



The investigation of phenol removal from aqueous solutions by zeolites as solid adsorbents

Ljiljana Damjanović^a, Vesna Rakić^{b,*}, Vladislav Rac^b, Dušan Stošić^{a,c}, Aline Auroux^c

^a Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11158 Belgrade 118, P.O. Box 47, Serbia

^b Faculty of Agriculture, Department of Chemistry, University of Belgrade, Nemanjina 6, 11080 Zemun, Serbia

^c Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 CNRS/Université Lyon1, 2 av. Albert Einstein, 69626 Villeurbanne Cedex, France

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ABSTRACT

This work reports results on phenol adsorption from aqueous solutions on synthetic BEA (β) and MFI (ZSM-5) zeolites, studied by heat-flow microcalorimetry. For the sake of comparison, the adsorption was performed on activated carbon, a solid customarily used for removal of phenol from water. The obtained values of heats evolved during phenol adsorption indicate the heterogeneity of active sites present on the investigated systems for the adsorption of phenol. In addition, the amounts of adsorbed pollutant were determined and presented in the form of adsorption isotherms, which were interpreted using Langmuir, Freundlich, Dubinin–Astakov and Sips' equations. The latter was found to express high level of agreement with experimental data. The results obtained in this work reveal that the adsorption of phenol on zeolites depends on both Si/Al ratio and on the pore size. Hydrophobic zeolites that possess higher contents of Si show higher affinities for phenol adsorption. Among investigated zeolites, zeolite β possesses the highest capacity for adsorption of phenol. The possibility of regeneration of used adsorbents was investigated by thermal desorption technique. It has been shown that in the case of β zeolite the majority of adsorbed phenol is easily released in the low temperature region.

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1. Introduction

Phenol and phenolic compounds are both naturally occurring chemicals and are manufactured by man [1–3]. Phenols are present in wastewaters of various industries, such as refineries, coking operations, coal processing, pharmaceuticals, plastics, wood products, as well as pesticide, paint and paper industries. The effective removal of phenol from wastewaters is a problem of great importance and interest, particularly because phenol is toxic even at low

concentrations. Excessive exposure to phenol may cause health effects on brain, digestive system, eyes, heart, kidney, liver, lungs, skin and it can cause genetic damage.

There are various technologies for the removal of phenol from the effluents and they can be divided in three categories: biological, chemical and physical. Among them, physical method, in particular adsorption process, is generally considered the best, very effective, low-cost and widely used for the removal of the phenolic pollutants. Review on available technologies for phenol removal from fluid streams has been recently published providing comparison of the experimental conditions and the performances of different techniques [1].

For the abatement of phenol from water streams various separation technologies as well as destruction technologies exist, but their application strongly depends on single cases, in particular on the concentration of phenol in the stream, the co-presence of other contaminants and the nature of the industry where this problem is found. In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of phenol compounds from wastewaters. Among vast number of different adsorbents, numerous studies report phenol adsorption on activated carbon, in fibrous or granular form. Adsorption of phenolic compounds from aqueous solutions presents the most widespread use of activated carbons in water treatment and it has been reviewed [4]. However, it is well known that regenera-

Abbreviations: EPER, European Pollutant Emissions Register; VOC, volatile organic compounds; AES-ICP, atomic emission spectrometry-inductively-coupled plasma; TG-DTA/DSC, thermogravimetry-differential thermal analysis/differential scanning calorimetry; XRD, X-ray diffraction; c_{eq} , concentration of solution at equilibrium (mol dm^{-3}); S_e , the amount of adsorbate bonded to adsorbent in equilibrium (mol g^{-1}); S_m , the maximum amount of adsorbate in a monolayer (mol g^{-1}); K_L , the adsorption intensity or Langmuir coefficient ($\text{dm}^3 \text{mol}^{-1}$); K_F , constant in Freundlich isotherm ($\text{mol g}^{-1})(\text{mol}^{-1} \text{dm}^3)^n$; n , constant in Freundlich isotherm; DA, Dubinin–Astakov; K , constant in Sips' isotherm ($\text{dm}^3 \text{mol}^{-1})^n$; R , gas constant; T , absolute temperature; N_a , the adsorbed amount (mol g^{-1}); N_{am} , maximum amount adsorbed in micropores (mol dm^{-3}); β_s , affinity coefficient; E_{os} , characteristic energy of adsorption; TPD, temperature programmed desorption; TG-DSC, thermogravimetry-differential scanning calorimetry; MS, mass spectrometry; Q_{diff} , differential heats.

* Corresponding author.

E-mail address: vesna.rakic@ffh.bg.ac.rs (V. Rakić).

tion of active carbon is complicated and expensive. Consequently, reviews reporting results about possible application of various adsorbents for phenolic compounds such as clays [5], different types of polymers [6,7], modified clays [8,9], surfactant-modified zeolites and mesoporous aluminosilicates [10–12], carbon nanotubes [13], hydroxyapatite nanopowders [14], can be found in the literature.

Zeolites are an important class of hydrated aluminosilicates: they possess cage-like structures with internal and external surface areas of up to several hundred square meters per gram. An important property of these materials is the capacity to be regenerated while keeping their initial properties. Synthetic and natural zeolites have been widely used as adsorbents, catalysts, ion exchangers, membranes and molecular sieves; however, the application of synthetic zeolites for removal of phenolic compounds from wastewaters is covered in a limited extent in literature [15–23].

