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ADSORPTION OF PHENOL AND BENZOIC ACID FROM WATER SOLUTIONS BY MODIFIED ADSORBENTS

Adsorption of phenol and benzoic acid from water and n-heptane solutions by macroporous silicas with chemically modified surface has been investigated. Grafting of branched functional groups into silica surface allows to increase the values of Henry's constants of these aromatic compounds at the adsorption equilibrium in n-heptane solutions. For some modified silicas they grow by two orders. The nature of interaction between the molecules of aromatic compounds and the modified surface of silica has been also considered, as well as the possibility of application of the adsorbent to wastewater treatment.

1. INTRODUCTION

The adsorption plays an important role in the advanced wastewater treatment because of its numerous advantages and in particular for its high treatment efficiency and economy resulting from the adsorbent regeneration and reuse and possibility of automation of the adsorption process [2]. Many types of activated carbons are most widely used in the advanced wastewater treatment despite relatively high cost, because some cheaper adsorbents (silica gels, clays and some other oxides) are highly hydrophilic and difficult to apply in practice. Therefore it is important to estimate the possibility of application for those purposes of silica gels with the modified surface.

2. EXPERIMENTAL

2.1. MATERIALS

The macroporous silica — silochrom Si-80 — with the unit surface area of 80 m^2g^{-1} and the average pore diameter of 60 nm was selected as the original sample, and trimethylchlorsilane, tetraethoxysilane, γ-phenoxypropyltriethoxysilane, γ-aminopropyltriethoxy-

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silane, and aminohexyl-N-aminopropyltriethoxysilane were used to modify the silica active surface. Phenol and benzoic acid dissolved in the fresh twice distilated water or in n-heptane stored with zeolite NaA were selected as sorbates.

2.2. METHODS

Prior to modification 10 g of silochrom were heated at 550 K during 4 hours and then introduced into the glass vessel containing 100 ml of dry toluene solution of organosilane. The content was mixed and boiled for 10 hours and then the modified silica sample was treated with dry solvent and dried in vacuum for 5 hours at 400 K [4]. Portions of the dried and modified silica were introduced into glass ampoules and mixed with the dilute solutions of aromatic compounds of a known concetration. The analysis of the solution samples was carried out with the help of differential refractometer ITR-2, after adsorption equilibrium had been attained.

The values of Gibbs adsorption, based on the excess of the sorbate in the solution at equilibrium and on its concentration in bulk solution, were calculated from the following formula:

$$\Gamma = n(c_0 - c)s^{-1}m^{-1}, \tag{1}$$

where:

n is the amount of solution, moles,

c_0 and c are initial and equilibrium concentrations of an adsorbate (aromatic compound), mg/g,

s is an unit surface area of the adsorbent, m^2/g,

m is the amount of adsorbent, g.

3. RESULTS AND DISCUSSION

The adsorption isotherms of phenol and benzoic acid from n-heptane solution are shown in figs. 1 and 2. All the adsorbents studied are characterized by positive adsorption values with the exception of silica sample modified by γ-phenoxypropyltriethoxysilane for which the adsorption of benzoic acid was negative. Modification of silica surface by alkylaminosilanes increases the adsorption of phenol and benzoic acid from dilute solution of n-heptane due to the energy growth resulting from the specific interaction between the molecules of aromatic compounds and the amino groups of the modified silica surface. Such a modification of silica surface or that of the other silanes studied leads to the adsorption decreases because of the substitution of the active hydroxyl groups of silica surface by alkyl (or aryl) groups unable to interact specifically with the functional groups of aromatic molecules. Thus, grafting of the branched functional groups of organosilane molecules into silica surface brings down the competitive adsorption of solvent molecules and increases the specific interaction of phenol molecules and benzoic acid with this surface.

The values of Gibbs' adsorption at two adsorbate equilibrium concentrations and those of Henry's constant K at equilibrium concentrations C below $\mathrm{mg \cdot g^{-1}}$ for the adsorption of phenol and benzoic acid on the original and modified silica samples are given in tab. 1. The K constant was calculated as being equal to

