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Removal of detergents from water by adsorption on activated carbons obtained from various precursors

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ABSTRACT

The adsorption of detergents—sulfonic and phenolic compounds—from aqueous solutions by activated carbons (AC), obtained on the base of different precursors, was studied. The carbon adsorbents used were prepared by water vapor pyrolysis of different raw materials: peach stones, olive stones, natural asphaltite, mixtures from coal tar pitch, and furfural. It was established that all the samples of ACs have close values of high adsorption capacities toward the studied detergents. Some factors affecting the adsorption process—the time of treatment and the amount of the adsorbent—were investigated. It was established that the amount of adsorbent has no significant influence on the adsorption process.

Keywords: Water purification; Detergent; Activated carbon; Biomass

1. Introduction

The surfactants are widely used in the domestic cleaning detergents, as well as in the textile, paint, polymer, pesticide, pharmaceutical, mining, oil recovery, pulp, and paper industries [1].

There are three major types of surfactants—ionic, nonionic, and amphoteric. Among the ionic surfactants, sodium alkyl sulfonates are among the most used ionic surfactants in a wide range of detergents—dishwashing liquids, shampoos, shaving foams, powders for washing machines, industrial detergents, engine degreasers, floor cleaners, car wash soaps, toothpastes, shampoos, shaving foams, etc. [1–3]. Sodium dodecylbenzenesulfonate $C_{12}H_{25}C_6H_4$-SO_3Na is a common component of laundry detergents. Linear alkylbenzene sulfonates (LAS), alkyl ethoxy sulphates, alkylphenol ethoxylates, and quaternary ammonium compounds are the most commonly used commercial surfactants, as the major surfactants used in our days are the LAS and the alkyl phenol ethoxylates. The industrial and house waste waters contain high content of sulfonic compounds as a

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result of surfactant use. Phenolic compounds can also be found in waste waters after production and using of surfactants [4].

Many detergents are very toxic and harmful pollutants because they are not easy degradable and they can be accumulated as industrial and household waste on land and in water systems. Some detergents are known to be toxic for animals, ecosystems, and humans; in addition, these substances can enhance the diffusion of other environmental contaminants [5].

In the last decades, many investigations connected with the potential contamination of water resources by detergents were performed [1–3,6–11]. The anionic surfactants, especially LAS, deserve special interest, since they have some specific negative effects on aquatic and terrestrial ecosystems. Many consumer products contain high quantities of LAS, which are discharged into the waste waters after use [12,13].

Some surfactants have been proposed for restrictions on their use. For example, the branched dodecylbenzenesulfonates, has been phased out in many countries, mainly due to the slow biodegradation of these substances [3]. The commercial surfactant perfluorooctanesulfonic acid (PFOS) was banned in USA and other countries, due to increased risk of chronic kidney disease and other negative health effects [14]. PFOS, Perfluorooctanoic acid and their precursors are also persistent organic pollutants, and in the last years their production has almost brought to an end [3].

The surfactants in commercial detergent products remain almost chemically unchanged during the washing process and they are discharged down in the drain together with the dirty wash water. Very often, the drain is connected to a sewage, and ultimately to a waste water treatment plant, where the surfactants in the sewage can be removed by biological and physico-chemical processes [6,7].

The removal of detergents from aqueous solution is very important from the environmental point of view. The Water Framework Directive sets the ambitious goal of attaining "good status" for Europe's rivers, lakes, groundwater bodies, and coastal waters by 2015 in accordance with a clearly defined timeline [8].

The conventional methods used for surfactant removal from water involve chemical and electrochemical oxidation, membrane technology, chemical precipitation, photo-catalytic degradation, adsorption, and various biological methods [1–3,6,7,9–11,15–21].

Until now, the interest has focused mainly on the biodegradation. Biological degradation of LAS under aerobic condition has been demonstrated by some authors [11,15]. Degradation processes in anaerobic systems depend on alternative acceptors, such as sulfates, nitrates, or carbonates [14,15].

