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Possibilities of using the aspen poplar seeds (*Populus tremula* L.) for the purpose of removing monoaromatic hydrocarbons from an aqueous solution

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ABSTRACT

Sorption of oil-related products (including mainly the propellants) is the very basic process that counteracts spreading these types of pollution into environment. Plenty of synthetic substances are used as sorbents for binding organic compounds (including the monoaromatic hydrocarbons) both from the surface and underground waters. The aim of this paper is to present results of the research on the possibilities of using the aspen poplar (*Populus tremula* L.) seeds as a sorbent of monoaromatic hydrocarbons from an aqueous solution. In order to increase sorption capacity, the seeds biomass was submitted for the process of mercerizing in diversified time and temperature in water and the NaOH solution. The removal of benzene, toulene, ethylbenzene, *o*-xylene, *m*-xylene, and cumene was carried out by means of the "batch method". All the conducted experiments have shown a high sorption level of the analyzed pollutions from an aqueous solution. The best sorptive qualities appeared in the seeds drenched in water for 15 d (G) and 14.9% more absorbed hydrocarbons in comparison with the control sample and the smallest sorption— seeds drenched in distilled water for an hour in the temperature of 80°C (H). The process of the seeds mercerizing, conducted with the use of hot water, appeared to be cumbersome, but with the use of NaOH it provided positive effects only after 4 h of process. Two-week seeds mercerization in water of a temperature 20°C (G) is actually the most time-consuming, but at the same time absorbs the least amounts of energy and material, therefore is the most effective one too.

Keywords: Sorption; Aspen poplar seeds; Mercerization; Aromatic hydrocarbons; BTEX

1. Introduction

In order to limit the negative effects of gas oil or mazut spillage, the usage of tankers that serve for their transport ought to be particularly careful. Nonetheless, as a result of catastrophes caused by terrestrial and marine movement, an accidental overflow at petrol reloading stations, as well as damage made on transfer lines, the spillages pose a serious danger, causing waters degradation and soil that are used for agricultural purposes. In this case, the oil-related pollution sorbents find a really wide range of usage here [1–6]. Especially important is the problem with hydrocarbons easily soluble in water, because a sorbent has to bind only organic compounds but not water [7].

The effectiveness of sorption depends on the adsorbent type that is used (mainly of its active surface, amount, and size of the pores), the adsorbent concentration, temperature, the contact time of the adsorbate and the adsorbant, as well as their reciprocal affinity. The most commonly used adsorbents are activated carbon, zeolites, colloidal silicon dioxides, aluminogel, metal oxide, fibrous materials of the natural origin, and the synthetic cross-link polymers [8]. A big number

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of sorbents can be regenerated through abstraction (decomposition) of the adsorbate molecules, due to which they can be reused. Nevertheless, in most cases, a waste sorbent has to be incapacitated [9–11].

Fibrous synthetic materials, used as sorbents, are mainly the products made from polyvinyl chloride or polystyrene. Their sorption capacity is huge and exceeds 100 g of the oil-related product per 1 g of sorbent (1,000%). Their neutralization is possible in the incineration of hazardous waste, due to which energy can be regained [12]. All in all, other authors point at the possibility of removing the absorbed hydrocarbons, for instance, by means of impressing or sluicing them with hexane, therefore a particular sorbent can be used once more [13].

The appliance of natural fibrous sorbents is usually limited to the high-ground peat or wasted woodchips. Waste natural resources (e.g., straw/hay) can be also used as fibrous sorbent. The removal mechanism is based on adsorption and absorption processes. Adsorption is in general restricted to the surface, related to chemical structure of straw tissues. Absorption is an interpenetration of sorbed substance and mostly depends on microstructure of the straw stalk [14]. Dissolved organic compounds (hydrocarbons) are extremely difficult to remove but at the same time using traditional sorbents is really expensive. The suggested aspen poplar seeds that are released after its finished process of blossoming are especially problematic in the urban environment. Waste character, nanotube structure of seeds needles, high hydrophobicity, and availability in many places cause a possibility of using them in various climatic conditions as a cheap and accessible hydrophobic sorbent [7]. Vegetable fibers have extremely low density and they are a natural part of environment, so they could be an interesting alternative for synthetic polymers in oil spills removal [15]. The aim of the research was to attempt to use the aspen poplar seeds for sorption of the monoaromatic hydrocarbons from an aqueous solution. For optimal price and sorption effectiveness estimation, different mercerization procedures were analyzed.

