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Chemical Structure of Phenols and Its Consequence for Sorption Processes

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Additional information is available at the end of the chapter

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Abstract

Sorption of phenolic compounds is a very complex process and many factors influence it. At the beginning, detailed chemical structure of phenols is presented with its consequence for physical properties, for example, values of melting and boiling points, solubility in water, pKa and Log P. Also influence of activating and deactivating substituents on the properties is explained. On this basis, interaction with the most frequently used sorbents, for example, chemically modified silicas, polymers and porous carbons, is described. Both sorbents characteristics including physical (porosity) and chemical properties (functional groups) and experimental conditions such as concentration of solutes, contact time, temperature, solvent effects and presence or absence of oxygen are taken into account. The explanations of irreversible adsorption and oxidative coupling phenomena are included. The mechanisms of phenolic compounds sorption are described.

Keywords: phenol's properties, phenol's sorption, phenol's interactions, structure, adsorbents

1. Introduction

There is a huge variety of phenolic compounds in our natural environment. Some like eugenol, thymol, pyrogallol, guaiacol or pyrocatechol are formed in natural way, but a vast majority of them are introduced as a consequence of industrial, agricultural and communal activities of humans. While the former are neutralized as the result of natural processes, the latter pose a serious risk to the environment.

Quantitative isolation of phenol and its derivatives from environmental matrices is usually difficult because of considerably different properties and low concentration. It was a stimulus to development of research on process of sorption and search for efficient sorptive materials.

This chapter is devoted to review of current state of knowledge on sorption process of phenolic compounds. Many different types of sorbents are used for phenols in chromatographic columns and solid phase extraction devices. Their efficiency is diverse and depends on many factors. As the most important chemical structure of adsorbate, a type of sorbent and its porosity as well as properties of solvent (or eluent) should be mentioned. Also other properties such as pH, temperature and presence of oxygen influence the process. For this reason, sorption of phenols is a very complex phenomenon. Although many researchers try to explain the mechanism of interaction of phenols with adsorbents, it is still an open problem.

Many groups of researchers tried to solve it using different scientific methods, for example, chromatography [1, 2], spectroscopy (UV, mass spectrometry [MS], Fourier transform infrared spectroscopy [FTIR]) [3–5], thermal analysis [6], and computer simulations [7]. Based on the obtained results, some authors proposed explanations of phenomena and mechanisms accompanying the sorption of phenol. Understanding the mechanism is important from scientific point of view. Elucidation of this process is essential for reasons of utility and finding an answer to the questions how to improve efficiency of sorption phenolic compounds in the processes of aqueous environment remediation. Effective removal of these species from industrial and urban waste water helps to protect aquatic ecosystem from toxic impact of phenols on the living organisms, which is an important aim all over the world.

2. Chemical structure and properties of phenols

Phenols are compounds possessing one or more hydroxyl groups (-OH) directly connected to the aromatic system (e.g. phenyl, naphthyl) [8, 9]. **Figure 1** presents some examples of phenols with their systematic and common names.

All carbon atoms forming aromatic ring are sp^2 hybridized. Therefore, phenyl has hexagonal planar structure with all bond angles 120° and delocalized π -electrons distributed over the ring. The C-O bond is formed from $\text{Csp}^2\text{-Osp}^3$ and the O-H bond is formed from $\text{Osp}^3\text{-H}1\text{s}$. Two other orbitals of oxygen atom are occupied by two nonbonded electron pairs. For this reason, hydroxyl functional group C-O-H has a bent shape with almost the tetrahedral bond angle of 109.5° as it is represented in **Figure 2**. Oxygen is more electronegative than carbon and hydrogen that makes both the C-O and O-H bonds polar [10].

Moreover, electron pairs of oxygen atom are conjugated with aromatic system that causes partial transfer of negative charge from oxygen to the ring and delocalization of the charge. This effect additionally strengthens polarization of O-H bond. In consequence, phenol gains acidic character and ability to form phenoxide (phenolate) ion [9, 10]. Both phenol and its conjugate base are resonance stabilized. Dispersion of the negative charge over the molecule can be illustrated with the resonance structures or as a resonance hybrid as in **Figure 3**.

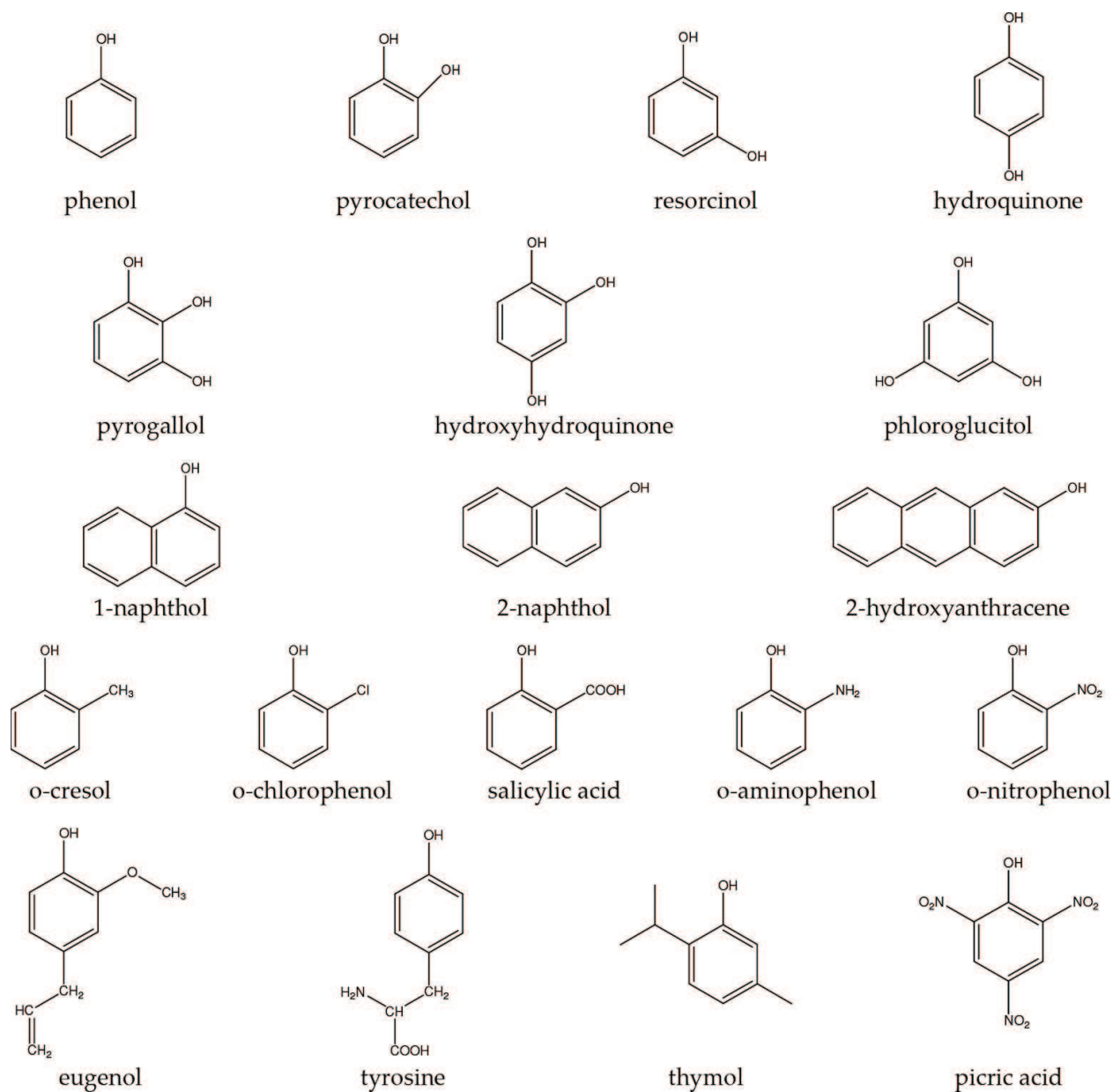


Figure 1. Examples of phenolic compounds.