Although a lot of processes have been used for detergent removal, adsorption is the best-known purification method from economical point of view. In the last decade, adsorption has become a well-established technique for removal of pollutants. In addition, carbon adsorbents, especially the activated carbons (ACs), have proved to be the most effective adsorbents for the purification of water containing pollutants in low concentrations [9,10,18–19].

In the literature, there are some investigations about removal of detergents from water solutions—all the authors investigate adsorption of definite compounds, but they do not study adsorption from mixtures of detergents (as they are present in commercial products).

The objective of the present study is to test the adsorption properties of the obtained carbon adsorbents—synthesized on the base of peach stones, olive stones, natural asphaltite, mixtures from coal tar pitch, and furfural—toward detergents in water solution of commercial washing products. We intend to investigate the adsorption of sulfonic and phenolic compounds (easy detectable by UV spectroscopy), which are present frequently in domestic detergents. The factors influencing the adsorption process will also be investigated. This work is a part of our efforts to develop a technology for complex purification with different types of adsorbents.

2. Materials and methods

2.1. ACs—production and characterization

The ACs samples have been prepared from various raw materials: peach stones, olive stones, natural asphaltite (from Sirnak deposit, Turkey), furfural, and coal tar pitch. The samples of natural asphaltite and peach stones (seeds were removed) were crushed before carbonization. For the preparation of synthetic carbon, the mixtures of coal tar pitch and furfural (in weight proportion 50:50%) were treated with concentrated H_2SO_4 (acid was added by drops to the mixture with continuous stirring) at 120°C until solidification.

All the raw samples (15 g each)—olive stones, crushed peach stones, crushed asphaltite, and the solid product from the mixture of coal tar pitch and furfural—were subjected to pyrolysis up to 550°C, with a heating rate of 10°C/min at atmospheric pressure, in a stainless steel vertical reactor placed in a tube furnace.

The obtained carbonizates were subjected to activation with water vapor at 800°C for 1 h.

We have prepared two samples of AC from peach stones with different surface area.

The porous structure of all ACs was studied by N_2 adsorption at 77 K using Quantachrome NovaWin2 porosimeter.

The content of oxygen-containing functional groups with increasing acidity on the carbon surface was determined applying Boehm's method by neutralization with basic solutions of increasing strength—$NaHCO_3$, Na_2CO_3, NaOH, and EtONa. About 0.5-g portions (± 0.0001 g) of the AC samples were put in contact with 100 mL of 0.05 N of every basic solution in sealed flasks. The suspensions were shaken for at least 16 h, and then filtered. The excess of base remaining in the solution was determined by back-titration using an excess of standard HCl solution [22]. The amount of basic sites was determined with 0.05-N HCl [23]. The procedure is the same as above mentioned, as back-titration of the excess of standard solution HCl was performed by titration with 0.05 N NaOH solution.

AC containing mineral substances and active groups on its surface may alter the pH of liquids to which it is added. To predict its behavior to a certain extent, a standard test has been devised, giving a good approximation of practical conditions. The pH of the solution after boiling of the samples of AC was measured according to the following procedure: 4.0 g of AC sample was weighed into a 250-mL beaker and 100 mL of distilled water was added. The beaker was covered with a watch glass and the mixture was boiled for 5 min. The suspension was set aside and the supernatant liquid was poured off at 60˚C. The decanted solution was cooled down to ambient temperature and the pH value was measured to the nearest 0.1 pH unit.

2.2. *Detergent adsorption measurements*

The adsorption experiments were carried out by using fractions of 0.1 g of AC samples with particle size ~2 mm. The adsorption capacity of the adsorbents toward sulfonic and phenolic compounds in a Bulgarian commercial product, used as washing liquid in domestic and social places, was investigated. The adsorbent portions of 0.1 g were added to the washing liquid samples with volumes 5–40 mL, and then water was added to each sample to reach the volume of 50 mL. All the solutions were shaken for 5–120 min to reach equilibrium.

The amount of the sulfonic compounds were determined at wavelength $220\,cm^{-1}$ and the amount of phenolic compounds at wavelength $269\,cm^{-1}$, using UV spectrophotometer Pharo 300 [24,25].

The following factors affecting the sorption of the investigated detergents from aqueous solution were studied: the adsorbent amount and the contact time.