Although the thermodynamic and kinetics of organic compounds adsorption from gas phase by zeolites have been investigated, Radeke et al. [24] have shown that straightforward extrapolation is not possible from the gas-phase adsorption of organics in the presence of water vapor to the separation of organics from liquid water using dealuminated Y zeolites as adsorbents.

It is known that for adsorption of phenols from aqueous solutions, zeolite adsorbents must be hydrophobic, i.e. possess a high Si/Al ratio [15,17,20,21]. Therefore, the adsorptive properties of various zeolites towards the adsorption of phenol from aqueous solutions have to be investigated and verified by adequate experimental methods. Microcalorimetry coupled with volumetry is undoubtedly the appropriate method. Calorimetric techniques are promising methods to study adsorption phenomena on the surface of solid in contact with a liquid phase for two main reasons: (i) the expected physical quantities are directly measured, and (ii) the experiments provide both thermodynamic (the heat evolved) and volumetric (the amount of introduced substance) data [25–27].

The aim of this work is to investigate the adsorptive properties of various synthetic zeolites for the removal of phenol from aqueous solutions using liquid phase (titration) calorimetry. The adsorptive properties of these adsorbents have been compared with that of high-surface activated carbon. In this study, two types of zeolites were used:

- (i) zeolite BEA (beta), which has a three-dimensional intersecting channel system, two mutually perpendicular straight channels, each with a cross section of $6.6 \text{ \AA} \times 6.7 \text{ \AA}$, and a sinusoidal channel with a cross section of $5.6 \text{ \AA} \times 5.6 \text{ \AA}$ [17];
- (ii) MFI (ZSM-5) type zeolite, which is a medium-pore zeolite presenting a three-dimensional interconnected channel system with 10-membered openings ($5.1 \text{ \AA} \times 5.5 \text{ \AA}$ and $5.3 \text{ \AA} \times 5.6 \text{ \AA}$), the size of the channels intersection is close to $8.5\text{--}9.0 \text{ \AA}$ [17].

The adsorption of phenol from aqueous solutions on investigated zeolites and activated carbon in this work has been studied by isothermal volumetry–microcalorimetry, at 303 K; temperature chosen as technically relevant in water purification.

2. Experimental

2.1. Materials

The solids used as adsorbents were supplied by Aldrich (activated carbon), Rhône-Poulenc (H β -zeolite, Si/Al=43), Zeolyst (HZSM-5(x) zeolites, where x denotes Si/Al ratio, which is 15, 40 or 140). Ion-exchanged form of HZSM-5(15) zeolite, containing Cu²⁺

was obtained using common ion-exchange procedure: HZSM-5(15) was suspended in 0.01 mol L^{-1} aqueous solution of copper acetate and stirred for 24 h at 298 K, followed by filtering, washing with de-ionized water and drying.

Phenol used in this work is high purity (Sigma–Aldrich, 99%); the solution of 0.03 mol L^{-1} (dissolved in de-ionized water, pH 6.5) was used for both microcalorimetric and adsorption studies.

2.2. Characterization

Surface areas and textural properties of investigated adsorbents were either determined by the BET method from the adsorption of nitrogen at 77 K after pre-treatment for 4 h at 673 K under vacuum (the adsorption was performed using ASAP 2020 equipment from Micrometrics), or supplied by producer (in the case of activated carbon). The Cu²⁺ content was determined by AES-ICP in a Spectroflame-ICP instrument after dissolution of zeolite in a mixture of HClO₄, HNO₃ and HCl. The results of chemical analysis and the values of BET surface areas are presented in Table 1.

The affinities of solids toward water were estimated by finding the amounts of water that the samples, previously exposed to air, possess. For that purpose, thermogravimetry (TG-DTA/DSC Labsys from Setaram) of all samples was performed in the temperature region 30–900 °C. The samples were heated under the flow of air ($30 \text{ cm}^3 \text{ min}^{-1}$), with a heating rate of 5 K min^{-1} .

The crystallinities of adsorbents were checked by X-ray diffraction (XRD). In order to verify whether the structures of applied zeolites have been affected by the adsorption of pollutant and the subsequent process of regeneration, these procedures have been followed by the XRD investigation. All powder X-ray diffraction patterns were recorded on a Bruker (Siemens) D5005 diffractometer at room temperature using Cu K α (radiation, 0.154 nm) from 3° to $80^\circ 2\theta$ in 0.02° steps with 1 s per step. These experiments revealed that all investigated zeolites preserved their structures unaffected after the adsorption of phenol and the performed procedure of regeneration.

The adsorption of phenol onto the investigated materials was studied by titration microcalorimetry, which was employed to obtain the heats evolved as a result of adsorption. Experimental set up for titration microcalorimetry allowed precise control of introduced amounts of phenol, but not the detection of phenol remaining in solution after adsorption. Therefore, the volumetric measurements were collected in separate experiments, in order to obtain the amounts of adsorbed phenol on investigated materials.

2.3. Titration microcalorimetry

The adsorption heats of phenol dissolved in water were measured in a differential heat flow reaction calorimeter equipped with a stirring system (TITRYS, from Setaram) which is fully described elsewhere [28]. Briefly, the samples were pretreated under vacuum at 423 K for 4 h before being transferred into the calorimeter cell. Using a syringe pump, successive pulse injections of known amounts of a solution (0.03 M) of the probe molecule were sent onto the sample maintained at 303 K at 2 h time intervals. A pre-heating furnace allowed the injection of the solution at the same temperature as the calorimeter. The reference and measurement cells contained the pure solvent (1.5 mL) and the solvent with a weighted amount of the outgassed solid sample (ca. 150 mg), respectively. A programmable syringe pump (PHD 2000, Harvard Apparatus) was linked to the calorimeter by capillary tubes. Each dose was accompanied by an exothermic peak. The evolved heat was evaluated by the SETSOFT acquisition and processing software from Setaram.

