Review on phenolic compounds: Occurrence and Properties

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Abstract

Phenols are aromatic compounds containing one or more hydroxyl groups attached to the aromatic ring. Phenols are weak acids in comparison to aliphatic alcohols, hence they can be extracted easily from the organic solutions using aqueous Sodium Hydroxide. When aliphatic one or more aromatic hydrogen atoms are replaced by alkyl groups, phenols are termed Alkylphenols.

In this paper, the occurrence and properties of phenols and its derivatives have been studied to understand their chemistry. This shall help to identify energy efficient and economically feasible wastewater treatment technique owing to the known hazardous impact of presence of phenols in industrial effluents on environment and human health.

1. Introduction

Phenol (hydroxybenzene) is a colourless crystalline compound of characteristic odour, soluble in water and organic solvents. Commercially, phenol is synthesized by extraction from coal tar since it is formed by transformation of high quantities of cumene present in plants used for tar production (Michalowicz and Duda, 2007). It is also obtained by reaction between chlorobenzene and sodium hydroxide, oxidation of toluene and synthesis from benzene and propylene. Phenol is produced as a result of chemical reactions occurring in the atmosphere in condensed water vapour forming clouds (Michalowicz and Duda, 2007). It is also formed during natural processes: biosynthesis by plants and decomposition of organic matter (USEPA, 1980). This compound is a result of amino acids contained in hemicellulose of plants under the UV irradiation influence (Davidson, 1996) and tyrosine transformation in mammalian digestive tract (Tsuruta, 1996). Phenols are present in environment due to their usage in production of several pesticides (phenoxyherbicides) like 2, 4 - dichlorophenoxyacetic acid (2, 4 - D), 4 -chloro -2 - methylphenoxyacetic acid (MCPA) and phenolic biocides like pentachlorophenol (PCP), dinoseb and diarylether pesticides. Phenols are formed due to natural processes like degradation of organic matter or synthesis of chlorinated phenols by fungi and plants (Michalowicz and Duda, 2007). These compounds are used to make synthetic resins, dyes, pharmaceuticals, pesticides, synthetic tanning agents, perfumes, lubricating oils and solvents (Michalowicz and Duda, 2007). Phenols are used in different industries including chemical production of alkyl phenols, cresols, xylenols, resins, aniline and other compounds (Bobrański., 1973), oil, processing of coal and metallurgic (Bruce et al., 1987). It also finds use in pesticides, explosives, dyes and textile production (Budavari et al., 2001).

The exposure to phenol causes skin irritation and necrosis. This exposure damages kidney, liver, muscles and eyes. The damage to skin is caused because of coagulation due to reaction of phenol with amino acids present in keratin of the epidermis and collagen in inner skin. The harmful effects are characterised by dryness in throat and mouth, dark coloured urine and strong irritation in mucous membranes (Michalowicz and Duda, 2007). Their presence even in low concentration can cause hindrance in use or reuse of water. This results in unpleasant taste and odour of water and imparts negative effects on different biological processes (Dąbrowski et al., 2005).

Phenols are one of the priority pollutant listed by Environment Protection Agency (EPA). Under section 313 of the Emergency Planning and Community Right to Know Act of 1986 (EPCRA), release of more than one pound of phenol into air, water and land must be reported annually and should be entered into Toxic Report Inventory (TRI). The EPA has developed National Recommended Water Quality Criteria (EPA Standards., 2009) to provide guidance to States and Tribes in adopting water quality standards under section 304(a) of the Clean Water Act (CWA). The United States Environmental Protection Agency (US-EPA) has limited phenol level in surface water to 0.5 mg/L. The permissible limit for discharge of phenol in drinking water defined by US-EPA (Ohio EPA 2002), European Union (Busca et al., 2008) and MINAS of CPCB, India is 0.5 mg/L.