The effect of carbon amount on the removal of sulfonic compounds was studied using 15 mL of solution from the initial washing liquid detergent. The determinations were performed as follows: portions of 50 mL solution, containing 15 mL washing liquid, were introduced into series of conical flasks, each containing 0.05–1 g portion of carbon adsorbent from peach stones ($800\,m^2\,g^{-1}$). After 2 h, the content of phenolic and sulfonic compounds in the flasks, after filtration through microporous filter paper, was determined spectrophotometrically.

The effect of pH of the solution on the equilibrium adsorption of sulfonic and phenolic compounds was investigated by using 0.1-g carbon adsorbent and 50-mL solution (containing 20 mL washing liquid) with 1-h time of treatment. The initial pH values of the solutions were adjusted with HCl and NaOH.

3. Results and discussion

3.1. *ACs characterization*

The N_2 adsorption isotherms of ACs from peach stones ($510\,m^2\,g^{-1}$) (sample 4), from olive stones (sample 2), from natural asphaltite (sample 1), and from synthetic carbon (sample 3) are presented in Fig. 1. The AC from peach stones and synthetic AC exhibit a type I isotherm in the BDDT classification [26], indicative of microporous materials. The N_2 isotherm curves of ACs from natural asphaltite and from olive stones are characterized with an opening of the knee at low relative pressures. This indicates the development of mesoporosity and a widening of the microporosity in these ACs.

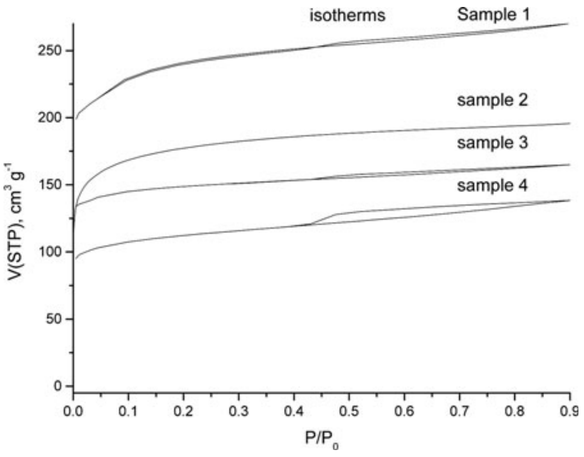

Fig. 1. N_2 adsorption isotherms at 77 K of obtained carbons: sample 1—AC from natural asphaltite; sample 2—AC from olive stones; sample 3—synthetic AC; and sample 4—AC from peach stones.

Table 1
Quantification of oxygen-containing groups on ACs surface (meq g^{-1})

Sample	pH	Acidic surface functional groups				Basic groups
		Carboxyl	Lactonic	Hydroxyl	Carbonyl	
AC from olive stones	8.2	BDL	BDL	0.21	1.69	1.19
AC from peach stones	9.4	BDL	BDL	0.29	1.07	1.04
AC from natural asphaltite	7.6	BDL	BDL	0.80	2.96	4.58
AC from coal tar pitch/furfural	8.1	BDL	BDL	1.25	2.39	0.78

Note: BDL—below detection limits.

The calculated surface areas of the obtained ACs are as follows: synthetic AC—620 $m^2 g^{-1}$; AC from peach stones—510 $m^2 g^{-1}$; AC from olive stones—760 $m^2 g^{-1}$; and AC from natural asphaltite—870 $m^2 g^{-1}$. The yield of the ACs after activation process, depending on the raw materials, is 58, 61, 56, and 50%, respectively. We have to note that the preparation process used has obtained high-yield ACs with relatively developed pore structures.

3.2. Surface oxygen-containing groups

The functional groups on the surface of ACs have strong effect on the adsorption properties. Table 1 shows the content of different oxygen-containing groups on the surface of ACs.

The presence of oxygen-containing functional groups on the surface of ACs is very important. The experimental data show that various oxygen-containing groups with acidic character (hydroxyl and carbonyl groups) and basic groups were detected. The content of hydroxyl groups on the surface of the AC from peach stones is higher than other ACs.