2. Materials and methods

The monoaromatic hydrocarbons sorption (benzene, toulene, ethylbenzene, *o*-xylene, *p*-xylene, and cumene, characteristics of which have been put in Table 1), was conducted through the "batch"-type experiments in the room temperature (20°C±2°C). The sorbents applied in the research were six types of materials, produced in the process of mercerization of the aspen poplar seeds biomass. What is more, all the reagents had a degree of purity appropriate to the chromatographic analysis.

2.1. The samples preparation

The seed samples were collected, cleaned off from the mechanical pollutions, and dried to a constant mass of 90°C. The process of mercerization was carried out in cold and hot conditions, due to which the following types of seeds biomass have been extracted:

S—blank test—without mercerization
H—drenching in the distilled water of temperature 80°C for 60 min
W—drenching in the distilled water of a temperature 80°C for 240 min [16]
N—drenching in the 5% solution NaOH of a temperature 80°C for 240 min [17]
Na—drenching in the 5% solution NaOH of a temperature 20°C for 2 d [18]
G—drenching in the stand water supply of a temperature 20°C for 15 d [14]

Testing over the hydrocarbons extracted from a water solution was carried out in glass vessels closed with microsection. The water solution was prepared through the process of dissolving hydrocarbons, mixed in equal proportions (500 μL): benzene (B), toluene (T), ethylbenzene (E), *o*-xylene (O), *p*-xylene (P), and cumene (C) in 1,000 $cm^{3,}$ of redistilled water containing ethylene glycol in the amount of 5 cm^3/dm^3. The characteristics of the tested compounds

Table 1
Basic parameters of investigated compounds

Compound CAS number	Molar mass (g/mol)	Water solubility (20°C) (mg/dm^3)	Density (g/cm^3)	Concentration in adsorbate (mg/dm^3)
Benzene 71-43-2	78.12	1,780	0.876	320.4
Toluene 108-88-3	92.15	500	0.867	141.5
Ethylbenzene 100-41-4	106.18	150	0.867	45.7
p-Xylene 1330-20-7	106.18	180	0.861	44.6
o-Xylene 108-38-3	106.18	170	0.897	51.3
Cumene 98-82-8	120.19	50	0.862	16.6

Concentration in adsorbate—this study.

have been presented in Table 1. The obtained water solution was kept in the temperature of 20°C without any light access. Each time about 0.15 g of the aspen poplar seeds were directly weighed out to the vessels. The proportion of sorbent to water solution was 1:250. Amount of water solution was calculated to obtain exactly 1:250 proportion in each experimental vessel. The sorption time was 15, 30, 60, 120, 240, and 360 min. After this time, the samples with the solution were taken and next submitted for extraction, by means of dichloromethane, through shaking them in laboratory glasses (4 cm^3) made from dark glass and cranked up with a teflon cap. Eluate was dried with Na_2SO_4, which was previously dried in 130°C. Each of the experiments was conducted in three independent repetitions. Aromatic hydrocarbons were marked in untreated extracts (or in blank samples) by the gas chromatography–flame ionization detection method, with the usage of a capillary column SPB-1701 of the length of 30 m, by constant helium flow, through a column in the amount of 1 cm^3/min. The injector temperature was 250°C and the detector's one was 280°C. The temperature program of the oven began at 40°C kept for 2 min and then the temperature rose in the rate of 7°C/min up to 100°C. The final temperature of the program (100°C) was kept for 1 min. The detection limit was 2.0–3.5 μg for a single compound. In order to make the calibration curve, the LGC Promochem formulas were used with an initial concentration of 200 μg/mL of each single compound. Recovery of single compound varied from 89%–92% (cumene) to 68%–75% (benzene). The total sorption capacity was assessed by the weighing method [18,19]. Two mathematical models were used to describe the kinetics: Lagergren's and Ho–McKay's [8]. The statistical calculation (regression analysis) was conducted by means of the Statistica 12 package.