Table 1
The chemical compositions and BET surface area values of investigated adsorbents.

Sample	Si/Al	Chemical composition	BET surface area (m ² g ⁻¹)	The capacity for water adsorption (wt.%)
HZSM-5	15	H ₆ (H ₂ O) ₁₆ [Al ₆ Si ₉₀ O ₁₉₂]	392	11.2
Cu-HZSM-5	15	H _{5.5} Cu _{0.5} (H ₂ O) ₁₆ [Al ₆ Si ₉₀ O ₁₉₂]	408	11.2
HZSM-5	40	H _{2.35} (H ₂ O) ₁₆ [Al _{2.35} Si _{93.65} O ₁₉₂]	425	7.4
HZSM-5	140	H _{0.7} (H ₂ O) ₁₆ [Al _{0.7} Si _{97.3} O ₁₉₂]	400	4
Hβ-zeolite	43	[H _{1.3}][Al _{1.3} Si ₅₇ O ₁₂₈]	650	2.1
Activated carbon	–	–	1600	–

2.4. Adsorption studies

Adsorption experiments were performed under same conditions as measurements in the titration microcalorimetry. The samples were pretreated in the same way. Each point of the obtained adsorption isotherms was collected in a separate experiment. 150 mg of dry sample was placed in a sealed flask which contained 1.5 mL of water and the appropriate amount of 0.03 M aqueous solution of phenol. After the continuous stirring at constant temperature (303 K), the solid and liquid phases were separated by centrifugation (Minispin from Eppendorf, 13 400 rotations per minute (rpm), duration of centrifugation 1 h). The amount of adsorbed phenol was determined by measuring the singular absorbance of phenol at 269.5 nm using UV-vis spectrophotometer GBC CiUltra 10e. Each absorbance was used to calculate the phenol concentration in solution at equilibrium, using an analytical curve. The difference between the amount of phenol in solution at equilibrium and the quantity added initially provided the amount of pollutant adsorbed by the solid.

The equilibrium concentrations at 303 K were achieved after 1 h of stirring, what was determined in the separate set of experiments. The same dose of phenol was introduced to the same amount of adsorbent in several flasks while time of stirring was varied. The concentrations of phenol which remained after particular periods were determined by spectrophotometry, as explained earlier. The equilibrium concentration was achieved after different periods of time: 20 min for some samples, 30 min or longer for others, but for all samples equilibrium concentration was achieved after 60 min of stirring at 303 K. It should be noted that the profiles of heat flow signals also indicated that adsorption is finished after 1 hour, in the case of all investigated systems—after that time, the heat flow signal reached the baseline values. Finally, the obtained results were expressed in the form of adsorption isotherms: the amount of adsorbed phenol as a function of the phenol amount remaining in the solution at equilibrium, at 303 K.

The isotherms obtained in this study were interpreted using different models; in each case the isotherm parameters were determined by fitting, using Microcal Origin 8 software.

In the literature, the Langmuir isotherm has been widely applied to interpret the data obtained for the adsorption of liquid pollutants—it has shown a good agreement with a wide variety of experimental data for the adsorption of solutes from liquid solutions [11]. This isotherm is known in the form:

$$S_e = \frac{K_L S_m c_{eq}}{1 + K_L c_{eq}} \quad (1)$$

where c_{eq} is the concentration of adsorbate in solution at equilibrium (mol L⁻¹), S_e is the amount of adsorbate bonded to adsorbent in the case of reached equilibrium (mol g⁻¹), S_m is the maximum amount of adsorbate bonded to adsorbent when a monolayer is formed (mol g⁻¹), and K_L is the adsorption intensity or Langmuir coefficient (L⁻¹ mol⁻¹).

The basic assumption of Langmuir's theory is that the adsorption of one single adsorbate molecule takes place at specific active sites of an energetically homogeneous surface of the adsorbent. By contrast, Freundlich isotherm is an experimental model that can be

applied to non-ideal adsorption on heterogeneous surfaces as well as for multi-layer adsorption [11]; it has been derived by assuming the heterogeneity of surface (exponentially decaying adsorption sites strength). It is expressed by the following equation:

$$S_e = K_F c_{eq}^n \quad (2)$$

where c_{eq} and S_e have the same meanings as previously, while K_F and n are constants; number n being often lower than 1.

Both Freundlich and Langmuir concepts are combined in the postulation of Langmuir–Freundlich (named also “Sips’ equation”): the interaction of one adsorbate molecule with one active site at heterogeneous surface possessing definite number of active sites is presumed [29]. This equation can be expressed as:

$$S_e = \frac{K S_m c_{eq}^n}{1 + K c_{eq}^n} \quad (3)$$

where symbols have the same meanings as previously.

Dubinin–Astakov (DA) model, often applied to interpret data obtained for the adsorption of phenol on activated carbons [30,31] is also used to fit the experimental data:

$$N_a = N_{am} \exp \left\{ - \left[RT \ln \left(\frac{c_s / c_{eq}}{\beta_s E_{0s}} \right) \right]^4 \right\} \quad (4)$$

where N_a is the adsorbed amount and N_{am} is the maximal adsorbed amount, R and T are the gas constant and temperature, respectively, β_s is the affinity coefficient (for phenol equal to 1.0), E_{0s} is the characteristic energy of phenol adsorption, and c_{eq} and c_s are the equilibrium phenol concentration and the saturation concentration at temperature T , respectively. This equation is a variation of well known Dubinin–Radushkevich isotherm, which is postulated for the adsorption from the gas phase. DA equation is applied for the adsorption on energetically heterogeneous solids, allowing describing a continuous distribution of pore sizes. If the exponent 4 is reduced to 1, the equation is reduced to well known Freundlich isotherm.

