Mutual influence of functional groups on the example of phenol molecule

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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, Mutual influence, physical properties, chemical properties, solute.**

I. 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.

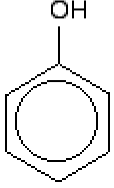
Quantitative isolation of phenol and its derivatives from environmental matrices is usually difficult because of considerably different properties and low concentration. It was a stimulus to development of research on process of sorption and search for efficient sorptive materials.

This paper 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.

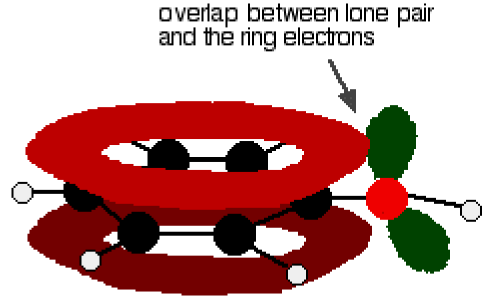
II. STRUCTURE OF PHENOL

The simplest way to draw the structure of phenol is:

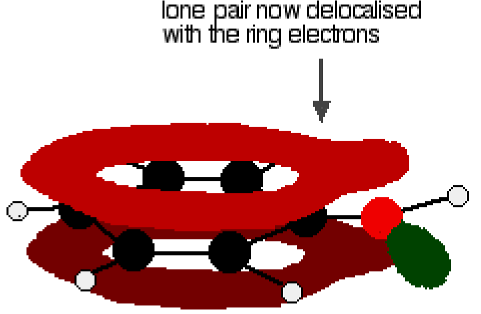


. . . but to understand phenol properly, you need to dig a bit deeper than this.

There is an interaction between the delocalized electrons in the benzene ring and one of the lone pairs on the oxygen atom. This has an important effect on both the properties of the ring and of the -OH group. One of the lone pairs on the oxygen overlaps with the delocalized ring electron system . . .



. . . giving a structure rather like this:



The donation of the oxygen's lone pair into the ring system increases the electron density around the ring. That makes the ring much more reactive than it is in benzene itself. That is explored in another page in this phenol section. It also helps to make the -OH group's hydrogen a lot more acidic than it is in alcohols. That will also be explored elsewhere in this section.

Physical properties

Pure phenol is a white crystalline solid, smelling of disinfectant. It has to be handled with great care because it causes immediate white blistering to the skin. The crystals are often rather wet and discolored.

Melting and boiling points

It is useful to compare phenol's melting and boiling points with those of methylbenzene (toluene). Both molecules contain the same number of electrons and are a very similar shape. That means that the intermolecular attractions due to van der Waals dispersion forces are going to be very similar.

	melting point (°C)	boiling point (°C)
C_6H_5OH	40 - 43	182
$C_6H_5CH_3$	-95.0	111

The reason for the higher values for phenol is in part due to permanent dipole-dipole attractions due to the electronegativity of the oxygen - but is mainly due to hydrogen bonding. Hydrogen bonds can form between a lone pair on an oxygen on one molecule and the hydrogen on the -OH group of one of its neighbors.

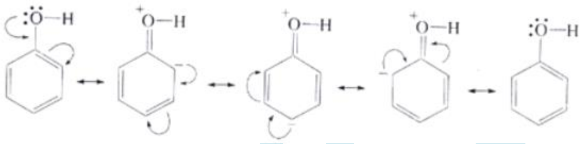
Solubility in water

Phenol is moderately soluble in water - about 8 g of phenol will dissolve in 100 g of water. If you try to dissolve more than this, you get two layers of liquid. The top layer is a solution of phenol in water, and the bottom one a solution of water in phenol. Phenol is somewhat soluble in water because of its ability to form hydrogen bonds with the water.

III. CHEMICAL PROPERTIES OF PHENOLS

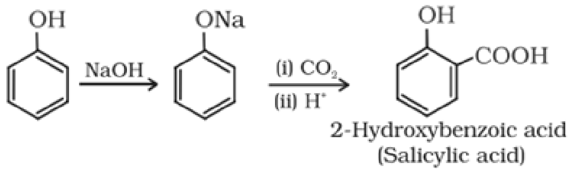
Electrophilic substitution reactions

The presence of OH group on benzene increases the electron density on the benzene ring making it more susceptible to attack by an electrophile. The reactions involving benzene ring are electrophilic substitution reaction. The presence of OH group makes the orthoand para carbon of benzene more electron rich than meta position. The OH group is called *o* –, *p* – directing group.