The existence of phenols and their derivatives in industrial wastewater is a major health hazard. Their presence in environment particularly in water is harmful both for human beings and flora and fauna. Therefore, the focus is on purification of wastewater containing phenol . The treatment of phenolic wastewater can be classified into two categories: destructive and recuperative processes (Banat et al., 2000). The former includes destruction oxidation with ozone (Hoigne., 1985), hydrogen peroxide (Kochany and Bolton., 1992) or manganese oxides (Ukrainczyk and McBride., 1992) while latter involves removal techniques like adsorption onto porous solids (Danis et al., 1998), membrane separation (McCary and Ray., 1987) and solvent extraction (Eahart et al., 1977). The techniques in practice for the removal include adsorption (Ahmaruzzaman & Sharma., 2005), reactive adsorption (Sharma et al., 2013), ion-exchange processes (Clifford), extraction (Pinto et al., 2005) etc. The presence of enormous diversity of chemical pollutants in water requires special treatment technologies for its decontamination to improve water quality and treated wastewater before it can be reutilized (Ania et al., 2004). The present study deals with comparing various methods used for removal of phenol and its derivatives and regeneration of spent adsorbent.

2. Phenol

2.1 Properties of phenol and its derivatives

Table 1 represents physical and chemical properties of phenol and its compounds. The knowledge of these values determines the range of operating conditions during commercial production of phenol and helps in handling such potentially harmful compounds.

Table 1 Physical and Chemical properties of phenol and derivatives

Compound Name	**bp(°C)**	**mp(°C)**	**Solubility in water**	**pK$_a$ value**	**Reference**
p-tert butylphenol	237	98	Soluble	10.16 at 25°C	Ishikwa., 2000
Catechol	245.5	105	Very soluble, 430 g/l at 25°C	9.25, 13	Suresh et al, 2012
2-Chlorophenol	174.9	9.3	28 g/l at 20°C	8.3-8.6	Czaplicka., 2004
3-Chlorophenol	214	33-34	26 g/l at 20°C	8.8-9.1	Czaplicka., 2004
4-Chlorophenol	217-219	42-44	27 g/l at 20°C	9.1-9.4	Czaplicka, 2004

o-Cresol	191	31	Soluble, 93 g/l at 25°C	10.20 at 25°C	Dąbrowski et al., 2005
m-Cresol	202	12	Slightly soluble, 25 g/l at 25°C	10.01	Dąbrowski et al., 2005
p-Cresol	202	35	Slightly soluble, 23 g/l at 25°C	10.17	Dąbrowski et al., 2005
2,4-Dichlorophenol	210	45	Slightly soluble, 4.5 g/l at 20°C	7.5-8.1	Czaplicka., 2004
2,5-Diclorophenol	211	58-59	-	7.51-8.1	Czaplicka., 2004
3,5-Dichlorophenol	233	68	Slightly soluble	6.9-8.3	Czaplicka., 2004
2,4-Dimethylphenol	211.5 (at 766 mm Hg)	25.4-26	Slightly soluble		
Hydroquinone	287	172	Soluble (59 g/l at 25°C)	9.9, 11.6	Suresh et al., 2012
4-Nonylphenol (branched)	293-297	-8	5.4 mg/l	-	Ying et al., 2002; ECB, 2002; Ahel and Giger., 1993
Pentachlorophenol	310	190	Slightly soluble, 0.014 g/l at 20°C	4.7-4.9	Czaplicka., 2004

