

INTERACTION OF AQUEOUS SOLUTION OF PHENOL WITH 5A ZEOLITE: ADSORPTION AND COMPARISON WITH COMMERCIAL CARBONS AS ADSORBENTS

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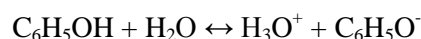
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Abstract: The commercial carbons have been used as adsorbents in decontamination processes due to their large specific surface, high adsorption capacity, microporous structure and specific surface reactivity. One of the most important applications of activated carbon concerns the water purification treatment. Water is often contaminated with phenol and allied pollutants where zeolites, as the adsorbents, also play a significant part. In this study, the comparison of parameters obtained from the adsorption isotherms of zeolites and commercial carbons has served to clarify the zeolite surface property, as an adsorbent, on the molecular level. The phenol aqueous solution of 2.0 – 4.0 mgL⁻¹ mass concentration has been used as adsorbate. The phenol content has been determined spectrophotometrically on the basis of the color intensity of quinoid-type compound which has originated from the phenol and 4-amino antipyrin reaction with the K₃Fe(CN)₆ as an oxidant in the alkaline medium.

Keywords: adsorption, zeolite, phenol, waste water.

1. INTRODUCTION

In general, adsorption comprises accumulation of molecules from the solution on the outer and inner surface of the adsorbent. That surface phenomenon represents a manifestation of complex interactions among three included components, i.e. adsorbent, adsorbate and solvent. The affinity between the adsorbent and the adsorbate is the main force of interaction controlling the adsorption. However, the affinity between the adsorbate and the solvent can play an important part in adsorption, especially due to the fact that the oxygen – hydrogen bond in the phenol –OH group is more polar than in the alcohol, which makes the hydrogen bonds among the phenol molecules stronger. Phenol is weak acid prone to disassociation in the aqueous solution:



A proton in phenol gets easily separated from the –OH group thanks to π - electronic system of the aromatic nucleus, which also includes p-orbital of

the oxygen atom. This makes the oxygen – hydrogen bond more polar. [1-3]

It is due to these characteristics of phenol that it was interesting to observe its reaction in the contact with two almost inert materials (activated carbon and lignite) and the synthetic 5A zeolite.

2. MATERIALS AND METHODS OF WORK

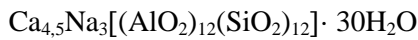
The following adsorbents have been used in the experimental part of the work:

Activated carbon, is a specially prepared type of carbon of porous crystal structure, which is usually used for adsorption. The pore space in the activated carbon does not exceed the size of 1nm. Producer *Kemika*, Zagreb.

Carbon of the *Stanari* Coal Mine, which is classified in the class of younger lignites. Carbon possesses very few reactive impregnations and has a low content of sulphur and a low content of ash (only 7.5 %), based on which it has been characterized as ecological fuel.

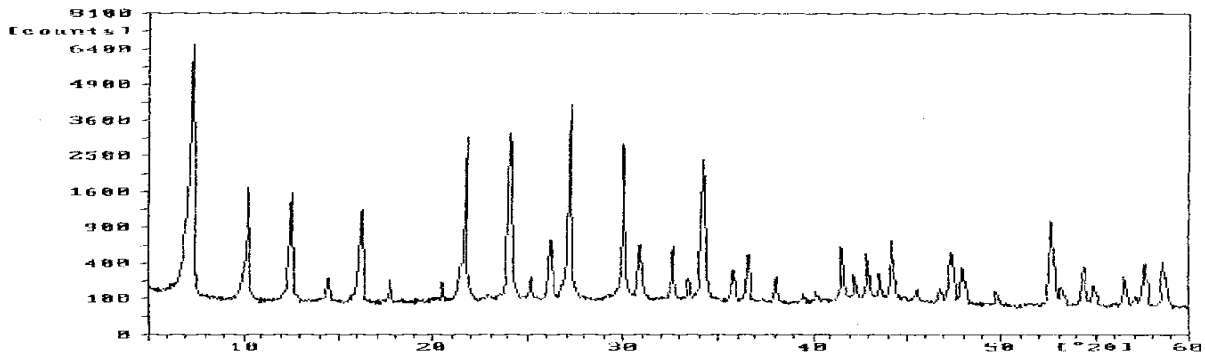
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Synthetic 5A zeolite, of the faujasite class, whose producer is Organisch – Chemisches Institut der Universitaet Goettingen. The formula of 5A zeolite, according to Linde, is:

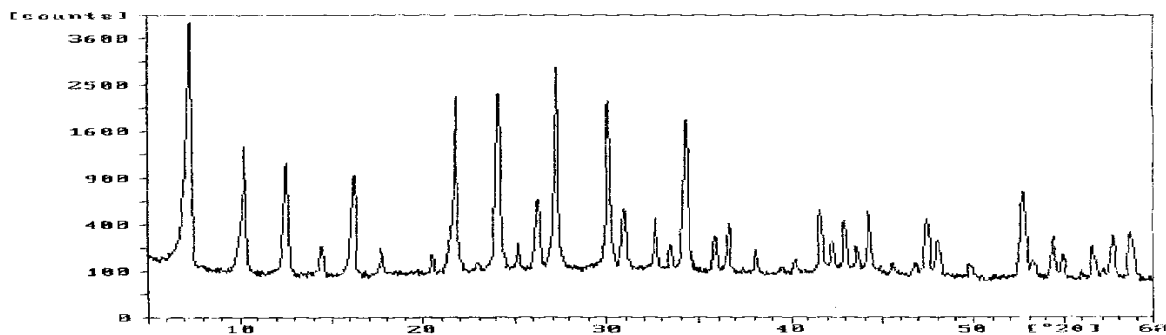


The adsorbate has been the aqueous solution of phenol with the mass concentration of $\gamma = 2.0 - 4.0 \text{ mgL}^{-1}$. The content of phenol before and after the adsorption was determined spectrophotometrically based on the color intensity of the quinoid-type

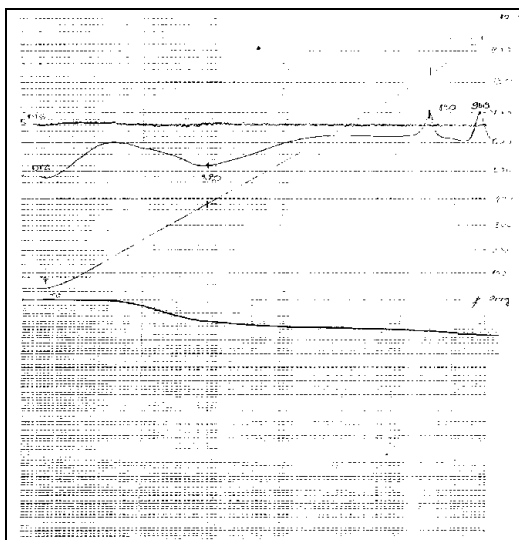
compound that originates from the phenol and 4-amino antipyrine reaction with $[\text{K}_3\text{Fe}(\text{CN})_6]$ as an oxidant in the alkaline medium. The spectrophotometer applied was Milton Roy, Spectronic 1201. The identification of the sample was performed by an x-ray diffraction analysis on the automatic PHILIPS PW 1710-type diffractometer along with the use of the Cu-anticathode and graphite monochromator and by the method of thermal analysis (DTA, TG and DTG) on the Mettler – thermoanalyzer



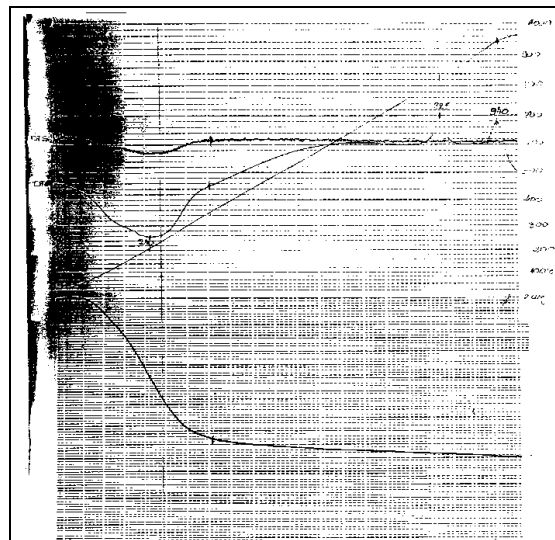
Picture 1. Diffraction of 5A sample



Picture 2. Diffraction of 5A sample (after adsorption)