$$K = \Gamma / c \quad \text{at } c \text{ below 1 mg/g.} \tag{2}$$

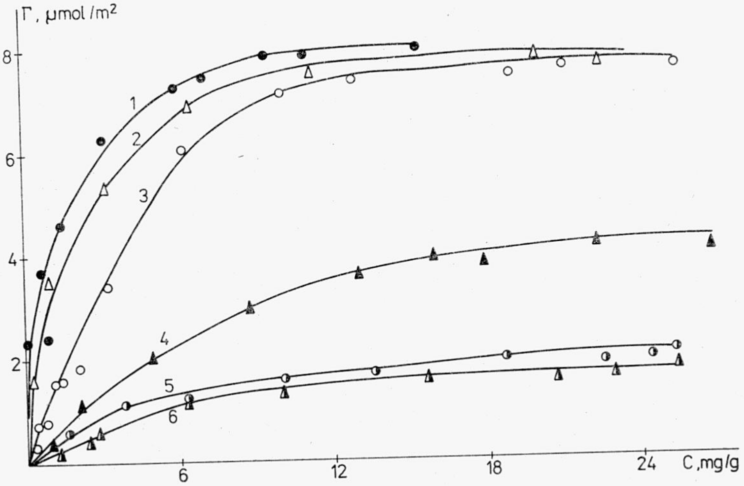

Fig. 1. The adsorption isotherms of phenol from n-heptane solutions by modified silica adsorbents: 1-Si-PP 2-Si-AH, 3-Si-80, 4-Si-TE, 5-Si-PP, and 6-Si-TM

Rys. 1. Izotermy adsorpcji fenolu z roztworów n-heptanu przez zmodyfikowane adsorbenty krzemionkowe 1-Si-PP, 2-Si-AH, 3-Si-80, 4-Si-TE, 5-Si-PP i 6-Si-TM

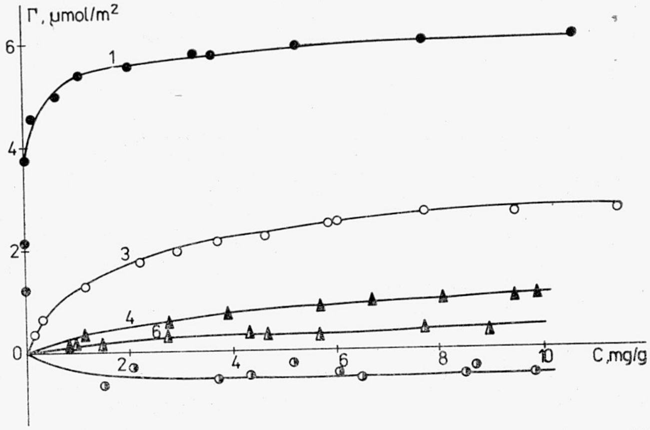

Fig. 2. The adsorption isotherms of benzoic acid from n-heptane solutions by modified silica adsorbents

Rys. 2. Izotermy adsorpcji kwasu benzoesowego z roztworów n-heptanu przez zmodyfikowane adsorbenty krzemionkowe

Table 1

The values of Γ and K for adsorption of phenol and benzoic acid

Wartości Γ i K dla adsorpcji fenolu i kwasu benzoesowego

Symbol of the adsorbent sample	Phenol			Benzoic acid		
	Γ, μmol/m²		K	Γ, μmol/m²		K
	$c = 2$ mg/g	$c = 10$ mg/g	sm³·m⁻²	$c = 2$ mg/g	$c = 10$ mg/g	sm³·m⁻²
Si-80	2.35	7.15	0.22	1.75	2.75	0.404
Si-TM	0.4	1.4	0.029	0.2	0.45	0.018
Si-PP	0.65	1.6	0.049	−0.45	−0.5	—
Si-TE	0.98	3.3	0.074	0.5	1.1	0.054
Si-AH	4.35	7.6	0.81	—	—	—
Si-AP	5.15	7.9	14.7	5.6	6.1	3.59

Note: Si-80 is the original silica sample, and the remaining ones are the modified samples using: trimethylchlorsilane (TM), γ-phenoxypropyltriethoxysilane (PP), tetraethoxysilane (TE), aminohexyl-N-aminopropyltriethoxysilane (AH), and γ-aminopropyltriethoxysilane (AP).

As it can be seen from fig. 1 and tab. 1, because of modification of the silica surface by monochlor- and ethoxysilanes towards hydrophobic, the adsorption and K constant values at the adsorption equilibrium in the system aromatic compound–n-heptane-silica are significantly diminished. The coating of silica surface by amino groups significantly increases those values at low and moderate concentrations.