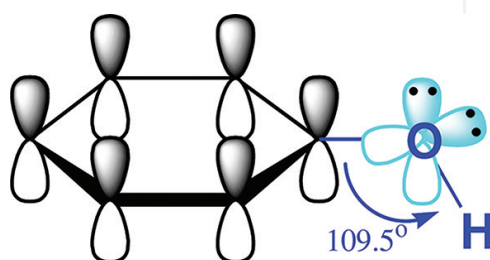


Figure 2. The structure of phenol.

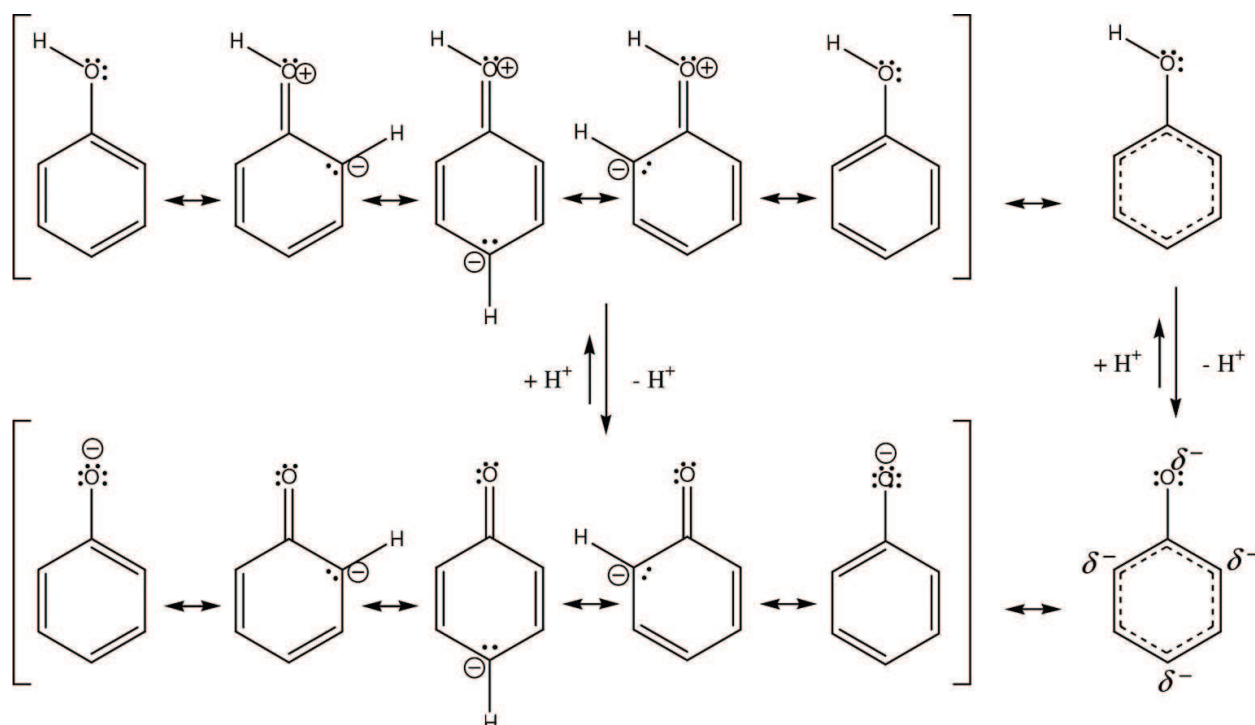


Figure 3. Resonance stabilized structures of phenol and phenoxide representing dispersion of negative charge and its resonance hybrid. Based on Refs. [9, 10].

All the above-mentioned structural features give the phenol specific physical and chemical properties. Phenol is a peculiar smelling, water-soluble crystalline solid, with low melting and high boiling point values. These attributes can be reinforced or weakened, if a substituent is connected to the aromatic ring. A chemical character (electron withdrawing or donating), the way of substitution—position and a number of functional groups attached to the ring—can alter properties of the phenol significantly. Some properties such as melting (MP) and boiling points (BP), density (D), water solubility (w.s.), acidity in water (pKa) and octanol-water partition coefficient (Log P) of phenol and its derivatives are presented in **Tables 1** and **2** [11, 12]. Comparison of these data allows to evaluate the impact of substituents on change of the properties.

Many monohydroxyl derivatives (alkylphenols, alkoxyphenols, halogenophenols, 2- and 3-nitrophenols) similar to phenol are crystalline solids with melting points below 100°C and boiling points ca. 200°C. Other nitrophenols, aminophenols, pentachlorophenol, hydroxybenzoic acids and species possessing two or more hydroxyl groups in a molecule have very high values both melting and boiling points. While some phenols are sublime, others decompose before reaching the boiling point. So, high temperatures are the consequence of intermolecular hydrogen bonds, which are formed between the molecules, thereby justifying water solubility of these compounds. The examples of intermolecular hydrogen bonds that phenols can form with their own molecules and with molecules of water are shown in the **Figure 4**.