2.5. Temperature programmed desorption—regeneration of the adsorbents

The possibility to perform the regeneration of adsorbents was investigated by temperature programmed desorption—TPD. The measurements were performed using a thermobalance coupled with differential scanning calorimeter (TG-DSC 111 from Setaram), equipped by a mass spectrometer (MS, Thermostar from Pfeifer) as a detector; capillary-coupling system was used. The TPD experiments were carried out in a flow, with helium as the carrier gas (30 cm³ min⁻¹). For each experiment, ca. 20 mg of a sample with phenol adsorbed in previously done microcalorimetric experiment was used. Solid material with adsorbed phenol on the surface was separated from liquid phase by drying at room temperature for two days; the sample was then placed in the DSC chamber. After being kept at 300 K for three hours, the temperature was increased up to 873 K, at 3 K min⁻¹. During the temperature increase, the mass spectrometer was set to collect mass fragmentations typical for water (18 and 17) and phenol (94, 66, 65, 40 and 39) [32].

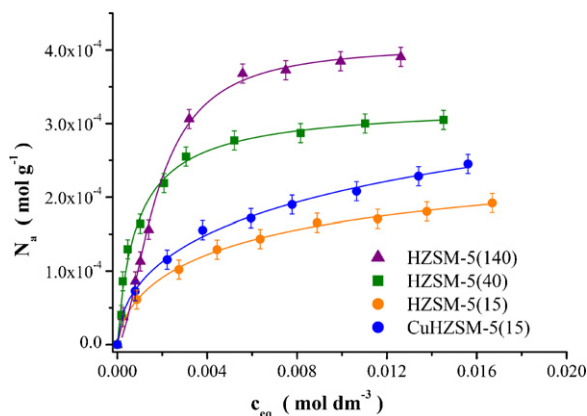


Fig. 1. The adsorption isotherms of phenol from aqueous solutions onto ZSM-5 zeolites with different Si/Al ratio and on Cu-HZSM-5(15) zeolite. The adsorption was done at 303 K, from 0.03 M aqueous solution of phenol (pH 6.5). Symbols present experimental data, while solid lines are obtained by calculation using Sips' equation.

3. Results and discussion

The chemical compositions, the values for BET surface area and the capacities for the adsorption of water, obtained by measuring the amounts of water removed from the samples by heating in temperature region 303–1073 K, are given in Table 1. It is evident that the affinity toward water is related to the Si/Al ratio, but also to the type of zeolite: H β -zeolite is the most hydrophobic, among the investigated solids. The values of internal surfaces and internal volume occupied by micropores are also dependent on zeolite type. In HZSM-5 sample, practically all internal volume is microporous ($S_{\text{micro}} = 378 \text{ m}^2$, $S_{\text{ext}} = 5 \text{ m}^2$; $V_{\text{micro}} = 0.17 \text{ cm}^3 \text{ g}^{-1}$; while the total volume is $V_{\text{total}} = 0.18 \text{ cm}^3 \text{ g}^{-1}$); in comparison with about 30% in the case of H β -zeolite ($S_{\text{micro}} = 452 \text{ m}^2$, $S_{\text{ext}} = 98 \text{ m}^2$; $V_{\text{micro}} = 0.21 \text{ cm}^3 \text{ g}^{-1}$; while the total volume is $V_{\text{total}} = 0.63 \text{ cm}^3 \text{ g}^{-1}$) [33,34]. Activated carbon is mainly microporous: $V_{\text{micro}} = 1.3 \text{ cm}^3 \text{ g}^{-1}$; while the total volume is $V_{\text{total}} = 1.5 \text{ cm}^3 \text{ g}^{-1}$.

Figs. 1 and 2 present the adsorption isotherms of phenol obtained in this work. In all presented isotherms, the number of moles adsorbed per gram of zeolite is denoted as N_a ; while the concentration of adsorbate determined at equilibrium is denoted as c_{eq} .

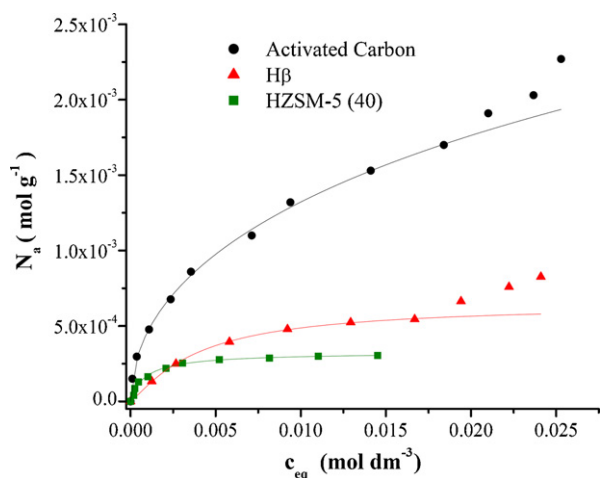


Fig. 2. The adsorption isotherms of phenol from aqueous solutions onto activated carbon, H β -zeolite and HZSM-5 zeolite with Si/Al = 40. The adsorption was done at 303 K, from 0.03 M aqueous solution of phenol (pH 6.5). Symbols present experimental data, while solid lines are obtained by calculation using Sips' equation. Error bars are not visible because they are smaller than symbols.