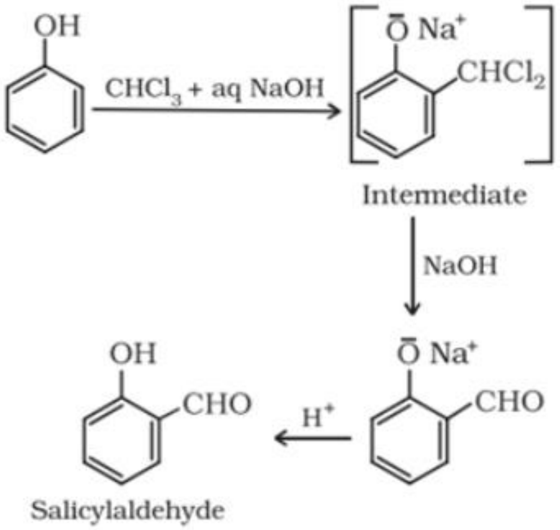


Reactions of phenol involving the cleavage of O–H bond

Kolbe's reaction:

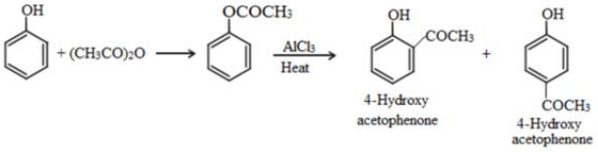


Reimer-Tiemann reaction:

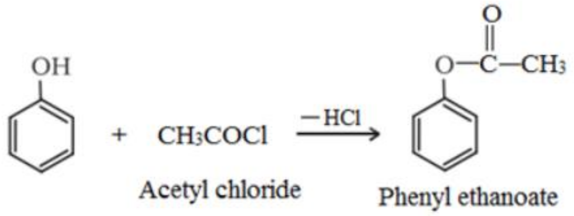


Fries rearrangement:

Esters of phenol gives phenolic ketones on rearrangement in the presence of anhydrous $AlCl_3$. This reaction is called fries rearrangement.

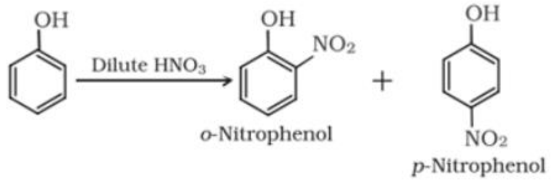


Acetylation:

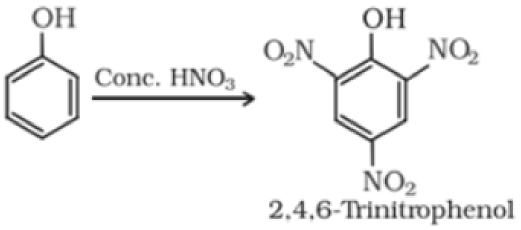


Nitration:

Reaction with dilute HNO_3 :

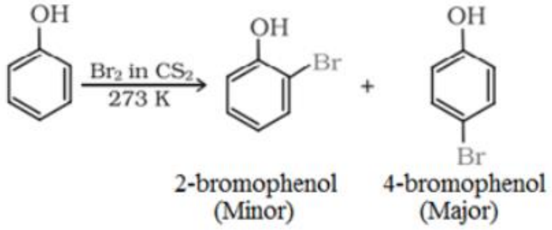


Reaction with conc. HNO_3 :

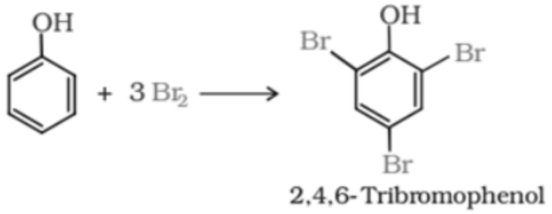


Halogenation:

Bromination in solvents of low polarity like CS_2 :

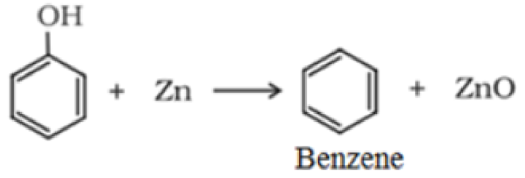


The reaction of phenol with bromine water:

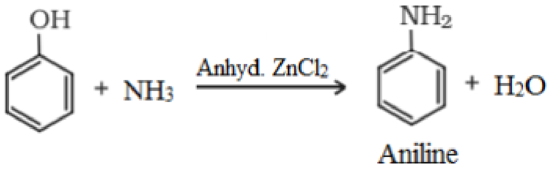


Reactions of phenol involving cleavage of the C-O bond

Reaction with zinc dust



Reaction with ammonia:



Uses of phenol

- It is used as an antiseptic.
- It is used as a disinfectant in household cleaners.
- It is used in the preparation of resins, dyes, explosives, lubricants, pesticides, plastics, drugs, etc.

IV. 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.

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 hypercrosslinked 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.

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 16 Phenolic Compounds - Natural Sources, Importance and Applications 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].

V. CONCLUSIONS & 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, donoracceptor 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. 22 Phenolic Compounds
- Natural Sources, Importance and Applications 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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