The AC from olive stones has the lowest content of hydroxyl groups. The AC from natural asphaltite exhibits higher content of carbonyl groups and basic groups—this could be due to the high mineral content of this carbon. All ACs have basic character of the surface (pH > 7.0).

3.3. Detergent adsorption measurements

We investigated the adsorption of detergents from solutions containing different volumes of washing liquid—5, 10, 15, 20, 30, and 40 mL. Figs. 2–6 show the detergent adsorption isotherms of the investigated carbons.

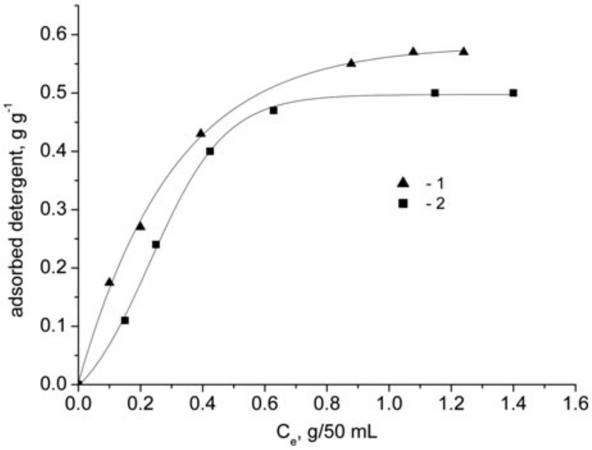

Fig. 2. Adsorption of detergents on AC from furfural and coal tar pitch: 1—sulfonic compounds and 2—phenolic compounds.

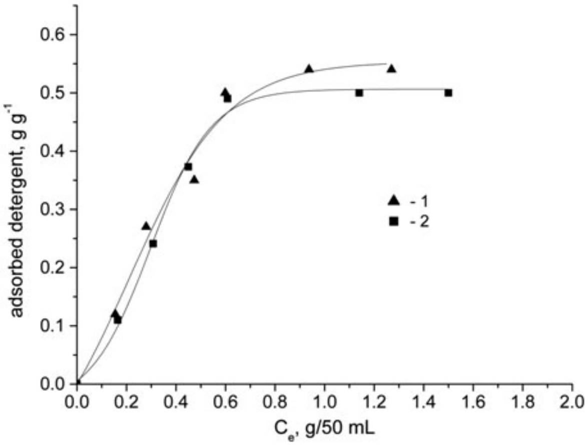

Fig. 3. Adsorption of detergents on AC from peach stones (BET surface area 800 $m^2 g^{-1}$): 1—sulfonic compounds and 2—phenolic compounds.

The shapes of all isotherms belong to type L of Giles classification [27]. This shows that the process of adsorption of detergents can be described by Langmuir theory, which states that the adsorption proceeds via a monolayer formation in the range of concentrations used. The results demonstrate that the ACs obtained from olive stones and ACs from the mixture

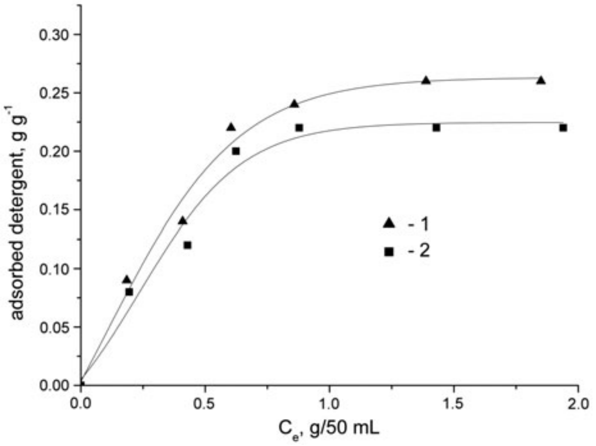

Fig. 4. Adsorption of detergents on AC from peach stones (BET surface area 500 $m^2\,g^{-1}$): 1—sulfonic compounds and 2—phenolic compounds.