Picture 3. Thermogram of 5A sample



Picture 4. Thermogram of 5A sample (after adsorption)

3. STUDY RESULTS AND DISCUSSION

The adsorption of phenol on the mentioned adsorbents was conducted by adding 100 mL of the aqueous solution of phenol ($\gamma = 2.0 - 4.0 \text{ mgL}^{-1}$) to 1.0 g of adsorbent. 10 mL of acetate buffer (pH=7) was added to each sample. The adsorption balance

was reached 24 hours later, and then the concentration of phenol was determined before and after the adsorption spectrophotometrically. [4-6] The results were presented in the form of functional dependence x/m on the balance concentration of the phenol solution in the tables (1, 2 and 3) and in the pictures (5, 6 and 7).

Table 1. Adsorption of phenol on carbon from Stanari; pH=7, $t=24^h$, $T=285 \text{ K}$ (12°C)

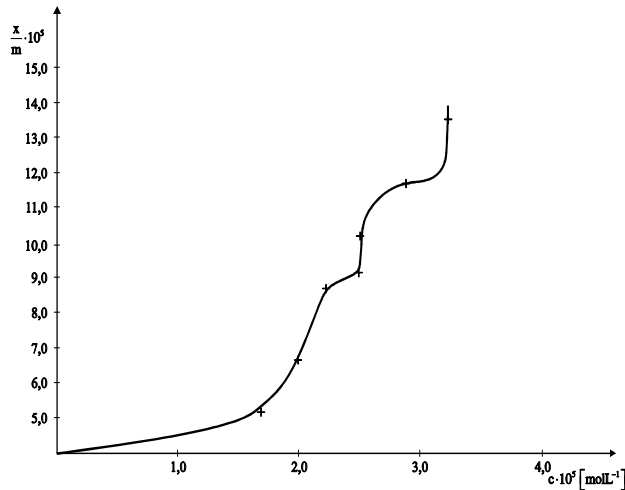
A_0	γ_0 [mg/L]	A	γ [mg/L]	$\frac{x}{m} \cdot 10^5$	$\log \frac{x}{m}$	$c \cdot 10^5 \left[\frac{\text{mol}}{\text{L}} \right]$	$\log c$
0,273	2,1338	0,209	1,6117	5,221	-4,2822	1,7146	-4,7658
0,325	2,5579	0,242	1,8809	3,770	-4,1694	2,0009	-4,6988
0,379	2,9984	0,272	2,1256	8,728	-4,0591	2,2613	-4,6456
0,406	3,2186	0,294	2,3051	9,135	-4,0393	2,4522	-4,6104
0,429	3,4062	0,303	2,3785	10,277	-3,9881	2,5303	-4,5968
0,488	3,8874	0,344	2,7129	11,745	-3,9301	2,8861	-4,5397
0,549	4,3850	0,383	3,0310	13,540	-3,8684	3,2245	-4,4915

Table 2. Adsorption of phenol on the activated carbon; pH=7, $t=24^h$, $T=285 \text{ K}$ (12°C)

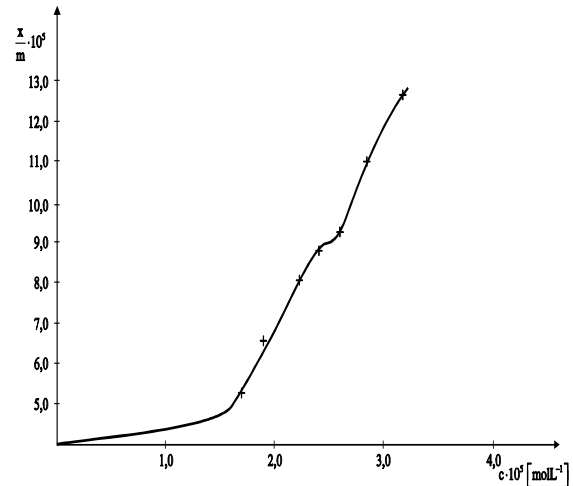
A_0	γ_0 [mg/L]	A	γ [mg/L]	$\frac{x}{m} \cdot 10^5$	$\log \frac{x}{m}$	$c \cdot 10^5 \left[\frac{\text{mol}}{\text{L}} \right]$	$\log c$
0,280	2,1909	0,215	1,6607	5,302	-4,2756	1,7667	-4,7528
0,320	2,5171	0,239	1,8564	6,607	-4,1799	1,9749	-4,7044
0,372	2,9413	0,272	2,1256	8,157	-4,0885	2,2613	-4,6456
0,396	3,1370	0,288	2,2561	80809	-4,0551	2,4001	-4,6198
0,423	3,3573	0,308	2,4192	9,381	-4,0278	2,5736	-4,5878
0,475	3,7814	0,340	2,6803	11,011	-3,9582	2,8514	-4,5449
0,533	4,2545	0,377	2,9821	12,724	-3,8954	3,1724	-4,4986