Phenol	182	43	Soluble, 93 g/l at 25°C	9.89 at 25°C	Dąbrowski et al., 2005
Resorcinol	277	111	1100 g/l at 25°C	9.2, 10.9	Suresh et al., 2012
2,3,4,6-Tetrachlorophenol	150	70	0.183 g/l at 20°C	5.3-6.6	Czaplicka., 2004
2,3,5,6-Tetrachlorophenol	188	114-116	0.1 g/l at 20°C	5.2-5.5	Czaplicka., 2004
2,3,5-Trichlorophenol	248-255	57-62	0.22 g/l at 20°C	6.8-7.4	Czaplicka., 2004
2,3,6-Trichlorophenol	246	58	-	6.0-7.1	Czaplicka., 2004
2,4,5-Trichlorophenol	Sublimes	67-70	0.948 g/l at 20°C	7.0-7.7	Czaplicka., 2004
2,4,6-Trichlorophenol	243-249	69	0.434 g/l at 20°C	6.0-7.4	Czaplicka., 2004
2-Nitrophenol	215	-	2.0 g/l at 25°C	7.17 at 25°C	Dąbrowski et al., 2005
3-Nitrophenol	194	-	1.35 at 25°C	8.28 at 25°C	Dąbrowski et al., 2005

2.2 Occurrence of Phenols

There are a total of 33 phenolic compounds that are classified into a periodic table using an algorithm based on information entropy (Castellano et al., 2012). Phenols are structurally classified in a hierarchical order based on five features. Depending on these features, the first three are marked as Group and the last two are called Period. Those present in the same group exhibit moderate similarity. Phenols occur both naturally and in synthetic compound form.

Table 2 Naturally occurring forms of phenols

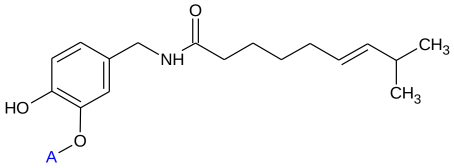
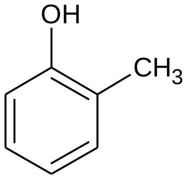
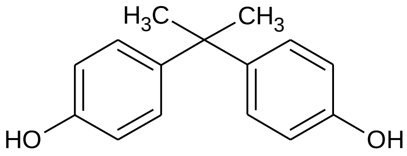
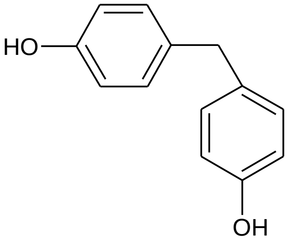
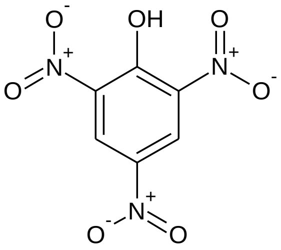
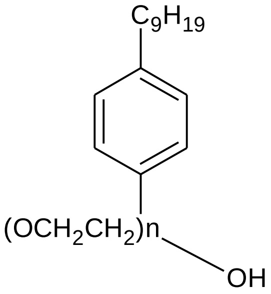
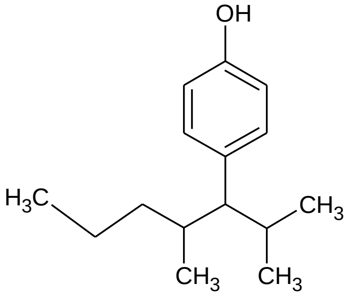
Compound Name	Occurrence in nature	Characteristic features	Compound Structure	Reference
Capsaicin	Hot chili pepper	Pungent taste, fat soluble alkaloid originating from Bolvia, Brazil, mostly present in trans - isomeric form		Arora R et al., 2011
Cresol	Coal tar and creosote	Non-biodegradable, toxic and corrosive		Fardhyanti et al., 2012; Dyreborg and Arvin, 1994
Cannabinoids	Glandular trichomes of plant	-	-	Meijer et al., 2003

Table 3 Synthetic forms of phenols and their applications

Compound Name	Applications	Remarks	Compound Structure	Reference
Bisphenol-A	Can coatings on, powder paints, additives in thermal paper, in dental fillings	Surface water: 0.0005 - 0.41 µg/L Sewage effluent: 0.018 – 0.702 µg/L Sediments: 0.01 – 0.19 mg/kg Sewage sludge: 0.004 - 1.363 mg/kg dry weight		Fromme et al., 2002
Bisphenol-F	Production of epoxy resins and polycarbonates for lining large foods containers and water pipes	Surface water: 0.0001 - 0.18 µg/L Sewage effluent: 0.022 – 0.123 µg/L Sewage sludge: 4.2 - 181 µg/kg dry weight		Fromme et a.l, 2002