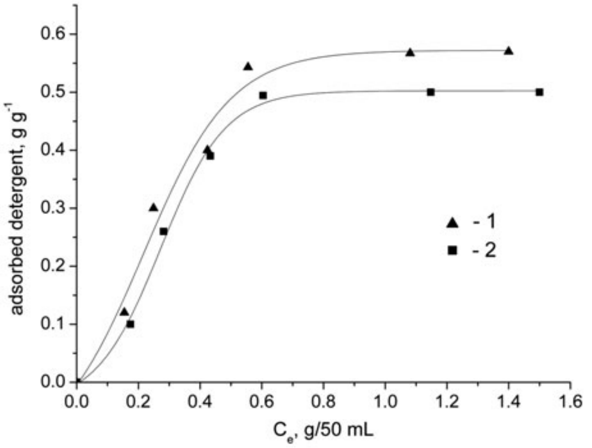

Fig. 5. Adsorption of detergents on AC from olive stones: 1—sulfonic compounds and 2—phenolic compounds.

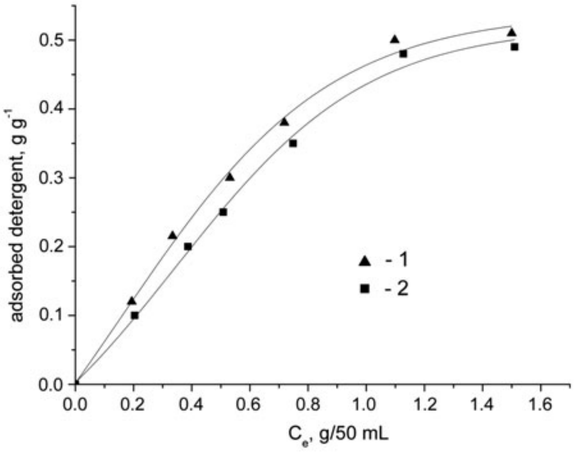

Fig. 6. Adsorption of detergents on AC from natural asphaltite: 1—sulfonic compounds and 2—phenolic compounds.

of furfural and coal tar pitch have the highest values of adsorption capacity.

The experimental data were successfully fit (Fig. 7) to the Langmuir isotherm, expressed by the equation [28]:

$$C_e/Q_e = 1/Q_0 b + C_e/Q_0 \tag{1}$$

where C_e is the equilibrium pollutant concentration remaining in the solution after reaching adsorption–desorption equilibrium ($mg\,L^{-1}$), Q_e is the amount of pollutant bound to the adsorbent ($mg\,g^{-1}$), Q_0 is the maximum amount of the pollutant per unit weight of adsorbent ($mg\,g^{-1}$), and b is a constant related to the affinity of binding sites ($L\,mg^{-1}$).

The Langmuir linear fitting of experimental data for detergent adsorption on AC from natural asphaltite are presented in Fig. 7. The linear plot of C_e/q_e vs. C_e shows that the adsorption obeys Langmuir isotherm model—correlation coefficients are 0.9950 for sulfonic and 0.9935 for phenolic compounds, respectively. This dependence is similar for the other ACs.

It should be underlined that for maximal adsorption capacity toward sulfonic and phenolic compounds for all the investigated samples we have obtained values in the range 0.5–0.6 $g\,g^{-1}$ (with exception of the AC from peach stones, which is distinguished by low surface area). These values are very close to the best adsorption capacity for Norit AC samples (with higher surface area) toward LAS, reported by Schouten et al. [19].

The small differences in the uptake of sulfonic and phenolic compounds for synthetic AC and AC from

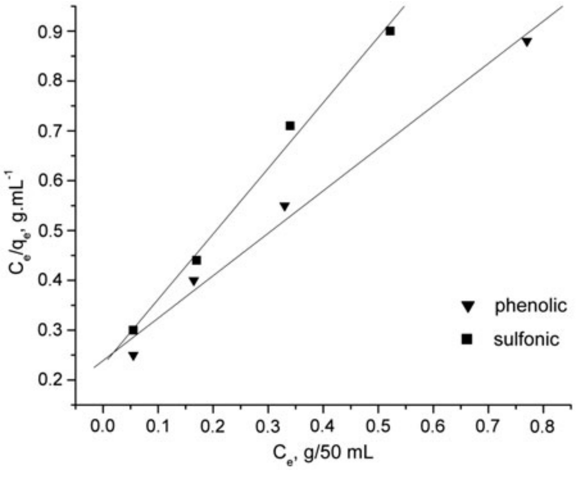

Fig. 7. Langmuir plot for adsorption of sulfonic and phenolic compounds on AC from natural asphaltites.