Compound	Case no.	M [g mol ⁻¹]	MP [°C]	BP [°C]	d [g cm ⁻³]	p.s.	w.s. [g L ⁻¹]	pKa	LogP	μ [D]
Chemical name										
IUPAC name										
Benzenol Phenol	108-95-2	94.11	40.91	181.7	1.071	c.s.	83	9.99	1.46	1.61
Pyrocatechol Benzene-1,2-diol	120-80-9	110.11	105	245.5	1.344	c.s.	461	9.45 12.8	0.88	nda
Resorcinol Benzene-1,3-diol	108-46-3	110.11	109.8	280	1.278	c.s.	1400	9.30 11.06	0.80	2.07
Hydroquinone Benzene-1,4-diol	123-31-9	110.11	171	287	1.330	c.s.	72	10.85	0.59	1.4
Pyrogallol Benzene-1,2,3-triol	87-66-1	126.11	133	309	1.453	c.s.	507	9.01	0.97	nda
Hydroxyhydroquinone Benzene-1,2,4-triol	533-73-3	126.11	141	nda	nda	c.s.	nda	nda	nda	nda
Phloroglucinol Benzene-1,3,5-triol	108-73-6	126.11	217 -219	S. D.	nda	c.s.	10	8.45	nda	nda
1-Naphthol Naphthelene-1-ol	90-15-3	144.17	96	288	1.095	c.s.	0.86	9.34	2.85	1.40
2-Naphthol Naphthelene-2-ol	135-19-3	144.17	121.6	285	1.28	c.s.	0.75	9.51	2.70	1.53
o-Cresol 2-Methylphenol	95-48-7	108.14	31.0	191.0	1.047	c.s.	25.9	10.287	1.95	1.60
m-Cresol 3-Methylphenol	108-39-4	108.14	12.2	202.2	1.034	l	22.2	10.09	1.96	1.44
p-Cresol 4-Methylphenol	106-44-5	108.14	34.77	201.9	1.0185	c.s.	21.5	10.26	1.94	1.64
m-Xylenol 2,4-Dimethylphenol	105-67-9	122.16	25.4 -26	211.5	0.965	c.s.	7.87	10.60	2.30	nda

Compound	Case no.	M [g mol ⁻¹]	MP [°C]	BP [°C]	d [g cm ⁻³]	p.s.	w.s. [g L ⁻¹]	pKa	LogP	μ [D]
Chemical name										
IUPAC name										
Mesitol 2,4,6-trimethylphenol	527-60-6	136.19	73	220	nda	s	1.01	10.88	2.73	nda
2-Ethylphenol	90-00-6	122.16	18	204.5	1.015	l	5.34	10.20	2.47	nda
3-Ethylphenol	620-17-7	122.16	-4	218.4	1.028	l	nda	9.9	2.40	nda
4-Ethylphenol	123-07-9	122.16	46	217.9	1.011	c.s.	4.90	10.0	2.58	nda
Guaiacol 2-Methoxyphenol	8000-58-9	124.14	28-32	205	1.129	l/ c.s.	18.7	9.98	1.32	nda
3-Methoxyphenol	150-19-6	124.13	-18 -16	244	1.131	l	nda	nda	nda	nda
4-Methoxyphenol	150-76-5	124.14	54-57	243	1.55	c.s.	40.0	10.05	1.41/ 1.34	nda
o-Aminophenol 2-Aminophenol	95-55-6	109.13	170 -174	153 11 mmHg	1.328	c.s.	20	4.72 9.71	0.62	nda
m-Aminophenol 3-Aminophenol	591-27-5	109.13	123	164 at 11mmHg	1.195	c.s.	26.3	4.37 9.815	0.21	1.83
p-Aminophenol 4-Aminophenol	123-30-8	109.13	187.5	284 D.	1.29	c.s.	1.6	5.48 10.46	0.04	nda
2,4-Diaminophenol	95-86-3	124.14	205 D.	nda	nda	c.s.	275	nda	nda	nda

M, molar mass; d, density; w.s., water solubility; MP, melting point; p.s., physical state; c.s., crystalline solid; l,– liquid; pKa acidity in water; BP, boiling point; D., decomposes; E., explodes; S, sublimes; Log P, partition coefficient; μ, dipole moment in benzene as solvent; nda, no data available.

Table 1. Comparison of physical and chemical properties of phenol and its derivatives with electron-donating substituents.

Compound	Case no.	M [g mol ⁻¹]	MP [°C]	BP [°C]	d [g cm ⁻³]	p.s.	w.s. [g L ⁻¹]	pKa	Log P	μ [D]
Chemical name										
IUPAC name										
o-Nitrophenol	88-75-5	139.11	44–45	216	1.49	c.s.	2.5	7.230	1.79	3.10
2-Nitrophenol										
m-Nitrophenol	554-84-7	139.11	96.8	194	1.485	c.s.	13.55	8.360	2.00	3.90
3-Nitrophenol				70 mmHg						
p-Nitrophenol	100-02-7	139.11	113	279	1.479	c.s.	15.6	7.15	1.91	5.05
4-Nitrophenol			–114	D.						
2,4-Dinitrophenol	51-28-5	184.11	114.8	S.	1.6683	c.s.	2.790	4.09	1.67	nda
Picric acid	88-89-1	229.10	122	300	1.763	c.s.	12.7	0.42	1.44	1.75
2,4,6-Trinitrophenol			–123	E.						
Salicylic acid	69-72-7	138.12	159	211	1.443	c.s.	2.240	2.98	2.26	2.63 ^d
2-Hydroxybenzoic acid				20 mmHg				13.6		
4-Hydroxybenzoic acid	99-96-7	138.12	214.5 D.	nda	1.46	c.s.	5.000	4.54	1.58	2.73 ^d
o-Fluorophenol	367-12-4	112.10	14–16	151-152	1.246	l	37.7	8.82	nda	1.84 ^d
2-Fluorophenol										
m-Fluorophenol	372-20-3	112.10	13.5	178	1.213	l	nda	9.28	nda	nda
3-Fluorophenol										
p-Fluorophenol	371-41-5	112.10	48	185	1.22	c.s.	80	9.96	nda	2.08
4-Fluorophenol										
o-Chlorophenol	95-57-8	128.56	9.8	174.9	1.264	l	11.3	8.52	2.15	1.39
2-Chlorophenol										2.11 ^d
m-Chlorophenol	108-43-0	128.56	33.5	214	1.245	c.s.	26	9.12	2.5	2.15
3-Chlorophenol										
p-Chlorophenol	106-48-9	128.56	42.8	220	1.2238	c.s.	24	9.41	2.39	2.15
4-Chlorophenol										
2,4-Dichlorophenol	120-83-2	163.00	45	210	1.4	c.s.	4.5	7.89	3.06	1.59
2,4,6-Trichlorophenol	88-06-2	197.45	69.5	249	1.4901	c.s.	0.500	6.23	3.69	1.62

Compound	Case no.	M [g mol ⁻¹]	MP [°C]	BP [°C]	d [g cm ⁻³]	p.s.	w.s. [g L ⁻¹]	pKa	Log P	μ [D]
Chemical name										
IUPAC name										
2,3,4,5,6-Pentachlorophenol	87-86-5	266.34	174	309–310 D.	1.978	c.s.	0.014	4.70	5.12	nda
o-Bromophenol	95-56-7	173.00	5.6	194.5	1.492	l	2.23	8.45	2.35	1.36
2-Bromophenol										2.36 ^d
m-Bromophenol	591-20-8	173.00	33	236.5	nda	c.s.	23	9.03	2.63	nda
3-Bromophenol										
p-Bromophenol	160-41-2	173.00	66.4	238	1.840	c.s.	14	9.17	2.59	2.12
4-Bromophenol										
o-Iodophenol	533-58-4	220.01	39–43	186 100 mmHg	nda	c.s.	nda	8.47	nda	nda
2-Iodophenol										
m-Iodophenol	626-02-8	220.01	40	D.	nda	c.s.	nda	8.88	nda	nda
3-Iodophenol										
p-Iodophenol	540-38-5	220.01	94	D.	nda	c.s.	nda	9.2	nda	nda
4-Iodophenol										
M, molar mass; d, density; w.s., water solubility; MP, melting point; p.s., physical state; c.s., crystalline solid; l, liquid; pKa, acidity in water; BP, boiling point; D., decomposes; E., explodes; S, sublimates; Log P, partition coefficient; μ, dipole moment in benzene as solvent; d, dioxane; nda, no data available.										

