toluene	1.01 (0.01)	-	-
Benzyl alcohol	2.22 (0.22)	-	-
1,4 benzoquinone	0.56 (0.06)	-	-
Benzyldehyde	-	-	0.25 (0.03)

The number in parenthesis shows the percent mass fraction (round off to two decimal numbers) of the by-products with respect to the initial concentration of parent VOC.

Table 4 Mass of by-products released from PCO of EXT (μg per mg of EXT removed per sq-meter surface area of catalyst coating in 12hour continuous operation; solid phase)

By-products	VOCs			
	Ethyl benzene	p,m- xylene	o- xylene	Toluene
Acetone	1.55×10^{1}	3.33	5.37×10^{1}	7.20×10^{1}
	(1.55)	(0.33)	(5.37)	(7.20)
Hexane	2.44×10^{1}	6.30×10^{1}	2.75×10^{1}	2.51
	(2.44)	(6.30)	(2.75)	(0.25)
Cyclohexane	1.25×10^{-2}	2.14×10^{-2}	3.03×10^{-2}	1.10×10^{-2}
	(0.00)	(0.00)	(0.00)	(0.00)
Benzene	3.93×10^{-6}	8.86×10^{-6}	1.75×10^{-5}	1.50×10^{-5}
	(0.00)	(0.00)	(0.00)	(0.00)
Crotonaldehyde	4.01	2.39	1.06	2.89×10^{-3}
	(0.40)	(0.24)	(0.11)	(0.00)
Toulene	1.26×10^{-4}	1.98×10^{-4}	7.80×10^{-5}	3.93×10^{-5}
	(0.00)	(0.00)	(0.00)	(0.00)
1,4-benzoquinone	4.80×10^{-1}	3.87×10^{-2}	9.30×10^{-2}	1.08
	(0.05)	(0.00)	(0.01)	(0.11)
Benzaldehyde	8.83×10^{-2}	7.06×10^{-2}	8.26×10^{-1}	7.77×10^{-2}
	(0.01)	(0.01)	(0.08)	(0.01)
Phenol	3.63×10^{-1}	2.89×10^{-1}	3.41×10^{-1}	6.16×10^{-1}
	(0.04)	(0.03)	(0.03)	(0.06)
Benzyl alcohol	3.16×10^{-1}	6.41×10^{-2}	9.13×10^{-2}	7.72×10^{-1}
	(0.03)	(0.01)	(0.01)	(0.08)
Cresol	2.73×10^{1}	5.53×10^{-1}	2.09	7.44×10^{-1}
	(2.73)	(0.06)	(0.21)	(0.07)
Hydroquinone	1.51	8.97×10^{-1}	4.23×10^{-1}	3.79
	(0.15)	(0.09)	(0.04)	(0.38)
Benzoic acid	2.81×10^{1}	4.03	3.98	5.18
	(2.81)	(0.40)	(0.40)	(0.52)

The number in parenthesis shows the percent mass fraction (round off to two decimal numbers) of the by-products with respect to the initial concentration of parent VOC.

Table 5 Indoor air concentration of by-products (vapour and solid phase) of PCO of ethylbenzene and health risk (Volume of room 195 m^3 and mass of ethylbenzene treated 1.1088 mg)

By-products	CA (mg/m^3)	CDI (mg/kg-day)	RfD (mg/kg-day)	Carcinogenic Risk(SF* × CDI)	HI
		Vapour phase			
Hexane	6.10×10^{-5}	5.79×10^{-6}	5.72×10^{-2}		1.01×10^{-4}
Benzene	2.28×10^{-6}	2.17×10^{-7}	N.A.	6.28×10^{-9}	-
Toluene	2.12×10^{-5}	2.01×10^{-6}	1.40		1.44×10^{-6}
Phenol	1.59×10^{-6}	1.51×10^{-7}	6.00×10^{-1}		2.51×10^{-7}
Benzoic acid	9.68×10^{-6}	9.18×10^{-7}	4.00		2.30×10^{-7}
Hydroquinone	3.68×10^{-6}	3.49×10^{-7}	N.A.		-
			Σ=	6.28×10^{-9}	1.03×10^{-4}
		Solid phase			
Acetone	3.22×10^{-5}	3.06×10^{-6}	1.00×10^{-1}		3.06×10^{-5}
Hexane	5.09×10^{-5}	4.83×10^{-6}	5.72×10^{-2}		8.44×10^{-5}
Cyclohexane	2.61×10^{-8}	2.48×10^{-9}	1.71#		1.45×10^{-9}
Benzene	8.21×10^{-12}	7.79×10^{-13}	N.A.	3.65×10^{-14}	
Crotonaldehyde	8.35×10^{-6}	7.92×10^{-7}	N.A.	2.43×10^{-6}	
Toulene	2.62×10^{-10}	2.49×10^{-11}	1.40		1.78×10^{-11}
1,4-benzoquinone	1.00×10^{-6}	9.49×10^{-8}	N.A.		
Benzaldehyde	1.84×10^{-7}	1.74×10^{-8}	1.00×10^{-1}ϴ		1.74×10^{-7}
Phenol	7.57×10^{-7}	7.18×10^{-8}	6.00×10^{-1}		1.20×10^{-7}
Benzyl alcohol	6.60×10^{-7}	6.26×10^{-8}	3.00E$\times10^{-1}$ϴ		2.09×10^{-7}
Cresol	5.70×10^{-5}	5.41×10^{-6}	5.00×10^{-2}		1.08×10^{-4}
Hydroquinone	3.15×10^{-6}	2.99×10^{-7}	N.A.		
Benzoic acid	5.85×10^{-5}	5.55×10^{-6}	4.00×10^{0}		1.39×10^{-6}
			Σ =	1.51×10^{-6}	2.25×10^{-4}
		Overall (vapour phase+solid phase) =		1.51×10^{-6}	3.28×10^{-4}

N.A.: *Not Available*

[33]

ϴ [34]

* *Slope factor (SF for Benzene =0.029/mg/kg/day; crotonaldehyde =1.9/mg/kg/day* [34])