Fig. 1 shows the adsorption isotherms obtained for phenol adsorption on HZSM-5 zeolites with different Si/Al ratios. It is evident from the figure that both the shape of isotherms and the maximum values of adsorbed phenol are dependent on the Si/Al ratio. The isotherms for the HZSM-5(15) and HZSM-5(40) are steeper at low phenol concentrations than for the HZSM-5(140), indicating higher efficiency of these adsorbents at low phenol concentrations. All isotherms obtained for ZSM-5 zeolites could be described as L shape isotherms—in the domain of high equilibrium concentrations of phenol they either reach the plateau or show low slope. The so-called L shaped isotherms are interpreted in the literature as an indication that there is no strong competition between the solvent and the adsorbate to occupy the adsorbent surface sites [29,31].

It is evident that silica rich HZSM-5(140) sample has shown the highest adsorption capacity for phenol solution; while HZSM-5 zeolites with lower Si/Al ratio have potential for application as adsorbents for dilute phenol solutions. Zeolites, porous crystalline aluminosilicates formed by different amounts of SiO_4 and AlO_4 tetrahedra connected by oxygen atoms, are basically hydrophilic materials. However, it is generally accepted that they turn hydrophobic when Si/Al ratio reaches 10 [35]. Shu et al. [15] and Khalid et al. [17] have investigated the adsorption of phenol on various zeolite types and noticed the improvement of adsorption capacity with increased hydrophobicity. Hence, the results presented in Fig. 1 are in agreement with previous reports in the literature.

Since HZSM-5(15) showed the lowest adsorption of phenol, we performed ion exchange of H^+ ions with Cu^{2+} , in order to investigate influence of extraframework cations on phenol adsorption. The adsorption isotherms of phenol from aqueous solutions onto Cu^{2+} exchanged form of HZSM-5(15) is also presented in Fig. 1. The ion exchange resulted in an increase of phenol adsorption, in the whole range of applied phenol concentrations.

The quantities of phenol adsorbed on activated carbon and H β -zeolite are significantly higher than values obtained for HZSM-5 zeolites. The adsorption isotherms obtained for adsorption onto activated carbon and H β -zeolite are shown in Fig. 2. Isotherm obtained for HZSM-5 zeolite with Si/Al = 40 is also shown at the same figure for comparison. The amount of phenol adsorbed on β zeolite is similar to already published in the literature [17].

It is evident from the results presented so far that, even though Si/Al ratios of HZSM-5(40) zeolite and H β -zeolite (Si/Al = 43) were similar, amounts of phenol adsorbed by these two zeolites differ significantly—H β -zeolites is better adsorbent for phenol solution.

It is well known that zeolites consist of three-dimensional framework with well-defined, regular channels and cavities of molecular dimensions, specific to the type of zeolite. Zeolites are size-selective adsorbents: molecules which are to be adsorbed should be smaller than the pore size of the adsorbent, Pollutant molecules with sizes larger than the pore opening of the zeolites can only be adsorbed on the external surface of the zeolite, and in this case adsorption capacity is highly decreased.

The interaction of phenol molecule with zeolite structures is dependent on several factors. The suspensions of zeolites in water, investigated in this work, exerted slightly acidic pH values (between 4.7 and 6.3). Besides, the phenol is a weak acid that exists in aqueous solutions as both neutral and deprotonated forms—at pH value measured in this work (weakly acidic) the phenol should exist as nondissociated in the solution [37]. The acidity of phenol prevents its adsorption over the acidic sites. It has been shown that hydrogen from nondissociated phenol molecule is attracted by oxygen from zeolites' framework [36,38], this hydrogen bonding is done through the shifting of π electrons of the aromatic ring; the other possible interactions are those between aromatic ring of phenol with extraframework cation, through a kind of charge trans-

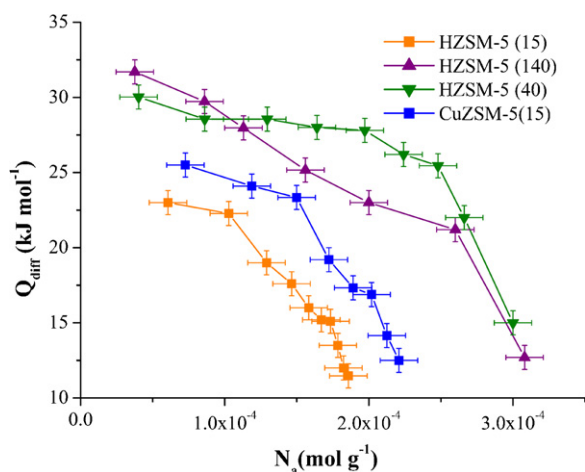


Fig. 3. Differential heats obtained for phenol adsorption as a function of adsorbed amount of phenol onto HZSM-5 zeolites with different Si/Al ratio. The adsorption was done at 303 K, from 0.03 M aqueous solution of phenol (pH 6.5).

fer from phenolate anion to empty orbital of metal [16,23,38]. All these interactions are dependent on the zeolite type (Lewis basicity of framework oxygens, the pore sizes and 3D structure), on the size of phenol molecule, its polarity and possible encapsulation in the pores of zeolite.

