

WASTELESS METHODS OF PHENOL CONTAINING INDUSTRIAL WATERS PURIFICATION AND NEW MODIFICATION OF THE METHOD OF THE ANALYSIS OF PHENOLIC TOXICANTS

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Effective methods of purification of phenol industrial wastewaters and wastes based on the different chemical phenol transformations to insoluble in water low toxic compounds with some valuable properties have been discovered. Chemical method of dephenolation using sulfochlorides may be applied for purification of industrial waters with any initial phenol concentration. Condensation method is based on the polycondensation reaction of phenol and formaldehyde in the conditions of acid catalysis with the addition of the special reagent. Method permits to purify the wastewaters, which contain phenols, phenolalcohols, aldehydes, oligomers, dyestuffs, etc. We have elaborated an analysis and express-analysis of different phenols using sulfochlorides, RSO_2Cl , as reagents which (especially aliphatic ones) are active and highly selective for phenols. The reaction is completed for 1-5 minutes in quantitative yield of arylsulfonates products, which are extremely stable compounds and can be easily determined.

Amongst the ecological dangerous organic pollutants of environment the most widespread are phenols. Arrival of phenols and its derived in environment: water, air, ground, products of feeding, some person activity products - bound as with processes occurring in nature, so and, in greater degrees - with the antropogenic influence on the ambience [1]. Phenol and its alkyl, chloro-, nitroderivatives often are present in sewages and surges (departures) of chemical, petrochemical, pharmaceutical, coke-chemical, woodworking and furnituric industry cellulose-paper enterprises and others. It is necessary also note that exactly phenols, particularly chloroderivatives are main sources of formation in biosphere such hightoxic and dangerous pollutions as dioxines.

Together with that phenols and other aromatic oxyderivatives are exceedingly important and deficit raw material for many branches of industry. Working out effective methods of dephenolation of waster waters is one of the most important aspects in the general problem of environmental protection and rational use of industrial wastes. Also questions of efficient analysis and express-analysis of phenols and its derived are important and actual.

In our Laboratory effective methods of purification and work of phenol industrial waste waters and wastes and also the technologies of processes, which are based on the different chemical phenol transformations to unsoluble in water small toxic compounds, which have some valuable properties, have been discovered.

CHEMICAL METHOD USING SULFOCHLORIDES

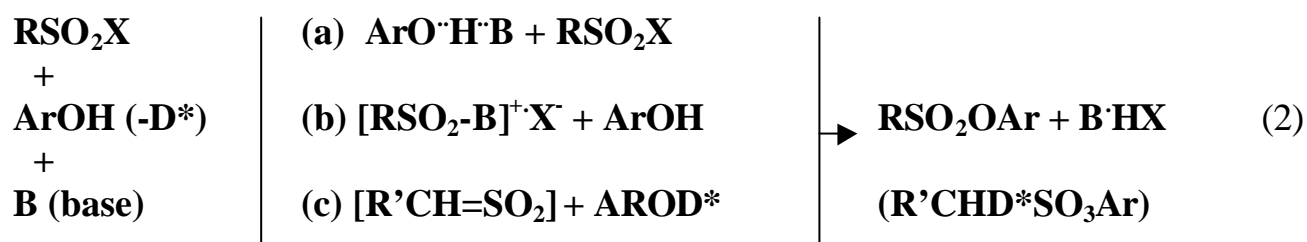
Chemical method using sulfochlorides developed on the basis of the results obtained in the research of kinetics and mechanism of sulfonylation reaction of phenols under base catalysis conditions [3].



Where: B – base catalyst

It has been studied the interaction of sulfonyl chlorides with phenols in the conditions of base catalysis in aqua and aqua-organic mediums. It has been shown that base-catalyzed phenolysis of sulfonyl chlorides in aqueous and aqua-organic proceeds predominantly and hydrolysis does not realize [2]. This fact is explained by the essential distinguish of catalytic action of bases in the case of phenolysis and hydrolysis. Thus, the catalytical effect of triethylamine for hydrolysis of benzene sulfonyl chloride is equal to $k_{\text{cat}}/k_{\text{incat}} = 5.6 \cdot 10^{-4} / 0.135 \cdot 10^{-4} = 41.5$ at the same time for phenolysis it is equal to $10^{-1}/10^{-7} = 10^6$. There k_{cat} , k_{incat} are the first order rate constants, s^{-1} , for the reaction between benzene sulfonyl chloride and phenol or water under pseudo-first-order conditions in the presence of triethylamine for k_{cat} . These results are explained according to the viewpoint of mechanism of general-base catalysis (2a), because phenol is more power acid than water.

It permits to use this process for dephenolation of industrial wastewaters and also for analysis and express-analysis of phenols and phenolic toxicants.



Where: R = Ar, Alk; ArOH or nucleophylic reagent HY;
 B = alkali, R₃N, Py...