Table 2. Comparison of physical and chemical properties of phenolic compounds with electron withdrawing substituents.

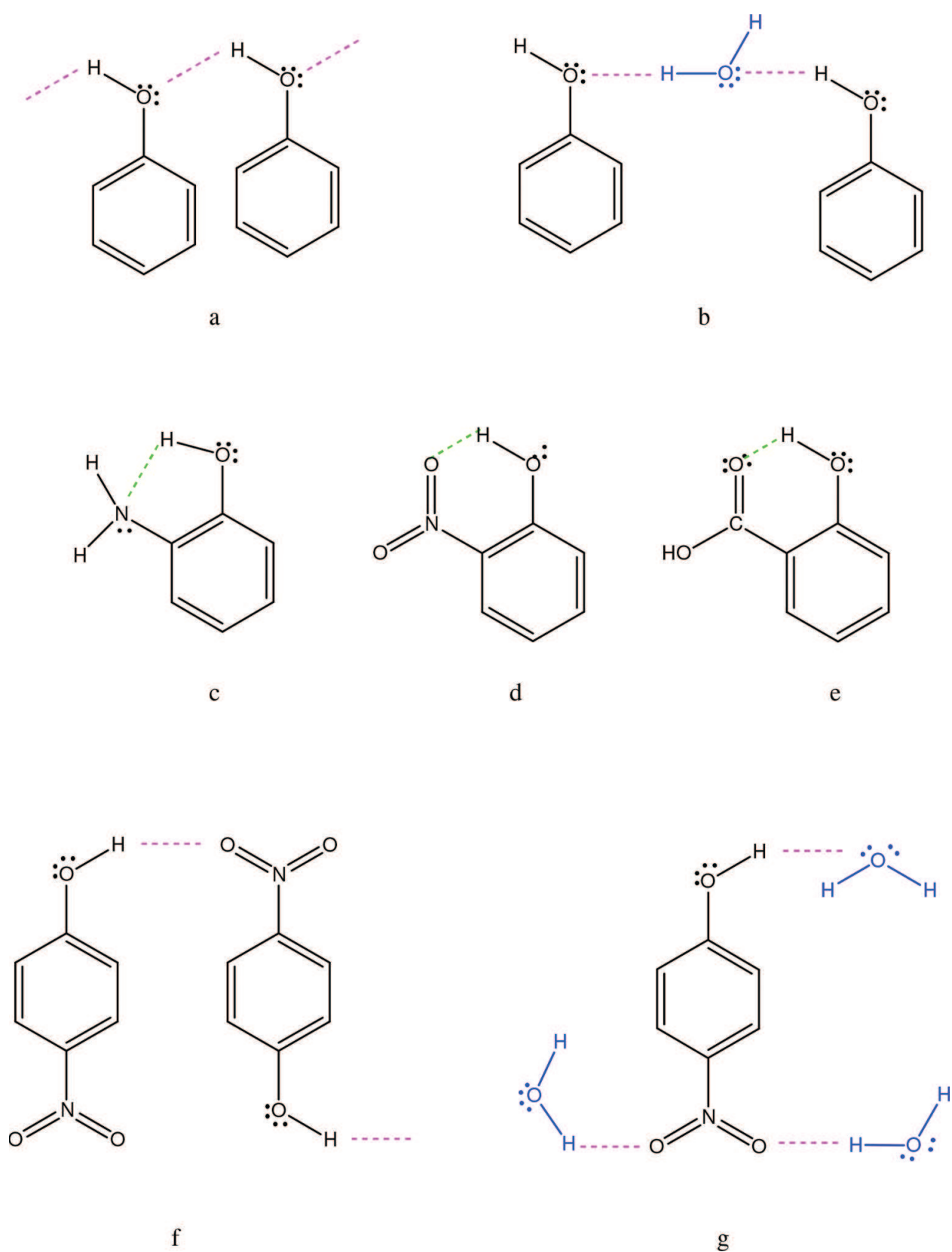


Figure 4. The intermolecular (purple dotted lines) and intramolecular hydrogen bonds (green dotted lines) formed by phenol and its derivatives. On the basis of Ref. [9].

The possibility to form hydrogen bonds suggests that phenols should have good water solubility, but this is not the rule. The unsubstituted phenol is relatively well soluble in water (83 g L^{-1}), while its substituted derivatives are not. For most of them, solubility does not exceed 30 g L^{-1} . Alkyl and halogen groups enhance hydrophobic character of aromatic ring resulting in decrease of water solubility. For phenols possessing functional groups with strong polar character, differences in ability to dissolve are more pronounced. Even for isomers of the same compound, they can be significant. The close proximity of the -OH group to substituents such as -NO_2 , -NH_2 and -COOH lead to formation of intramolecular hydrogen bonds. In this way coordinated the hydroxyl group becomes less active in the solvation process. Due to this fact, solubility of ortho-isomer is lower than meta or para ones (e.g. nitrophenols, hydroxylbenzoic acids).

Very interesting behavior demonstrates benzenediols and benzenetriols. Increasing number of hydroxyl groups implies their solubility should be better in comparison to phenol. It is indeed, but hydroquinone and phloroglucinol are exceptions. Solubility of these two compounds is lower and amount 72 and 10 g L^{-1} , respectively. This apparently abnormal behavior is the result of the presence of hydrogen bonds whose strength are additionally enhanced by symmetry of the molecules. The adjacent molecules form a kind of network in which each of them is strongly bonded with others by infinite chains of hydrogen bonds (**Figure 5**) [13–15]. In this way, a compact structure is created that prevents the penetration of solvent/water molecules into the interior. For this reason, dissolution process is significantly hindered. In