Turkish asphaltite (distinguished with the highest BET surface area) confirms that the adsorption does not exclusively depend on the porosity and surface area; it also depends on the chemical nature of the ACs, outlining the importance of the affinity of the adsorbate ions toward the surface of the adsorbent.

It is noteworthy that despite its moderate porosity development, AC prepared from mixture of furfural and coal tar pitch has high amount of oxygen-containing groups on the surface and this AC presents adequate adsorption capacity toward sulfonic and phenolic compounds, comparable to those of other carbons with higher surface areas (Figs. 2–6). This indicates that the determining factors for the adsorption properties of the samples are the porous structure and the chemical character of the surface. We have to note the considerably high equilibrium concentration of saturation of the surface of the AC from natural asphaltite (Fig. 6)—this may be due to the high content of mineral components with basic character, which could react with phenolic and sulfonic compounds.

Fig. 8 shows the effect of time of treatment on the removal of sulfonic compounds by AC from peach stones (surface area 800 $m^2 g^{-1}$). Data show that the removal of sulfonic compounds increases with time and attains equilibrium in 30 min for all initial concentrations.

Adsorption of sulfonic compounds increases sharply for a short time and enhances slowly and gradually when equilibrium is approaching. This behavior can be attributed to the decrease in the number of available sites on the carbon surface as the adsorption proceeds. The plots show that the amount of sulfonic compounds adsorbed ($g g^{-1}$) change gradually—this is represented by smooth and continuous curves, leading to saturation, which suggests the possibility of the formation of monolayer coverage of sulfonic compounds on the surface of the carbon adsorbent. The kinetic curves of the removal of sulfonic and phenolic compounds for all the samples are similar to those found in Fig. 8.

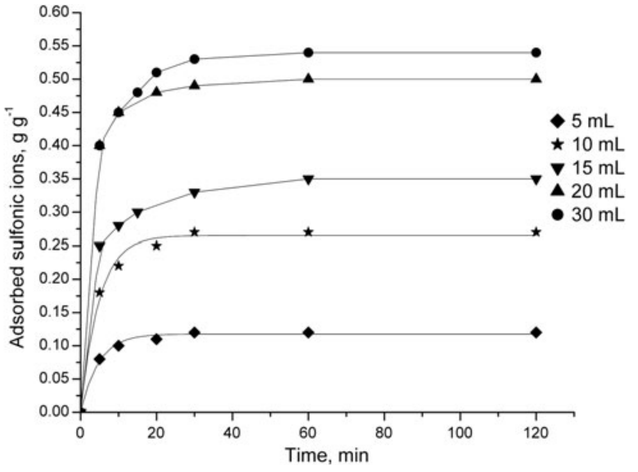

Fig. 8. Effect of contact time on adsorption at different concentrations (5–30 mL liquid detergent in 50 mL) of sulfonic compounds on the AC prepared from peach stones (BET surface area 800 $m^2 g^{-1}$).

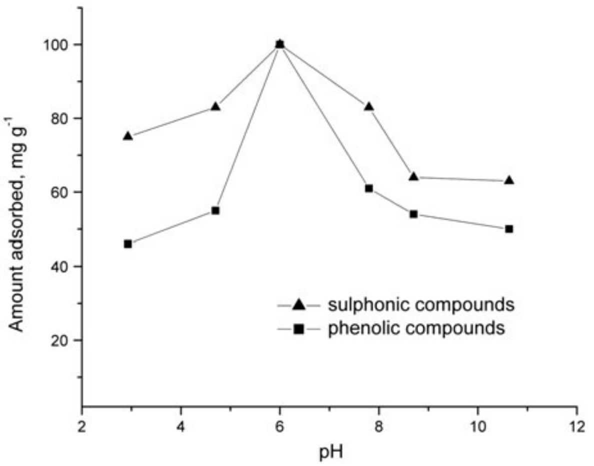

Fig. 9. Effect of pH on the retention of sulfonic and phenolic compounds on the AC prepared from peach stones (800 $m^2 g^{-1}$) from 50 mL solution (containing 20-mL washing liquid).