Table 3. Adsorption of phenol on zeolite 5A; pH=7, $t=24^h$, $T=285 \text{ K}$ (12°C)

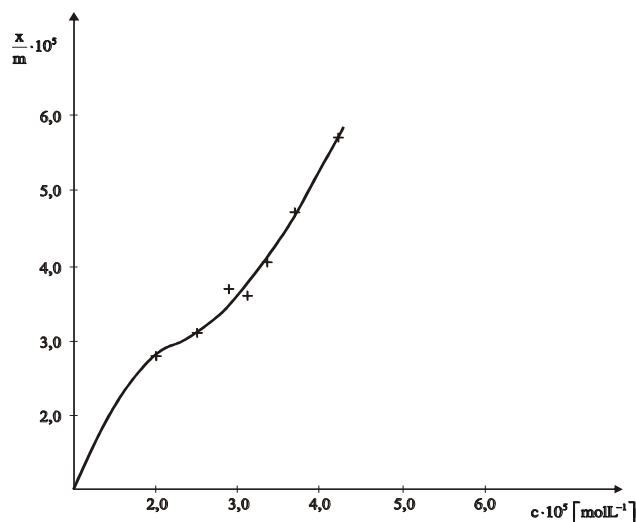
A_0	γ_0 [mg/L]	A	γ [mg/L]	$\frac{x}{m} \cdot 10^5$	$\log \frac{x}{m}$	$c \cdot 10^5 \left[\frac{\text{mol}}{\text{L}} \right]$	$\log c$
0,280	2,1909	0,246	1,9135	2,774	-4,5569	2,0356	-4,6913
0,342	2,6966	0,304	2,3866	3,100	-4,5086	2,5389	-4,5954
0,396	3,1370	0,350	2,7618	3,752	-4,4257	2,9381	-4,5320
0,419	3,3246	0,375	2,9657	3,589	-4,4450	3,1550	-4,5010
0,452	3,5938	0,402	3,1860	4,078	-4,3895	3,3894	-4,4699
0,504	4,0179	0,446	3,5449	4,730	-4,3251	3,7712	-4,5235
0,572	4,5726	0,502	4,0016	5,710	-4,2434	4,2570	-4,3709



Picture 5. Adsorption of phenol on Stanari carbon, time of adsorption = 24^h, t = 12 °C, pH = 7



Picture 6. Adsorption of phenol on activated carbon, time of adsorption = 24^h, t = 12 °C, pH = 7

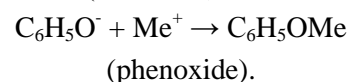


Picture 7. Adsorption of phenol on 5A zeolite, time of adsorption = 24^h, t = 12 °C, pH = 7

Adsorption was examined according to the Freundlich adsorption isotherm. The results indicated that this was a physical and multi-layer adsorption. In Freundlich equation $\frac{x}{m} = k \cdot c^{1/n}$, k and $1/n$ there are Freundlich coefficients that respectively represent the capacity and affinity of the adsorption. When taking a look at table no. 4, one can see that there is a certain correlation between the Freundlich coefficients and molecular characteristics of the components of this adsorption system. [7]