Dimensions of phenol molecule estimated by WINMOPAC program are $0.80 \text{ nm} \times 0.67 \text{ nm} \times 0.15 \text{ nm}$ [39]. Also, Shu et al. [15] considered phenol molecule as a disk and calculated the smallest cross-sectional distance for phenol as 4.3 \AA ; stating that, if the smallest cross-sectional distance is larger than the pore opening, phenol molecule cannot enter the pore (these calculations give static distances between nuclei which do not include van der Waals radii, so actual molecular distances are larger).

Based on presented results, it can be concluded that phenol molecule can enter pores of both HZSM-5 and H β -zeolites. However, β zeolite expresses favourable characteristics for phenol adsorption in comparison with ZSM-5: it is more hydrophobic, so the competition between water and pollutant molecules for adsorption is less pronounced; it possesses significantly larger pores and higher surface area. It is also worth to mention that H β can be taken as a prototype for Lewis active sites-rich zeolite (it possesses both Brönsted and Lewis acidic properties) while HZSM-5 zeolite possesses mainly Brönsted active sites. The existence of

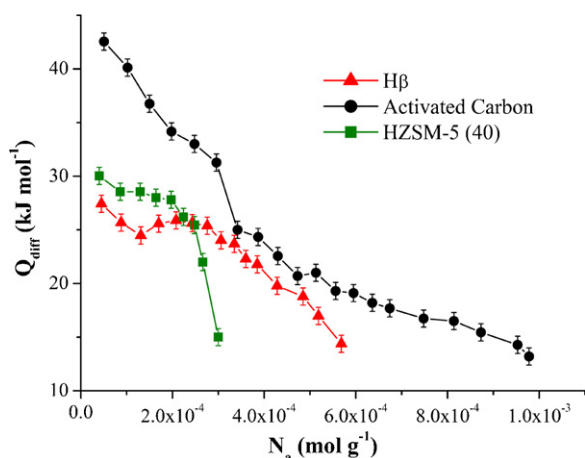


Fig. 4. Differential heats obtained for phenol adsorption as a function of adsorbed amount of phenol onto activated carbon, H β -zeolite and HZSM-5 zeolite with Si/Al=40. The adsorption was done at 303 K, from 0.03 M aqueous solution of phenol (pH 6.5).

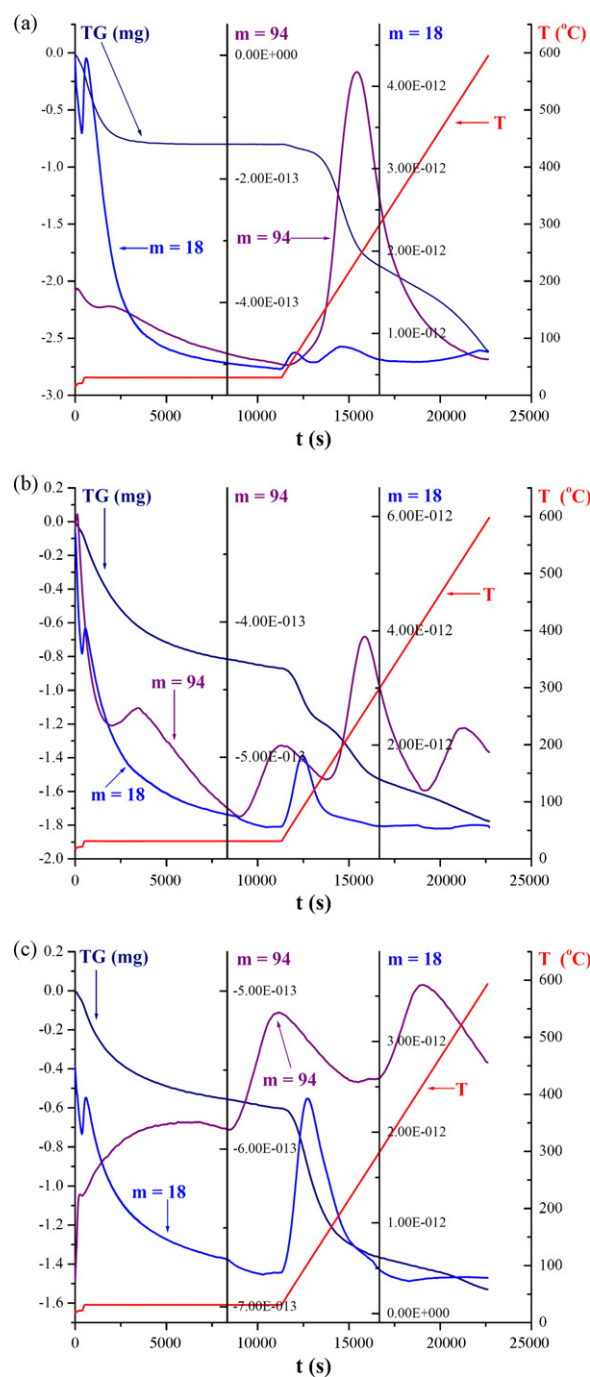


Fig. 5. The regeneration of solid materials after the adsorption of phenol. Figure presents the results obtained during the temperature programmed heating of polluted (a) activated carbon, (b) H β -zeolite, (c) HZSM-5(15): TG signal and TPD profiles of water ($m = 18$) and phenol ($m = 94$). The temperature performed from 300 K to 873 K, heating rate 3 K min^{-1} , in He ($30 \text{ cm}^3 \text{ min}^{-1}$).

framework Al and extraframework cations alter the internal and external electrostatic field of zeolite surface. It is also well known from the literature reports that the presence of framework Al and extraframework cations alter the ζ -potential of zeolite nanocrystals, what influence the interactions between them and species such as water or any adsorbate molecule [40]. The results presented in this work prove that electrostatic interactions are of importance for phenol adsorption on the investigated systems.