Picric acid (2,4,6-Trinitrophenol)	Explosives, dyes, germicides, analytical agents, tissue fixatives, tanning agents, photo-chemicals, pharmaceuticals	Toxic and acidic		Mohan et al., 2011
Alkylphenol ethoxylates (APE's)	Surfactants, domestic detergents, wetting and foaming agents, dispersants, emulsifiers, solubilizers; Industrial applications include paper and pulp, textiles, coatings, agricultural pesticides, lube oils and fuels, metals and plastics	Metabolites more toxic than parent substances, ability to mimic natural hormones by interacting with estrogen receptor, solubility depends on number of polar groups forming hydrophilic part of molecule		Ying et al., 2002

Nonylphenol	Non-ionic surfactants, manufacture of antioxidants, lubricating oil additives; Industrial applications include detergents, emulsifiers, wetting and dispersing agents, antistatic agents, demulsifiers and solubilizers	Low solubility, high hydrophobicity; Naturally occurs in rain and snow. Rain Sample: Urban sites: 0.062 µg/dm^3 Rural sites: 0.099 µg/dm^3 Snow Sample: Urban sites: 0.478 µg/dm^3 Suburban sites: 0.03 µg/dm^3		Fries and Püttmann., 2004 and Soares et al., 2008

Typically phenols are found in water bodies where industries discharge their effluents. Table 4 represents areas where phenols and their derivatives can be found.

Table 4 Concentration of phenols at various locations reported in literature

Name of compound	Location	Concentration	Reference
Alkylphenols	Surface water	0.7-21,000 (µg/L)	Michalowicz & Duda., 2007
Bisphenols A	Estuaries of Elba river, Germany	4-92 (µg/L)	Nelson et al., 2000
Bisphenols A	Sediments of Elba river, Germany	10-380 (µg/kg)	Nelson et al., 2000
2,3-Dimethylphenol	Buriganga river (Sowarighat), Bangladesh	0.946 (mg/L)	Hossain & Salehuddin., 2009
Bacteriside Triclosan	Lakes & rivers, Switzerland	74 (ng/L)	Buser et al., 2002
Chlorophenols	Oceanic waters	5-10 (ng/L)	Michalowicz & Duda., 2004
Chlorophenols	River water	2-2000 (µg/L)	Michalowicz & Duda., 2004
2,4,5-trichlorophenol & tetrachlorophenol	Drinking water	0.2-0.3 (µg/L)	Michalowicz J., 2004

Methyl Triclosan	Lakes & rivers, Switzerland	2 (ng/L)	Buser et al., 2002
4-Methylphenol	Hayashida River, Japan	204 (µg/L)	Michalowicz & Duda., 2004
2-Nitrophenols	Rain water & Snow	0.03-5.7 (µg/L)	Michalowicz & Duda., 2004
2-Nitrophenols	Ebro River, Spain	0.1-5.0 (µg/L)	Michalowicz & Duda., 2004
4-Nitrophenol	Ebro River, Spain	0.1-5.0 (µg/L)	Michalowicz & Duda., 2004
2,4-Dinitrophenol	Ebro River, Spain	0.1-5.0 (µg/L)	Michalowicz & Duda., 2004
Phenols	Natural water	0.01-2.0 (µg/L)	Michalowicz & Duda., 2004
Phenols	Surface Water, Netherlands	2.6-5.6 (µg/L)	Michalowicz & Duda., 2004