Chemical method of dephenolation may be applied for purification of waters with any initial phenol concentration. The purification degree is more as 99.9 %, residual phenol content equals 0.5 to 5 mg/l. The optimum temperature lies within the limits of 10 to 30 C. The influence of the catalyst nature on the process has been studied. Application of pyridine is rather uneffective, the use of ammonia, alkali, soda, triethylamine yields good results.

It has been demonstrated that process also successfully proceeds in the case of other phenols. In artificial mixtures with the initial phenol concentration 5 g/l dephenolation reached 99.9% and more, residual phenol concentration equalled 0.5-5 mg/l and less. The method has been tried on industrial wastewaters of coke-chemical plant. Dephenolation degree comprises 99.4 %, residual phenol content equals 5 to 10 mg/l. Simultaneously rhodanide content is brought down to 30 %, cyanides to 3 or 5 times and hydrogen sulfide is rendered completely harmless. Besides, tests on high-concentration phenol sewers of chemical plants were carried out (phenol content from 15 to 80 g/l). Dephenolation degree reached over 99.99%.

Sulfonyl acid phenyl esters are the products of the reaction (1), they are insoluble in water and one is lightly separated from water by settling. Sulfonate esters have series different useful properties. In particular, some phenyl esters of sulfonyl acids are widely known as plastisizers and softeners of high-molecular compound and rubber. Beside, certain phenyl esters evince acaricide properties. Series such compounds are produced for struggle against "tetranychus". It is known other fields of possible using of sulfonyl acid phenyl esters. The using of ones may compensate for purification expenses and give a direct economical effect.

On the basis of the obtained results a method of purification of wastewaters from phenol has been elaborated and technological parameters for the process have been established. Chemical method of dephenolation may be applied for purification of waters with any initial phenol concentration. The

purification degree is more as 99.9 %, residual phenol content equals 0.5 to 5 mg/l. The optimum temperature lies within the limits of 10 to 30 C.

The method for phenol analysis elaborated in our laboratory is also based on the reaction of sulfoester formation (1). It consists in treatment of the phenol solution in aqueous, aqua-organic and organic media by sulfochloride (especially aliphatic ones) with subsequent chromatographic determination of sulfoesters formed. The reaction proceeds with quantitative yield, therefore, the mole portion of the ester coincides with the mole portion of phenol in original solution.

METHOD OF CHEMICAL CONDENSATION

Method of chemical condensation is based on the polycondensation reaction of phenol and formaldehyde in the conditions of acid catalysis with the addition of the reagent [3]. The present addition increases phenols, formaldehyde condensation degree and their extraction from water. The process proceeds with the space-network polymer formation. Dependent on phenol, formaldehyde, reagent correlation, and acidity of medium, different products has been obtained, which distinguish on the structure, physical and other properties. For the maximum phenol extraction from the water the process was optimized. It has been shown that the optimum temperature is 95-100 C. This permit over the process during two hours. The higher medium acidity, the more rapidly and effectively process proceeds. The optimum pH is at two.

Condensation-chemical method permits to purify the wastewaters, which contain phenols, phenolalcohols, aldehydes, oligimeres, dyestuffs and etc. For purification of tar-waters of phenol-formaldehyde resins production the use of worked out method is most effective. The initial phenol concentration may be in range 30-40 g/l. The purification degree is more than 99.9%, the residual phenol concentration in water is equal to 0.1-0.5 mg/l.

The dephenolation product ("Formopor") is the powder with 0.1-1 mm dispersity. It has white or low-saturated colour in dependence on the wastewater colour. The powder is untotoxic and has fourth class of dangerous. Tests showed the possibility of it use as promoting filler for aldehyde resins and some kind of rubbers. Besides, the powder has large adsorption surface, contains active functional groups and may be used as adsorbent for heavy metal ions.

EXTRACTIVE-CHEMICAL METHOD

The effective complex extractive agent of basic character, which allows obtaining the wastewater dephenolation degree 99-99.5% during the periodic one-stage treatment, has been prepared. Phenol and different substituted phenols are easily removed. The extractive agent capacity in phenol attains 60%. Thanks to high thermal and chemical extractive agent stability the absorbed phenol discharge becomes simpler. At the rectification of complex extractive agent saturated by phenol absorbed water is first removed with azeotropizer, for example, toluene. Then, the rectification temperature being increased (the pressure being normal or with vacuum use) phenol, cresols are distilled off. After the phenol distillation the extractive agent without additional regeneration is once again subjected to dephenolation and it is capable to be used repeatedly.