It is important to notice that, quite different from the isotherms found for HZSM-5 structure, in the case of β zeolite and activated carbon investigated here, the isotherms can be comprehended as

Table 2
Isotherm constants for phenol adsorption onto activated carbon and different zeolites.

	Activated carbon	Beta zeolite (Si/Al = 43)	HZSM-5 zeolite (Si/Al = 15)	HZSM-5 zeolite (Si/Al = 40)	HZSM-5 zeolite (Si/Al = 140)	CuZSM-5 zeolite (Si/Al = 15)
<i>Sips equation</i>						
N_{am} (mol g ⁻¹)	0.0087	0.00064	0.0003	0.00033	0.00041	0.00055
K (dm ³ mol ⁻¹) ⁿ	1.83	766.99	26.13	711.53	59 634.37	7.13
n	0.51	1.20	0.66	0.94	1.73	0.54
R^2	0.99840	0.99964	0.99672	0.98896	0.99534	0.99400
<i>Langmuir equation</i>						
N_{am} (mol g ⁻¹)	0.002	0.00072	0.00022	0.00032	0.00051	0.00028
K (dm ³ mol ⁻¹)	215.80	200.69	340.31	1187.25	351.47	327.85
R^2	0.97280	0.99692	0.98253	0.98839	0.97406	0.97038
<i>Freundlich equation</i>						
K (mol g ⁻¹)(mol ⁻¹ dm ³) ⁿ	0.011	0.0037	0.00083	0.0011	0.0032	0.0012
$1/n$	0.446	0.454	0.352	0.284	0.451	0.374
R^2	0.99785	0.95611	0.98450	0.90864	0.90570	0.99082
<i>DA equation</i>						
N_{am} (mol g ⁻¹)	0.0019	0.00069	0.00022	0.00034	0.00052	0.00027
E_{0s} (kJ mol ⁻¹)	15.01	14.46	15.77	18.54	15.57	15.71
R^2	0.95780	0.99865	0.98251	0.98840	0.97457	0.97020

composed of three main regions. In the domain of low equilibrium concentrations of phenol, the slopes are high; then, the isotherms express either plateau (H β -zeolite) or a continuous slope (activated carbon) in the range of middle equilibrium concentrations of phenol; and finally, in the domain of high equilibrium concentrations of pollutant, both isotherms express steep increase (Fig. 2).

The adsorption of phenol solutions on activated carbons has been widely investigated and it was well established that it involves the formation of electron donor–acceptor complexes where the basic surface oxygen and/or carbon surface electron rich regions act as donors and the aromatic ring of the adsorbate serves as acceptor [16,29–31].

The isotherms similar to those presented in this work for phenol adsorption on activated carbon and β zeolite have been already reported in the literature, for the adsorption of same pollutant onto the activated carbons [29,31]. For activated carbons, such isotherms are found for lower phenol concentrations in solution. However, with increasing phenol concentrations, both displacement of water and pore filling happen in the same time, leading to the changes in the shapes of isotherms [31]. This is particularly important in the case of larger micropores and in the mesopores.

Finally, it can be comprehended that H β -zeolite is a good adsorbent due to its large pore structure and favorable electrostatic characteristics of its framework; activated carbon possesses a high surface area thus it has a high capacity for adsorption although it is not size selective adsorbent [43]; while HZSM-5 zeolite is microporous solid which express a limited possibility for phenol adsorption.

From all previously stated, it is evident that adsorption from aqueous solution is a complex phenomenon. In order to clarify the process of phenol adsorption, the microcalorimetric experiments were performed in this work. The evolved heats indicate the strength of interaction phenol–surface of the used samples.

In the solvent, the active sites of solid material are covered by solvent which in the first step has to be removed before the molecules of the adsorbate are retained by the solid. The evolved heats measured upon adsorbate (phenol) adsorption from aqueous solutions originate from the exothermic enthalpy of adsorption on the active sites and the endothermic enthalpy of the solvent displacement. In the case of differential methods, the thermal effects due to stirring, dispersion, dilution and solvation by water are compensated by the reference cell, which contains the solvent only [41]. The affinity of the adsorbent for the probe molecule is reflected

by the evolved heats. As the affinity increases, the evolved heat increases and the thermal balance shifts in favour of the contribution of the adsorption effects. The evolved heat during adsorption of the probe molecule on the active site of adsorbent reflects the strength of that site. Moreover, the dependence of the heat of adsorption on coverage provides information about heterogeneity of the active sites [42].

The experimental results of microcalorimetric measurements are shown in Figs. 3 and 4. The differential heats of phenol adsorption from aqueous solution versus amount of adsorbed phenol obtained for all investigated ZSM-5 zeolites are shown in Fig. 3.

The profile obtained in the case of HZSM-5(15) shows a continuous decrease, in the whole range of surface coverage. Differential heats of phenol adsorption on the same sample has been reported recently, and presented as a function of amount of introduced phenol [34]. In the case of HZSM-5(40), the profile for differential heats (Q_{diff}) versus adsorbed amount of phenol (N_a) decreases slightly at the beginning, then it presents a plateau-like part (up to 200 μ mol g⁻¹), followed by abrupt decrease, indicating that all available sites for phenol adsorption have been covered. Lower values for Q_{diff} in the case of HZSM-5(140) compared to HZSM-5(40) zeolite have been found, indicating the existence of stronger active sites in the case of HZSM-5(40). For Cu-exchanged form of HZSM-5(15), again the decreasing of Q_{diff} values upon increasing the coverage is evident; however, the heats of adsorption have higher values for Cu-ZSM-5(15) zeolite over the whole range of coverage.