The value of parameter n indicates that zeolite 5A is a good adsorbent for phenol. This is confirmed by the calculated heat of adsorption ($\Delta_{\text{anc}}H = -3376.52 \text{ Jmol}^{-1}$). However, the low value of coefficient k compared to the same one for the activated carbon and Stanari carbon could be a direct consequence of the adsorbent – adsorbate interaction. Namely, as mentioned before, phenol based on

its characteristics is an acid adsorbate, and therefore, the synthetic zeolite 5A with its active centers on the zeolite surface (Brönsted and Lewis acids and bases) might not be the best choice for this adsorption. [8] We also do not exclude a possibility of chemical reaction between the cations of zeolite (adsorbent) and phenolate ion (adsorbate):



The value of the constant k for the activated carbon and Stanari carbon indicates a much better affinity of adsorbent – adsorbate. Good interaction is also proved by the high values of x/m ratio, and the number of adsorbed molecules of phenol by 1g of the sample, Table 5. The reason for this reaction of carbon is explained by the inertness of the material.

Table 4. Constants n and k , $\Delta_{\text{ad}} H$ of Freundlich adsorption isotherm, height of plateau for adsorption of phenol on buffered samples

Name of sample	n	$k \cdot 10^4$	$\Delta_{\text{ad}} H$ [Jmol ⁻¹]	Plateau height $\frac{x}{m} \cdot 10^5$ [g · g ⁻¹]
5A (pH=7)	1.425	1.15	-3376.52	I=2.75
Stanari carbon (pH=7)	0.757	6025,59 · 10 ⁴	-1793.70	I=4.50 II=9.00 III=11.70
Activated carbon (pH=7)	0.706	5495,41 · 10 ⁴	-1672.86	I=4.30 II=9.00

Table 5. Number of adsorbed molecules (buffered) of phenol solution by 1 g of the sample

Name of sample	$\frac{x}{m} \cdot 10^5$ [g · g ⁻¹]			Number of adsorbed molecules · 10 ⁻²¹			From adsorbed molecules · 10 ⁻²¹ [nm ²]		
	I plateau	II plateau	III plateau	I plateau	II plateau	III plateau	I plateau	II plateau	III plateau
5A (pH=7)	2.75			176.18			44.87		
Stanari carbon (pH=7)	4.50	9.00	11.70	288.28	576.57	749.55	73.42	146.85	190.91
Activated carbon (pH=7)	4.30	9.00		275.47	576.57		70.16	146.85	

4. CONCLUSION

The analysis of the relationship between the Freundlich isotherm and molecular characteristics of adsorbents, adsorbates and solvents indicates that the activated carbon and Stanari lignite are better adsorbents for phenol than zeolite 5A due to less complex interactions among the components of the system of adsorption [9–10].

Namely, with zeolite 5A, in addition to physical adsorption, a possibility of chemical adsorption is not excluded either, and it originates from potential ionization of phenol, which makes it get adsorbed by the physical adsorption, cation exchange and also through the adsorption on the surface acid centres of zeolite 5A. All this results in high heat of adsorption, lower constant k and lower x/m ratio, i.e. smaller number of adsorbed molecules by 1g of sample.

5. REFERENCES

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ИНТЕРАКЦИЈА ВОДЕНОГ РАСТВОРА ФЕНОЛА СА
ЗЕОЛИТОМ 5А: АДСОРПЦИЈА И КОМПАРАЦИЈА СА
КОМЕРЦИЈАЛНИМ УГЉЕВИМА КАО АДСОРБЕНСИМА

Сажетак: Комерцијални угљеви се користе као адсорбенси у процесима деконтаминације због своје велике специфичне површине, великог адсорпционог капацитета, микропорозне структуре и специфичне површинске реактивности. Једна од најважнијих примјена активног угља је у третману пречишћавања вода. Често је вода контаминирана са фенолом и сродним загађивачима, при чему и зеолити имају важну улогу као адсорбенси. У овом раду је компарација параметара добијених из адсорпционих изотерми зеолита и комерцијалних угљева као адсорбенаса послужила да се појасне особине зеолитне површине, као адсорбенаса, на молекуларном нивоу. Адсорбат је био водени раствор фенола масене концентрације 2,0–4,0 mgL⁻¹. Садржај фенола одређиван је спектрофотометријски на основу интензитета боје једињења хиноидног типа која настаје реакцијом фенола са 4-амино антипирином уз оксидационо средство K₃Fe(CN)₆ у базној средини.

Кључне ријечи: адсорпција, зеолити, фенол, отпадна вода.

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