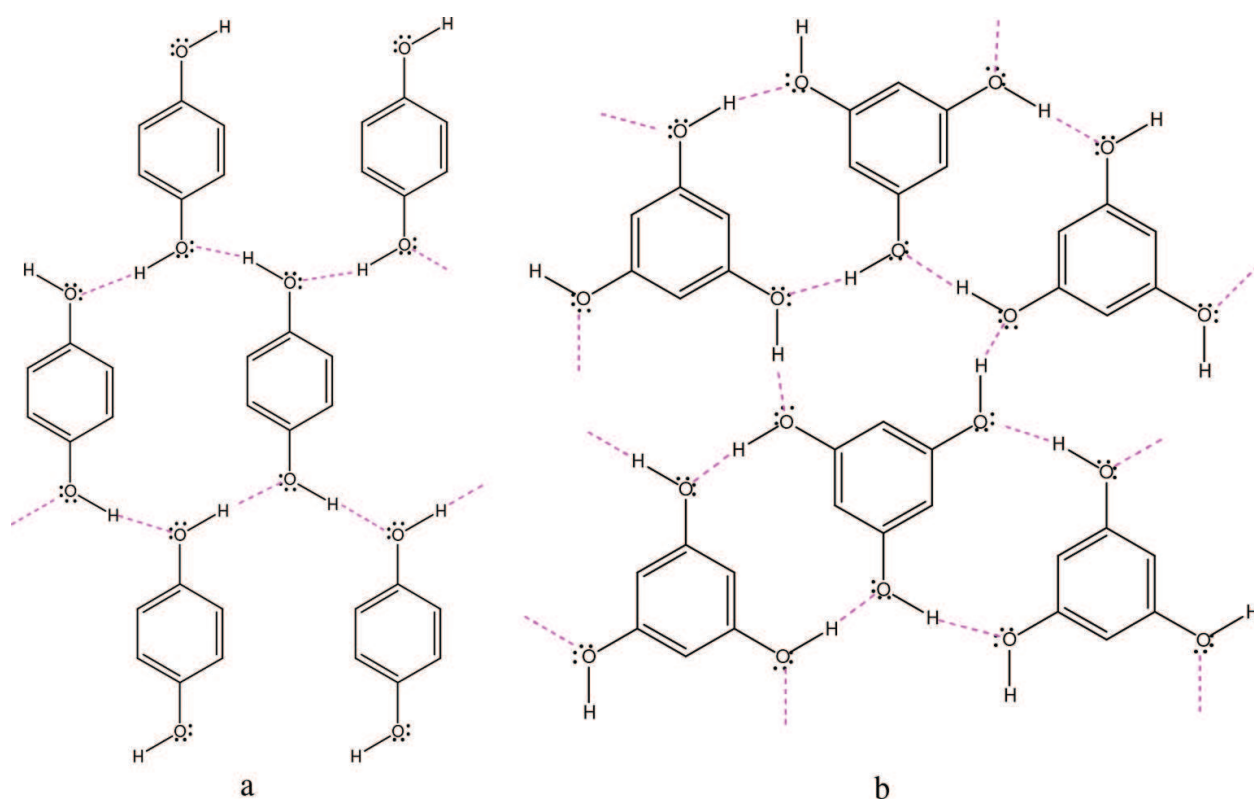


Figure 5. Hydrogen bonds enhanced by symmetrical structure of the molecules in (a) hydroquinone and (b) phloroglucinol. Based on Refs. [13–15].

the similar way, slight solubility of other phenols (4-aminophenol/para-isomers, multi-substituted phenols) can be explained.

Acidity values (pKa) of most phenols are in the range of 8–10, which means they are acids stronger than water (pKa of water 15.7) but weaker than carbonic acid (pKa of 6.4). As it was mentioned above, acidity of phenol is the result of delocalizing of negative charge over the aromatic ring and resonance effect. Dipole moment is sensitive to this kind of changes. Entering an *electron donating* ($-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{OCH}_3$, $-\text{NH}_2$, $-\text{OH}$) or *electron withdrawing* ($-\text{COOH}$, $-\text{NO}_2$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$) group to the ring causes changes in its electron density. As a consequence, altering of dipole moment of the molecule and its acidity is observed. For this reason, alkylphenols are less acidic and nitrophenols are more acidic than phenol. This effect is particularly well visible in case of picric acid. Three symmetrically situated nitro groups exert so strong electron-withdrawing effect that the pKa value for this phenol decreases up to of 0.42 and is comparable with acidity of mineral acids, for example, HBrO_3 (pKa = -0.69), H_3PO_4 (pKa = 2.12) or strong organic acids CF_3COOH (pKa = 0.2) and CCl_3COOH (pKa = 0.6). Similar effect is also observed for chlorophenols. The higher is a number of chlorine substituents the more acidic is character of phenol (decrease of pKa value) particularly in case of tri- and pentachlorophenols.

3. The way of interaction with sorbents

Great varieties of physicochemical properties make phenols very difficult compounds to adsorb or extract, especially they occur at extremely low level of concentration. Although so many different sorbents are commercially available, none of them is universal. For this reason, researchers are constantly working to develop new, better and more efficient materials for phenols sorption processes. All accessible sorbents due to their origin and chemical structure can be divided as the following classes:

1. Natural and mineral based (clay, silicas, zeolites) [16–23]
2. Polymer based [2, 17, 18, 20, 21, 24–28]
3. Carbons and carbonaceous materials (porous, activated, graphitized) [1, 17–20, 29–35]
4. Bioadsorbents: chitin, chitosan, peat, biomass [16]
5. Waste materials or by-products from agriculture or industry [16, 36–39]
6. Nanocomposites [40] and hybrid materials [41]

Independently of the above division, in each class, the materials can have hydrophobic or hydrophilic character due to the lack or presence of polar functional groups.

Retention of phenols from aqueous solution by nonpolar reversed phase adsorbent, for example, silica sorbents (RP-C_8 , RP-C_{18} , RP-cyclohexyl , RP-phenyl), is the result of apolar Van der Waals forces that play the key role in reversed phase mechanisms. Differences in the polarity and solubility of the phenols between the aqueous and the solid apolar phase cause the mass transfer leading to partition process. For this reason, the efficiency of sorbent is related to the

octanol-water partition coefficient, Log P (**Tables 1 and 2**), which is a measure of hydrophobicity (or lipophilicity) of the compound. The smaller is the value of Log P, the more limited is sorbent efficacy towards the compound. Conversely, increase in Log P provides its better affinity to the sorbent.

In sorption of phenols using hydrophobic polymers (e.g. PS-DVB (copolymer styrene-divinylbenzene) or hypercrosslinked resins) and graphitized carbons, the possible interactions are also hydrophobic ones. The partition process occurs due to combination of apolar Van der Waals and π - π electrons interactions of the aromatic rings of the adsorbate and adsorbent. Therefore, the retention is the result of the reversed phase mechanism, too [18].

Unfortunately, for very polar phenols, the described interactions in many cases are insufficient to carry out the process of sorption efficiently. In order to facilitate the retention, two methods can be applied:

- Introduction of polar groups (acetyl, hydroxymethyl, benzoil, o-carboxybenzoil, carboxylic, sulfonic, amino [24]) to the hydrophobic skeleton of already existing sorbent [27, 42]. This method is applicable to preparation of chemically modified polymers, activated or grafted carbons [42].
- Synthesis of a new sorbent using compounds with polar moieties. In this way, silica-based materials: RP-cyano, RP-hydroxyl, RP-amine [43], polar polymers [2, 21, 25–28] and chemically activated or porous carbons [21, 27–29, 39] can be produced.

Resulting materials still retain the high capacity towards less hydrophilic compounds and gain possibility to specifically interact with polar molecules due to stronger interactions including: dipole-dipole, hydrogen bonding or even ionic if sulfonic or carboxylic or amine groups are present. Additionally, polar surface is more wettable and consequently support mass transfer of the more polar species from aqueous solution to the sorbent [18], thus influencing the selectivity of sorption process and the capacity of the sorbent [26].