The heats evolved as a result of phenol adsorption from aqueous solutions onto activated carbon and H β -zeolite are shown at Fig. 4. Differential heats obtained for HZSM-5(40) zeolite are also shown in the same figure, for comparison, since this zeolite has similar Si/Al ratio as studied H β -zeolite. Evidently, the heats evolved in the case of activated carbon are the highest, thus indicating the significant affinity of carbon for the interaction with phenol. It is also interesting to point out here that the profile of differential heats obtained in the case of H β -zeolite differs from those obtained for other zeolites presented in this work: instead of abrupt decrease at the end of profile, it expresses continuous decrease of Q_{diff} values similar to that one found for activated carbon. Similar continuous decrease of Q_{diff} values with increasing coverage was found for H β -zeolite (Si/Al = 12.5) [34].

It can be inferred from microcalorimetric results obtained in this work that all investigated systems express energetic heterogeneity

in the process of phenol adsorption. Importantly, comparison of differential heats obtained for all zeolites investigated here leads to the conclusion that the interactions of phenol molecules with the surfaces of more hydrophobic zeolites, such as HZSM-5(140) and H β -zeolite are weaker than in the case of activated carbon and HSZM-5(40).

Energetic heterogeneity is also indicated by the analysis of adsorption isotherms presented in this work. All mathematical models for adsorption, mentioned in Section 2 were fitted to the experimental data. Based on R^2 values (presented in Table 2) it can be noticed that Sips' method has the highest level of agreement with experimental data, and fits well all experimentally obtained isotherms, as presented in Figs. 1–3.

This fact is another indication of energetic heterogeneity since Sips' equation is postulated with the assumptions that surface active sites are of different strengths and that one molecule of adsorbate interacts with one active site. The values obtained for all four adsorption models, the constants and their accordance with experimental data, are given in Table 2. It is important to notice that the Sips' equation could fit well the adsorption isotherms obtained for activated carbon and H β -zeolite only up to certain point, where these isotherms shows steep increase. It is well known that in the case of activated carbon, such a change is connected with the change in the mechanism of adsorption: at higher concentrations, phenol can displace water molecules even from the stronger active sites; in addition, the filling of larger micropores and even mesopores can happen. The shape of the isotherm obtained here for H β -zeolite could be interpreted in a similar way: the fact that Sips' model fits well this isotherm up to certain point (point 7, Fig. 2) indicates firstly the interaction of one phenol molecule with one active site at the heterogeneous surface, at low phenol concentrations; while at higher concentrations of pollutant, the filling of zeolitic porous system could be the event that predominates.

In this work, the possibility of regeneration of the samples applied for phenol adsorption from aqueous solution has been also tested. Phenol has been desorbed from the solids using thermal desorption method; these experiments have been performed using thermogravimetry coupled with mass spectrometry. Fig. 5 shows the mass loss and desorption profiles of water ($m/z = 18$) and phenol ($m = 94$), obtained as a result of temperature programmed heating, for activated carbon, H β -zeolite and HZSM-5(15). It is evident from the results presented in this figure that in the case of H β -zeolite, one significant amount of adsorbed phenol was desorbed without heating, in the flow of helium at 303 K—this part of phenol could be comprehended as physisorbed on the surface. In addition, another part of pollutant is desorbed by heating up to 473 K, in the case of both H β and HZSM-5(15). By contrast, in the case of activated carbon, a part of phenol that was physisorbed on the surface is very low, and the majority of pollutant has been desorbed by heating in the temperature region 373–773 K. It could be also important to notice that in accordance with these findings, lower initial heats were obtained for the adsorption on HZSM-5(15) and H β -zeolites, in comparison to activated carbon.

4. Conclusion

The results obtained in this investigation confirm that the adsorption of phenol from aqueous solution is more pronounced on hydrophobic zeolites. Both adsorption and microcalorimetric measurements have shown that the higher is Si/Al ratio, the higher is the adsorption of phenol.

All investigated systems showed the heterogeneity of sites active for phenol adsorption. The profiles of differential heats of phenol adsorption and the fact that the adsorption on the investi-

gated solids generally fits to Sips' equation, support this conclusion.

Among all zeolites tested as adsorbents, β zeolite has shown the higher affinity for phenol adsorption. Complex shape of adsorption isotherm obtained in the case of β zeolite is similar to that one obtained for high surface area activated carbon. It indicates the changing of adsorption mechanism: after all energetically heterogeneous active sites are covered with phenol molecules, it seems that pore-filling by phenol molecules takes place; this event results in steep increase in the amount of adsorbed pollutant. Therefore, it could be inferred from the results presented in this work that the adsorption of phenol from aqueous solution on investigated zeolites depends on both Si/Al of zeolites ratio and on their pore shapes and sizes.

Although the amount of adsorbed phenol is higher in the case of H β -zeolites, it is important to notice that the heats evolved by phenol adsorption on β zeolites are lower than in the case of ZSM-5 zeolite, thus indicating weaker interaction. Consequently, it has been found that the regeneration of β zeolites can be performed either by flushing the sample with the inert gas at near room temperature; or by heating up to moderate temperatures.

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