Phenols	Natural water	0.01-2.0 (µg/L)	Michalowicz & Duda., 2004
Phenols	Domestic water supply, USA	1 (µg/L)	Michalowicz & Duda., 2004
Phenolic compounds	Surface Water, Malaysia	1-2 (µg/L)	Abdullah et al., 2006
Phenolic Compound	Sewage & Industrial effluents, Malaysia	1-5 (mg/L)	Abdullah et al., 2006
Tetrachlorocatechol	River water, Central Poland	2 (µg/L)	Michalowicz & Duda., 2004

Based on Table 4, it can be inferred that high concentration of phenolic compounds is present in sewage & industrial effluents. It is found in Malaysia and 2,3-Dimethylphenol near Buriganga river (Sowarighat), Bangladesh. Bisphenol A (BPA) in Elba River, Germany is found in significant quantity while 4-Methylphenol in Hayashida River, Japan is detected in much less amount.

2.3 Phenol Toxicity

Table 5 represents phenol concentration in different industrial effluents.

Table 5 Phenol concentration in various industries

Name of industry	Phenol concentration (mg/L)	Reference
Refinery	6 – 500	Busca et al., 2008
Coking operations	28-3900	Busca et al., 2008
Plastic factory	800-8000	Veeresh et al., 2005
Manufacture of petrochemicals	2.8 – 1220	Busca et al., 2008
Paper and pulp industries	0.1 – 1600	Busca et al., 2008
Phenol resin production glass	800 – 2000	Meikap et al., 1977
Pharmaceutical industries	10 – 100	Luthy., 1979
Aircraft maintenance	200 – 400	Veeresh et al., 2005
Wood processing industries	Alkyl phenol: 0.02-2.8 (µg/L) & max: 43.3 (µg/L)	Fries & Püttman, 2003

It is seen that industrial wastewater from plastic industry contains highest phenol concentration. Phenol are used during production of surfactants, fertilizers, explosives, paints and removers, textiles, rubber , plastic plasticizers, anti-oxidants and curing agents etc (Busca et al., 2008).

2.4 Phenol Analysis

The various techniques presented in Table 6 help in estimating qualitative and quantitative analysis of the compound.

Table 6 Comparison of techniques for phenol analysis

Name of the method	Detection range	Remarks	Reference
Calorimetric	-	Time consuming, complicated sample pre-treatment, low sensitivity	Encyclopaedia of Analytical Science, 1995
Spectroscopic	-	Time consuming, complicated sample pre-treatment, low sensitivity	Textbook of Quantitative Chemical Analysis, 1998
Flow injection with Electrochemical detection	-	Fast method (sampling frequency 60 h^{-1}), precision: 0.1- 4.0 %, improved accuracy of determination of total Phenols (substituted Phenols: p- and nitro-Phenols) in sample	Christopheresen and Cardwell., 1996
Crystallization-Photometric technique	Max permissible concentration for	Sensitive to sample crystallisation rate	Eksperiandova et al., 1995

	chlorinated water (0.001 mg/L)		
Pervaporation Flow Injection technique	Limit: 0.9 mg/L Sampling frequency: 5 h^{-1}	Phenol determination in natural water containing suspended particulate matter, no preliminary filtration of sample/solid phase extraction required	Sheikheldin et al., 2000
Optical Detection using Chitosan film	2.5-70.0 µM	Good sensitivity, reproducibility,	Abdullah et al., 2006
GCMS	As low as 100 ng/L	Sensitive, rapid, simple, environment friendly	Hossain and Salehuddin., 2009

3. Conclusion

It is inferred that industrial wastewater from plastic industry contains highest phenol concentration. Throughout the study, various sources of phenolic compounds can be identified and their likely composition in the wastewater from various industries. This paper can help to determine the most area surrounding the respective production units, where immediate remediation can be started.

The first step towards this would include control the amount of phenols released in the effluent, finding its suitable alternative in the manufacturing of products and lastly, wastewater treatment using appropriate treatment method.

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