In a situation when a solution consists of phenols with significantly different properties, one sorbent may be insufficient to trap all the compounds quantitatively. In such cases, the possibility to achieve high retention and selectivity for all analytes is the preparation of device containing mixed or layered sorbents with different chemical characters [18, 20, 21].

4. Influence of different factors on process of phenols sorption

Process of sorption of phenolic compounds is very complex and many factors exert influence on its efficiency. Some of them were already described above. Others are presented below. The factors are arranged into three groups: the first, connected with adsorbents; the second, associated with adsorbate properties; and the last, related to environmental conditions. Nevertheless, one should remember that none of the factors is working as separate. All of them make a system in which each element is closely linked with others, and changing one of them affects the rest.

4.1. Adsorbent properties

4.1.1. Physical properties of an adsorbent

Many studies were carried out to find the correlation between specific surface area of sorbent and uptake of phenolic compounds. It is clear that as higher is the value of specific surface area, the higher are microporosity and the larger number of active sites available to interact with adsorbate. Consequently, extraction efficiency increases [23]. That is why, for hyper-crosslinked polymers, higher sorption capacity is observed in comparison with traditional polymeric sorbents [18, 21].

On the other hand, there are many works indicating lack of correlation between the value of specific surface area and ability to adsorb phenols [16, 24, 25, 27, 33, 41]. However, specific surface area is still put into characteristic in order to define the morphology of the adsorbent and for comparative purposes.

In general, an adsorption process consists of three following steps:

- transport of the adsorbates from the bulk solution to the adsorbent exterior surface,
- diffusion of molecules to the pore of adsorbent, although a small amount of adsorbate is retained on the external surface and
- proper adsorption of the solutes on the interior surface of the micropores and in capillary spaces of the adsorbent. This final step is assumed to be rapid and leads to state of equilibrium [16, 33]. A driving force of that process is an adsorption potential near the walls of micropores [23].

Consequently, adsorption of phenols is controlled by diffusion processes which are the slowest stage of the overall process. Therefore, characteristic features of porous structure like type of pores, their shape, size, a way of their connection and a size distribution are the most important factors determining the adsorption process and deciding on proper application [31, 44].

In case of sorption processes realized in a dynamic mode (e.g. chromatography, solid phase extraction), size, shape and uniformity of sorbent particles also play significant role. These parameters have an impact on a length of diffusional path, availability of pores for adsorbed molecules, mass transfer resistance and contact time. Not meaningless is the geometry of a device (e.g. column, cartridge, sampler) as its length and diameter decide on the rate and efficiency of the process.

4.1.2. Chemical properties of an adsorbent

Chemical composition of the adsorbent surface determines the mechanism of phenols adsorption. As it is described above, the retention of phenols on the solid surface is the result of specific and nonspecific interactions. The main role is played by strong dipole-dipole interactions and hydrogen bonds between phenolic compounds and surface functional groups. Equally important are π electrons interactions of the aromatic systems of the adsorbate and adsorbent (if contains) [26, 32].

Thus, retention of the polar phenols is enhanced by the presence of polar moieties on the sorbent surface, while sorption of the hydrophobic molecules and those forming strong intramolecular hydrogen bonds is not influenced by the polarity of an adsorbent surface [25].

The studies show that functional groups being active in retention of phenolic species are mainly located in larger micropores, and the increase in their concentration on the surface leads to the favoring of adsorption in larger pores. Consequently, the competition takes place between filling of the smallest micropores and the adsorption on active sites located in larger micropores [33].

The moderately and slightly acidic oxygen groups are as considered as the most important ones influencing the mechanism of phenols adsorption. The vital surface groups for this process are bases and carbonyls [18, 33, 45]. According to Su et al., the increase in concentration of carbonyl groups on the surface provides more sites for the donor-acceptor interactions resulting in the improvement in phenol adsorption [23].

In addition, other polar moieties, for example nitrile [25], amine [24] or bicarbonate [27] on the sorbent surface, can positively influence the uptake of phenol and its derivatives by the formation of hydrogen bonds.

Many researchers observe decrease in adsorption of phenol with the increase in surface acidity and with surface oxidation [33, 46, 47]. This phenomenon can be explained by

- strong interactions of phenols with the surface groups that lead to the creation of polymorphic forms of phenol [33],
- hydration process of polar groups (e.g. carboxyl) leading to creation of water clusters, which occupy active sites. The formed water complexes block the pore entrances and thus reduce surface available for sorption resulting in decrease of phenol adsorbability [23, 48].

In case of adsorption from solutions, the role of surface functionalities increases more and maybe even dominant [49]. The surface of adsorbent can be treated as a huge molecule covered with uniform (e.g. polymers) or various (e.g. active carbons) in chemical character functional groups. If they are able to dissociate, ions are released to the solution. Their presence affects the acid-base equilibrium of the solvent. In order to characterize this process, point of zero charge (PZC) [44, 50], contents of acidic and basic groups [47] and their pKa [45, 50], or pH of sorbent slurry [48], are determined.

The ions on surface, those in solution and adsorbate molecules interact with one another by electrostatic attraction or repulsion. Confirmation of this phenomenon was presented in Tamon and Ozaki's studies, who found that sorption characteristic of phenols in aqueous solution depends on electronic states of adsorbent surface and adsorbate [51]. The same phenomenon controls adsorption of acids on surface with basic groups and bases on the acidic ones of ion exchangers or porous carbons [32].

4.2. Adsorbate properties

Adsorption of small organic molecules, especially containing functional groups, is affected by surface chemistry. The bigger is the molecule, the weaker is the effect due to the steric

hindrance. As phenols possess in their molecules aromatic ring and at least one polar group (-OH), both these parts are active in competition for high-energy adsorption sites. The strength of retention of the molecule depends on size of molecule (the number of carbon atoms) and specific interaction caused by polar moiety [32]. The presence of substituents in the ring changes physical, chemical and energetic characteristics of the molecule, resulting in additional strengthening or weakening impact on the sorption process. It was also found that solutes with electron-donating groups show a tendency to irreversible adsorption, while those with electron-withdrawing groups do not [51].

Thus, for example, chloro or nitro groups which reduce the electron density of the aromatic ring cause growth of molecule hydrophobicity and decrease in water solubility. In consequence, interactions between the adsorbed molecules and hydrophobic surface of adsorbent become stronger and an increase in adsorption capacity is observed [17, 46, 49, 52, 53]. For polar adsorbents, the effect will be opposite [25, 35].

4.2.1. Size of molecule

The molecular size of the adsorbate has a crucial meaning for adsorption process. The rate of mass transfer is controlled by diffusion of adsorbates in porous structure of the adsorbent. However, availability of the pores strictly depends on size of the molecule. The smallest molecules penetrate almost all pores, while for the larger ones, not all of them are accessible. This elimination of large molecules from entering the pores describes size exclusion mechanism. As a result, porous materials act as a molecular sieve. An increase in adsorption resulting from the rise of adsorption energy is supposed if the pore size is about twice the size of kinetic diameter of adsorbate molecule [46].