3.4. Effect of pH

pH of the solution is one of the key factors that control the adsorption process, since it influences the electrostatic interactions between the adsorbent and the adsorbate. The adsorption of sulfonic and phenolic compounds, as a function of pH of the solution, was studied using AC from peach stones (800 $m^2 g^{-1}$) over a pH range of 2–12 units (Fig. 9).

The aimed pH value is obtained by adding adequate amounts of NaOH or HCl diluted solutions to the initial non-buffered solution containing the sulfonic and phenolic compounds. The uptake of both compounds was found to be maximal at pH 6–7. As expected, these results confirm that both compounds are preferentially adsorbed in their neutral form and that the effect of pH of the solution seems to depend to a large extent on the nature of the adsorbent [29].

For both pollutants, the amount adsorbed appeared to be much altered at acidic pH (below 6). As the pH increases, the surface of the ACs is being negatively charged (the amount of negative charges becomes predominant on the carbon surface) until reaching solution $pH > pH_{PZC}$. At this point, the fall in the uptake is probably due to the repulsive interactions that appear between the anionic form of the adsorbates and the charges on the carbon surfaces. Other possible reason is the competitive adsorption between sulfonic/phenolic and chlorine ions (probably present as impurities) which hinders detergent uptake.

These results also explain why the affinity of the sulfonic compounds is higher for AC from peach stones (800 m^2/g).

3.5. Influence of the carbon amount on the adsorption process

The influence of different amounts (0.05–1 g/50 mL solution) of AC from peach stones (surface area 800 $m^2 g^{-1}$) on the removal of sulfonic compounds at fixed concentration (50-mL solution containing 15 mL washing liquid) is shown in Fig. 10.

The increase of AC amount leads to an enhancement of percent removal of sulfonic compounds only for the range 0.05–0.10 g of AC. However, increasing of carbon adsorbent dose in the range 0.1–1 g does not affect the adsorption process.

When the amount of carbon adsorbent is 0.1 g, most probably a monolayer coverage of detergent molecules on the carbon surface is formed, thus hindering further adsorption due to the absence of accessible active sites.

The dependence of sulfonic compounds adsorption on the carbon amount is presented in Fig. 10 and is similar in the case of phenolic compounds.

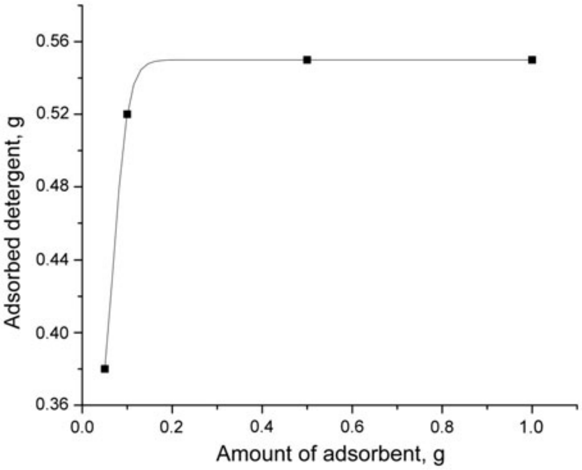

Fig. 10. Effect of amount of the adsorbent (AC prepared from peach stones with BET surface area 800 $m^2 g^{-1}$) on the adsorption of sulfonates from 50-mL solution.

4. Conclusions

The results reported in this work show that ACs obtained from agricultural by-products (peach stones and olive stones), from natural asphaltite, and from the mixture of coal tar pitch and furfural (synthetic AC) exhibit good adsorption activity toward phenolic and sulfonic compounds in aquatic solution.

The adsorption capacity of the ACs toward phenolic and sulfonic compounds depends on their porous parameters and surface chemistry, the latter governing the retention mechanism. Our results outlined the importance of the carbon surface chemistry for the removal of aromatic compounds. The effect of basic/acidic nature of the surface functionalities should also be taken into account.

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