The adsorption isotherms of phenol and benzoic acid from water solution on modified silica samples are represented in figs. 3 and 4. The silica modified with trimethylchlor- and tetraethoxysilanes were not investigated, because its samples could not be wet with

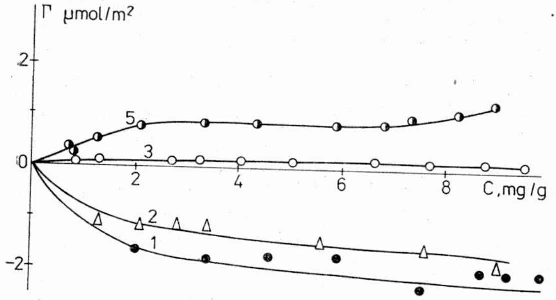

Fig. 3. The adsorption isotherms of phenol from water solutions by modified silica adsorbents

Rys. 3. Izotermy adsorpcji fenolu z roztworów wodnych przez zmodyfikowane adsorbenty krzemionkowe

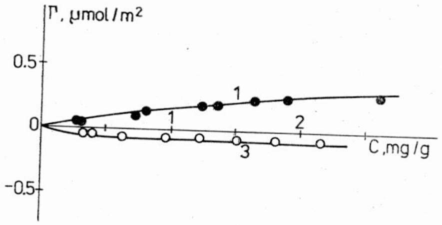

Fig. 4. The adsorption isotherms of benzoic acid from water solutions on modified adsorbents

Rys. 4. Izotermy adsorpcji kwasu benzoesowego z roztworów wodnych przez zmodyfikowane adsorbenty krzemionkowe water. The adsorption of phenol from water solution on the silica samples modified by aminosilanes is negative due to the strong interaction between water molecules with amino and ethoxy groups of the modified silica surface. The negative adsorption of benzoic acid from water solution on hydroxylated silica results from stronger interaction of water molecules with hydroxyl groups of silica surface. Grafting of amino groups into silica surface causes the positive adsorption of benzoic acid as a result of the specific molecular interaction between the acidic and basic groups. Thus, the modification of silica surface changes the properties of adsorbents and increases significantly the selectivity of adsorption in wastewater treatment.

The values of Gibbs adsorption at two equilibrium concentrations of sorbate in water and those of Henry's constant for phenol and benzoic acid are given in tab. 2. The results show to what extent the adsorbent properties are changed because of its surface modification.

Table 2

Values of Gibbs adsorption of phenol and benzoic acid and Henry's constant for modified silica adsorbents

Wartości adsorpcji Gibbsa dla fenolu i kwasu benzoesowego oraz stała Henry'ego dla zmodyfikowanych adsorbentów krzemionkowych

Sample symbol	Phenol			Benzoic acid		
	Γ, μmol·m^{-2}		K	Γ, μmol·m^{-2}		K
	$c = 2$ mg·g^{-1}	$c = 5$ mg·g^{-1}	cm^3·m^2	$c = 0.5$ mg·g^{-1}	$c = 2$ mg·g^{-1}	cm^3·m^{-2}
Si-80	0.1	0.15	0.01	−0.06	−0.1	—
Si-PP	0.75	0.85	0.045	—	—	—
Si-AP	−1.6	−1.95	—	0.1	0.28	0.024

Note: Sample symbols as those described in tab. 1.

Comparing the values of Henry's constant and the adsorption isotherms of phenol and benzoic acid from water and n-heptane solutions, the effect of solvent type on the interaction of molecules of aromatic compounds with modified silica surface may be estimated. Polarity of solvent is an important factor in the adsorption on polar adsorbents.

It is known that microporous activated carbons are able to uptake the organic compounds from water solutions due to the strong system of pores. However, the adsorption process proceeds at a very low rate because of a slow diffusion of the adsorbate molecules in the micropores, the sizes of which are close to the molecule hydrodynamic radius [1]. Penetration of molecules of aromatic compounds into the macropores of silica sample Si-80 proceeds extremely rapidly.

Figure 5 gives kinetic curves of adsorption of phenol and benzoic acid from water and n-heptane solutions by silica and activated carbons at the same dispersion degree of the adsorbents.

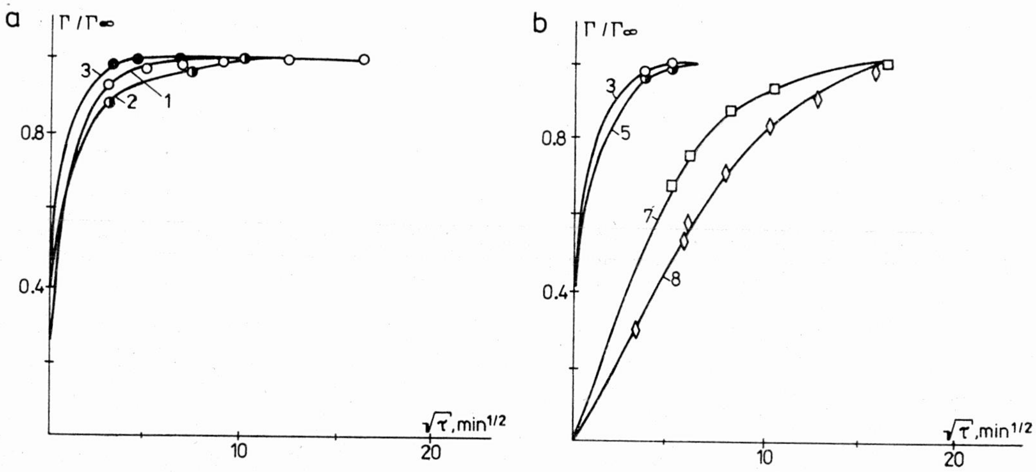

Fig. 5. Adsorption kinetics

a) of phenol (*1* and *2*) and benzoic acid (*3*) from n-heptane solution on silicas, b) of phenol from water solution on silicas (*3* and *5*) and BAC (*7*), KAC (*8*)