The species with branched or bulky substituents, which are too large to reach interior of micropores, are retained in mesopores [31]. Desorption of such solutes can be hindered due to being trapped inside pores.

4.2.2. Multicomponent effect

For multicomponent solutions additional effects become apparent. If the mixture consists of solutes having molecules of similar size, a competition between them for the active sites takes place. Compounds possessing higher affinity to adsorbent interact stronger with its surface and displace molecules interacting weaker [22, 27]. Hence, it follows a selectivity of adsorbent towards the specific compounds.

On the other hand, if molecules that are significantly different in size are present in the mixture, the larger of them can block entrances of some pores effectively preventing adsorption of the smaller species [31].

Both the effects adversely affect the sorption and reduce the overall efficiency of the process

4.2.3. Initial concentration and contact time

Increase in the phenols concentration in solution leads to an increase in the amount of adsorbed compounds. This can be attributed to a rise of the driving force of the concentration gradient

with the rise in the initial phenols concentration and different arrangements of solute molecules on the surface of adsorbent [30]. At low concentrations, phenol molecules are lying flat in parallel with the surface. As a result, the surface occupied per molecule corresponds to the largest of its dimensions [54, 55]. At higher concentrations, accessibility of the surface for the individual molecules is considerably less. Consequently, the molecules have to change their position for upright to allow closer packing in parallel to each other. Then the area occupied in conversion to a single molecule is smaller that is observed as rise in adsorption density [55].

Different studies show that the contact time required for phenols solution to reach the equilibrium is in the range of 1–24 h [30, 56, 57]. However, the uptake of phenols is the most rapid during the initial 30 min [56, 57]. It was also observed that the higher initial concentration, the longer equilibrium times were needed [30, 56]. Shaarani and Hameed explained the run of the process as follows: “initially the adsorbate molecules have to first encounter the boundary layer effect and then diffuse from the boundary layer film onto adsorbent surface and then finally, they have to diffuse into the porous structure of the adsorbent. This phenomenon takes relatively long contact time” [30].

Moreover, it was noted that at relatively large phenol adsorption values, when interactions between adsorbate molecules predominate, phenol uptake is higher for the more oxidized surfaces, whereas, in case of diluted phenol solutions, the competition between phenol molecules and water leads to substantial reduction in adsorption of phenol on oxidized surface. “Competition between water adsorbing in pores and phenol is mainly responsible for the changes in adsorption” [33].

4.3. Environmental conditions

4.3.1. Water and other solvents

Water molecules interact very weakly with the hydrophobic surface unless their concentration in adsorbed mixture is low (e.g. sorption from gas phase). If the contents of water rise like in case of sorption from aqueous solution or in head space techniques, the influence of water interaction with the surface is no longer negligible. Water begins to interfere with adsorption of organic compounds. Due to the better affinity to the surface, organic solutes are able to replace preadsorbed water. That impacts the kinetics and efficacy of the process. The effect is even stronger, if the surface is hydrophilic. The polar functional groups are predominantly adsorption centers capable of forming the hydrogen bonding. Interactions between water molecules lead to formation of clusters, which block entrances of pore as well as “the condensation of water in micropores at much lower humidity than that at which it happens on a fully hydrophobic surface” can take place [32, 33]. In consequence, adsorption of phenols diminishes.

From practical point of view both adsorption and desorption processes are equally important. Adsorption of phenols is usually carried out from aqueous solution. However, to desorb retained compounds, organic solvent is necessary. It should be chosen so that its properties (solvating power, good wettability of adsorbent, miscibility, chromophoric nature and purity) provided quantitative, quick and simple process of recovery.

For elution of adsorbed phenolic compounds, the most frequently used solvents are methanol [58], acetonitrile [59], acetone [18], ethyl acetate [18], tetramethylammonium hydroxide [17] and others [43]. If a single eluent is ineffective, a mixture of solvents can be considered. The volume of applied eluent depends on its eluting strength, polarity of the phenols, amount and surface chemistry of adsorbent, and type of device [18].

Bruzzoniti et al. in their paper presented efficiency of different eluents in desorption of phenolic compounds from graphitized carbon black. They noted the effectiveness of eluent was affected by the value of pKa phenolic solute. Phenols with pKa about 7 were effectively eluted with tetramethylammonium hydroxide, while for phenols with higher pKa, methanol was better [17].

For newly synthesized sorptive materials, studies on eluent selection and optimization of desorption process should be conducted [18, 59].

4.3.2. *Electrolytes: ionic strength*

The presence of electrolytes, for example salts in the solution, affects the strength of electrostatic interaction between phenolic solutes and the surface of the adsorbent. If these interactions are attractive and surface concentration of adsorbates is low, then the rise in ionic strength of solution causes decrease in uptake. But if they are repulsive or concentration of adsorbates on the surface is high, increase in ionic strength of the solution enhances the adsorption [60].

The presence of salts can influence the adsorption of phenols also by the effect of salting out. The electrolytes dissolved in the solution reduce or even destroy the hydration layer of organic compound causing decrease in its solubility, which affects favorably on adsorption.

Kuśmiderek and Świątkowski have compared the influence of an electrolyte on the adsorption of 4-chlorophenol on active carbon and multiwalled carbon nanotubes (MWCNTs). They used three different salts: Na₂SO₄, NaCl, NaNO₃ at various concentrations. The presented results proved higher uptake of 4-chlorophenol on the active carbon in the presence of salts in all cases, whereas no significant difference was observed for adsorption on MWCNTs. It was also indicated that the desorption of the 4-chlorophenol increased with the increase in the ionic strength of the solution [60].

Dissimilar results were obtained by Mukherjee and De for sorption of catechol on mixed matrix membrane in the presence of NaCl. They justified their outcome by weakening forces between sorbent and phenols resulting in decrease of the uptake. They also defined this phenomenon as the shielding effect [22].

4.3.3. *pH*

The change in pH affects chemistry of both the adsorbate and the adsorbent by shifting the equilibrium dissociation process of solutes and surface functional groups of the sorbent towards ionized or unionized form. Thus, adsorption of phenols is limited by the acid-base characteristic of the adsorbent and its microporosity, which subsequently influences kinetics

and effectiveness of the overall process. Higher values of uptake are observed for the compounds in undissociated form [30, 61]. Therefore, most of phenols such as weak acids are better adsorbed from neutral or acidic solutions. At lower pH values, oxonium ions are present in solution and they prevent dissociation of surface acidic groups. In these conditions, formation of hydrogen bonds and π - π interactions between phenolic adsorbates and sorbent surface is privileged. Accordingly, adsorption capacity is the highest [19]. The same applies to phenols, their transition point between acidic and basic form is associated with their pKa value. Below this value dominates acidic form and above it the conjugated base-phenoxide ion takes advantage.