NEW MODIFICATION OF THE METHOD OF THE ANALYSIS OF PHENOLS AND PHENOLIC TOXICANTS

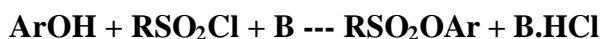
In the world practical person today accepted specifically to select so named "priority" phenols: phenol, 4-methylphenol, 2,6-dimethylphenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol,

pentachlorophenol, 4-chloro, 3-methylphenol, 4-nitrophenol, 2-nitrophenol, 2,4-dinitrophenol, analysis which in different objects of environment (water, ground, air, other) is obligatory. Besides, in earned one's living regions of different enterprises it is necessary to check a contents and dynamics of entering in ecosphere such phenolic deriveds as naphthols, pesticides, containing oxyaromatic group, polyphenols and different intermediate products of organic syntheses. In connection with need to identify a source of contamination of biosphere by phenols, as well as for getting an exhausting feature of condition of environment, should define not less than 10-15 derived phenols.

Known greater number of methods of analysis of phenols in objects of surrounding ambience, using physical and specific chemical characteristics of oxyaromatic compounds. These multiple ways are based on spectroscopic methods, typical colorimetric reactions, and interaction of phenols with different chemical reagents. For the analysis of low, threshold of quantity concentrations of phenols, so named "trace-quantity" amounts, as main methods are used liquid and gas chromatography. In these cases use such different methods of preliminary concentrating of phenols: the extraction, adsorption, forming the complexes and others.

Many phenols are unstable highreactivity compounds, they easily oxidize that greatly obstructs their quantitative determination and study. At the analysis of such labilic phenols last, usually, transform beforehand in stable products by means of different specific reactions: acylation under the action of anhydrides or haloidanhydrides of carbonic acids, different fluor reagents; reactions of phosphorylation, -alkylation and others. As a rule, these reactions of conversion of phenols in more stable products run slowly, yields of final products do not reach quantitative, reactions insufficiently specific with respect to oxyaromatic compounds. Recently final products of the conversion of analysing phenols also insufficiently stable and in these cases tests of analysis can not long is kept and used as arbitration and checked.

In our Laboratory effective methods of analysis and express-analysis of the phenol and various phenolic compounds, which are based on the different chemical phenol transformations to unsoluble in water compounds have been discovered [4].



The reaction of sulfonation of phenols streams in conditions of catalysis quickly and irreversibly; when using of alkanesulfochlorides, methanesulfochloride the interaction ends for 0.5-5 minutes. Products of the reaction, arylsulfonates - RSO_2OAr , stand out with the quantitative yield, easy and packed extracting by organic solvent, particularly in the event of the transfer of analysing tests in water-organic two-phase ambience, for instance, water-toluene. Products to reactions, arylsulfonates, are extremely stable materials (to thermal and hydrolitical treatment) in neutral conditions not only, but in ambiances 5-30 % acids and bases even. So suit analysed test of any objects of environment at the condition of full conversion of phenols to stable products can remain unlimited long and be used as arbitrage samples. For quantitative analysis of arylsulfonates it is possible to use gas-liquid chromatography with the electronic claw detector or the highly effective liquid chromatography. Aryl esters of sulfoacides are determined quantitative easy and due to essential differences of its indexes of holding can certain be analysed in complex mixtures and in different objects of the environment. For illustrations of the applicability of the sulfochloride method for the analysis of phenols and its derivatives give an example the table of experimental results of the testing a method of analysis of micro concentrations of phenols in water.

Water solutions of phenols were prepared in the box, filled by inert gas. Beforehand phenols were thoroughly cleaned, for the preparation of solutions used water - special bidistilat. For the

determination of low concentrations of phenols at level of microquantity it is necessary its preliminary concentrating, which possible make by the method of solid phase - or liquid phase extraction. We carried out such concentrating of phenols by the sorbtion its from solution with use of special absorbing cartridges Seppak C₁₈, Pressen C₁₈ (short microcolumns, filled by silicagel, chemical modified of the alkylsilane with final aminogroups). In the event of the analysis of natural water, soils, containing in the test other soluble and colloidal materials it is necessary the concentrating before the analysis, to add in the test 0.1 M KH₂PO₄ solution for the destroying of diverse complexes of phenols and raising a quality of analysis. Acetonitril or high-purity toluene was used as a solvent-eluent. The treatment of the phenol, phenols to stable arylsulfonates is realized by the influence of the dissolving alkanesulfochloride or arylsulfochloride and triethylamine as catalyst (~1 : 1.2). Method allows analysing concentrations of phenols in the interval 2-0.001 mg/l, analysis mistake forms 8-25%. Advantages of such modified method of the analysis of phenols that it allows be analysed any phenols and oxyderivatives practicaly, appears very sensitive and selective with respect of other oxyderivatives. The presence of another organic and inorganic admixtures in analysing objects doesn't worse analysis. Stabilizing test by means of sulfochlorides can be saved long-term unlimited.

Donetsk Botanical gardens and ecological inspectorates used our methods for the content study of any phenols in foliages of trees in Donetsk region, for example in the field of Donetsk cokefactory. In our Laboratory efficient methods of the purification and treatment of phenolic industrial waster waters and also technologies of processes, which are based on other chemical transformations of phenols to unsoluble in water intoxycal compositions with some valuable properties also has been discovered.

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