Rys. 5. Kinetyka adsorpcji

a) fenolu (*1* i *2*) i kwasu benzoesowego (*3*) z roztworu n-heptanu na krzemionce, b) fenolu z roztworu wodnego na krzemionce (*3* i *5*) oraz na BAC (*7*) i KAC (*8*)

Table 3

Parameters of phenol adsorption kinetics

Parametry kinetyki adsorpcji fenolu

Adsorbent	τ, min	
	n-heptane	water
Si-80	0.4	0.05
Si-PP	0.1	0.05
BAC	—	12
KAC	—	28

Note: BAC and KAC represent the activated carbon samples.

From fig. 5 it can be seen that the adsorption of aromatics by silica of different chemical characteristics of surface proceeds rapidly. However, penetration of phenol molecules into microporous carbons is a slow process.

The values of time corresponding to one half of equilibrium concentration τ are given in tab. 3. They indicate the rapid diffusion of phenol molecules in macropores of silica Si-80 and the slow diffusion of these molecules from n-heptane solution. This may be due to the fact that the enters into the pores are blocked by the adsorbed clusters of phenol molecules.

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ADSORPCJA FENOLU I KWASU BENZOESOWEGO Z ROZTWORÓW WODNYCH PRZY UŻYCIU ZMODYFIKOWANYCH ADSORBENTÓW

Badano adsorpcję fenolu i kwasu benzoesowego z roztworów wodnych n-heptanu przez makroporowate krzemionki o chemicznie zmodyfikowanej powierzchni. Zaszczepienie rozgałęzionych grup funkcyjnych w powierzchni krzemionki pozwala zwiększyć wartości stałych Henry'ego tych związków aromatycznych w roztworach n-heptanu w stanie równowagi adsorpcyjnej. Wartości te dla pewnych zmodyfikowanych krzemionek wzrastają w dwa rzędy wielkości. Wzięto również pod uwagę charakter interakcji między cząsteczkami związków aromatycznych a zmodyfikowaną powierzchnią krzemionek oraz możliwość zastosowania tego adsorbentu do oczyszczania ścieków.

ADSORPTION VON PHENOL UND BENZOESÄURE AUS WÄSSRIGEN LÖSUNGEN UNTER ANWENDUNG VON MODIFIZIERTEN ADSORPTIONSMITTELN

Untersucht wurde die Adsorption von Phenol und Benzoesäure aus wässrigen n-Heptanlösungen durch makroporöses Siliziumdioxyd dessen Oberfläche chemisch modifiziert wurde. Durch Bearbeitung der Oberfläche der Kieselerde mit verzweigten Funktionsgruppen, ermöglicht man eine Erhöhung der Henry--Konstanten dieser aromatischen Substanzen in n-Heptanlösungen im Adsorptions-Gleichgewicht. Für bestimmte, modifizierte Kieselgurerden, wachsen diese Werte um zwei Zehnerpotenzen an. Betrachtet wurde auch die Art der Interaktion zwischen den aromatischen Substanzen, der modifizierten Kieselgurfläche, sowie die Möglichkeit der Anwendung dieses Adsorbens zur Abwasserreinigung.

АДСОРБЦИЯ ФЕНОЛА И БЕНЗОЙНОЙ КИСЛОТЫ ИЗ ВОДНЫХ РАСТВОРОВ ПРИ ИСПОЛЬЗОВАНИИ МОДИФИЦИРОВАННЫХ АДСОРБЕНТОВ

Испытывалась адсорбция фенола и бензойной кислоты из водных растворов нормального гептана через макропористые кремнезёмы с химически модифицированной поверхностью. Прививка разветвлённых функциональных групп в поверхности кремнезёма позволяет увеличить значения постоянных Генри этих ароматических соединений в растворах нормального гептана в состоянии адсорбционного равновесия. Эти значения для некоторых модифицированных кремнезёмов возрастают в два порядка величины. Учитывался также характер взаимодействия между молекулами ароматических соединений и модифицированной поверхностью кремнезёмов, а также возможность применения этого адсорбента для очистки сточных вод.