The uptake of phenols decreases at higher pH, when the molecules turn into phenolate ions and the surface of the adsorbent is negatively charged. The presence of electrostatic repulsive forces impedes adsorption [16, 57]. Thus, the more acidic the surface of sorbent, the lower the adsorbability of phenols.

However, some researchers report that in certain pH range, adsorption for most phenols initially increases with the rise in pH to reach a certain value and then decreases with further increase in pH [16, 56]. This phenomenon can be explained by the fact that, in the presence of oxonium ions the surface functional groups of adsorbent gain a positive charge. As a result, adsorption of water increases and cluster formation takes place. Consequently, some of more active sites are not available. Second, already adsorbed molecules of phenols can block the entrances to fine pores and cause decrease in uptake. This effect is stronger at the lowest pH values [33].

4.3.4. Temperature

Due to the fact that process of physical adsorption is exothermic in nature, increase of temperature causes decrease in phenol's uptake [56]. Moreover, the rise in temperature increases the rate of the sorption process and leads to the disappearance of the effects associated with surface chemical composition [33].

In contrast, chemisorption is an endothermic process. Therefore, Shaarani and Hameed observed the increase of temperature slightly increases the uptake of 2,4-dichlorophenol at a higher concentration. They also found that the change of temperature alters the equilibrium capacity of the adsorbent for particular adsorbates [30].

4.3.5. Oxic and anoxic conditions

Influence of oxygen for process of phenols sorption was at first perceived for carbon adsorbents; hence, the facts presented here have been developed only based on the results obtained for these materials.

When phenols are adsorbed under oxic and anoxic conditions, differences in the uptake can be observed. The sorption capacities of some sorbents are higher under oxic conditions that imply promoting action of molecular oxygen in this process [3, 49]. The increase in adsorption is attributed to the oxidative coupling reaction leading to formation of dimers or more substituted derivatives of phenols (multimers) that are attached to the surface of adsorbent [33, 55].

The course of the process can be explained as follows: the molecules of phenols and those of oxygen diffuse to the surface of carbon, where they are preadsorbed. The adsorbed oxygen molecules form superoxo ions that yield rearrangements and further reactions with surface functional groups and adsorbed phenols leading to creation of various surface compounds. Thus, described reaction occurs only on the surface of carbon and is catalyzed by it [33].

Studies on this phenomenon revealed that

- the small pore size precludes oligomerization, thereby the presence of molecular oxygen has no significant effect on adsorption [3];
- narrow pore size distribution (PSD) reduces the oligomerization of phenols to some extent while the wider PSD favors it [1];
- 2-methylphenol shows oligomerization under oxic condition. The oligomerization of 2-chlorophenol depends on the overall competitive effect of 2-nitrophenol and 2-methylphenol [1];
- surface concentration of carboxylic groups diminishes the oxidative coupling in the whole range of coverages [62];
- the lower ability of carbon to adsorb ions on the surface, the more significant differences in adsorption determined at oxic and anoxic conditions [33];
- oxidative polymerization (spontaneous and/or electrochemical) of chlorophenol is responsible for a lack of anodic peak during voltammetric cyclization [5].

4.3.6. Irreversible sorption of phenols

Irreversible adsorption of phenols is closely related to process of chemical adsorption involving chemical reaction between adsorbates and surface functional groups of adsorbent [55]. As it was described above, the hydrogen bonding arising in the system adsorbate-active centers of adsorbent strengthens interactions and sorptive capacity, but also can cause difficulties related to irreversible sorption [18]. It can be also considered that phenol molecules or phenoxide radicals can react with active sites on a carbon surface, which leads to creation of covalent bond between them [33].

Tessmer et al. investigated this problem and found that "grater structural ordering and delocalized electrons on the carbon surface may increase the basicity of the carbon but do not enhance its ability to promote irreversible adsorption. The presence of oxygen containing basic groups (chromene-type or pyrone-type) is likely the key factor promoting irreversible adsorption" [48].

Other studies demonstrate that lactone surface groups are responsible for both irreversibility of phenol adsorption due to chemical reaction and decrease in the difference between adsorption in oxic and anoxic conditions [33].

And another one proves that irreversible adsorption to carbon surfaces does not depend on oxidative coupling reaction, but oxidative coupling may enhance irreversible adsorption

when experimental conditions are conducive (pH of solution high enough, microporosity of adsorbent) [63].

The discrepancies in this matter indicate that it is a topic still open for discussion and further research.

5. Conclusions and future prospects

A lot of scientific research was performed in order to study and understand the process of sorption of phenolic compounds. This chapter presents the complexity of this process and shows how many different factors have influence on it. The starting point is chemical structure and overview of physical and chemical properties of phenol and its ring-substituted derivatives. This characteristic is the basis to explain the behavior of the molecules in solution and during sorption. Next, the way phenols interact with the most popular sorbents are shortly described. Finally, factors influencing the sorption process were characterized.

Factors promoting the sorption:

- matching of the size of adsorbate molecules to the porous structure of adsorbent;
- the retention process of phenolics is mainly due to reversed phase mechanism, but in case of polar sorbents, it is also supported by specific attractive interaction (dipole-dipole, donor-acceptor and ionic);
- elongation of contact time of a phenols solution with an adsorbent;
- salting effect;
- pH. Sorption characteristic depends on electronic states of both an adsorbent surface and an adsorbate. Phenols uptake is higher for compounds in unionized form as formation of hydrogen bonds and π - π interactions are favored;
- increase in temperature in case of chemisorption process.

Factors hindering the sorption:

- polar functional groups of the sorbent acts as adsorption centers. Their presence in larger pores can limit access to micropores (pore blocking effect) and lead to competition between the process of micropore filling and adsorption on active sites;
- steric effects and size exclusion mechanism;
- pore blocking caused by adsorption of large molecules or water clusters;
- multicomponent effect and displacement phenomena;
- shielding effect;
- increase in temperature in case of physisorption process.

Irreversibility of phenols adsorption can be the result of

- a chemical reaction between adsorbate and surface functional groups;
- an oxidative coupling process in oxic conditions;
- trapping molecules (especially large or branched ones) in pores of adsorbent;
- the presence of electron donating substituents in phenol molecule enhances the effect of irreversible adsorption.

Although so many works were devoted to studies on phenols sorption, the general mechanism of the process is still not fully understood and explained. There are some issues and unsolved problems requiring further investigations:

- There is still no consensus in the matter, what kind of the adsorbent functional groups has favorable and which undesirable influence on adsorption of phenols.
- Process of irreversible adsorption due to oxidative coupling requires additional studies confirming the proposed in literature mechanisms.
- Most of the studies concern the process of sorption of single compounds. Only a few research studies relate to multicomponent system, in which competitive adsorption take place. This aspect is particularly important from environment protection point of view. Interferents, such as ions from salts or organic contaminants of natural or anthropogenic origin, impede quantitative analysis of phenols in waste water.
- Relatively little studied are processes of cyclic adsorption—desorption, reproducibility of the adsorption properties and regeneration of adsorbent, which are extremely important for utility reasons.

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