3. Results and discussion

The hydrocarbons submitted for the research are considered to be difficult to dissolve in water and usually perceived as a group of compounds which create fraction light non-aqueous phase liquid after being released to water environment. However, the qualities of hydrocarbons make them possible to migrate to the water phase (Table 1). The concentrations of the extracted analyzed compounds (despite of the ethylene glycol appliance) were lower than the maximum ones, possible to be obtained for water of the temperature of 20°C. When consulting the dissolubility of the particular compounds, it needs to be assumed that they were dissolved in water and did not exist in the emulsion state. Mercerization was shown as main chemical treatment which was used to improve the mechanical performance of fibers—also for improve hydrocarbons sorption capacity [17]. The analyzed sorbents—aspen poplar seeds obtained from a homogenous material—were different in terms of their apparent density and maximum sorption capacity. The greatest apparent density (Table 2) was noted down for the N and Na materials—submitted for the NaOH activity and the lowest one for G and S, which is characteristic for seeds propagated by wind and of similar density of the sisal and cotton fibers [15,20]. Apparent density was increasing together with the intensification of the mercerization process in the series G < S < H < W < N < Na. The maximum sorption capacity (44.47 g/g) was marked for the S material; however, the G seeds proved twofold lower total capacity, despite its similar apparent density. That can be caused by its partial disintegration of waxen fibers surface during the process of the oxygen-free mercerization that lasted for 15 d or degradation of cellulose fibers bunches. In the analogical research by other authors who studied the sorption of gas–oil on the black poplar (*Populus nigra* L.) seeds, 100 g/g of the total sorption capacity was obtained, indicating that they can be used for the purpose of removing the bottling of oil-related products at the same time [7]. Low density of the seeds analyzed here can lead to certain problems when using them for sorption. The ability to lift makes the applied material drift under the wind influence [7,11,21]. In case of sorbents use for clean-up in areas where water is not involved, the best solution is S material due to maximum oil capacity.

The verified, studied amounts of the total sorption capacity were higher for the expanded perlite, cellulose fibers and the polypropylene sorbent which was absorbing the greatest amount of an oil-related product, however still four times smaller than the noted capacity of the aspen poplar seeds [18]. Fibrous materials of vegetative origin (corn and soya waste), after its mechanical working and the process of mercerizing with sodium hydroxide, become a good sorbent, which sorption capacity for oil-burning products amounts to 450%–500% m/m [12]. In case of own studies, the aspen poplar seeds mercerization with NaOH showed the total sorption capacity between 321%–370%, which was at the same time the lowest and the highest value for the S and H seeds (4,014%–4,447%), so that it can be claimed that NaOH can be used only for dense materials (e.g., corn stem). Nevertheless, using this method of processing does not increase the natural capacities of fluffy materials, for instance, of the aspen poplar seeds. Similar amounts (40–50 g/g) of the absorbed oil-based products have been stated when kapok fibers were applied (*Ceiba pentandra* L.) [19]. Much higher amounts (nearly 100 and 85 g/g 24h each) have been noted down when silk fibers were used as a sorbent, but their usage is strictly dependent on the accessibility of wastes coming from textiles [15].

Table 2
Characteristic of sorbents used in experiments

Weed sample	S	H	W	N	Na	G
Bulk density (g/dm^3)	1.666 (0.036)	1.681 (0.128)	1.998 (0.110)	2.292 (0.572)	2.308 (0.129)	1.632 (0.078)
Sorption capacity (g/g)	44.47	40.14	36.74	3.207	3.700	21.87
Mass of adsorbed hydrocarbons from solution t = 360 min (mg/g)	95.8	94.4	97.2	100.1	98.6	110.1
Sorption change (%)	100	98.5	101.5	104.5	102.9	114.9

In the study carried out by the static method (batch), it has been shown that particular amount of the absorbed monoaromatic pollutions is dependent on the time of contact between polluted water and a sorbent, as well as on the type of the mercerization method applied. Notwithstanding, in all the cases, the process of sorption was flowing quite slowly and no balanced concentration has been noted down, as far as the studied cases are concerned. Sorption speed (k1 and k2 factors) calculated with Lagergren's and Ho–McKay's models show predominance of G and N-types materials in case of all analyzed compounds (Tables 3 and 4) with high correlation factors (over 0.98) for pseudo-second order equation. However the highest total capacity was noted for S material, G material was the best effective in BTEX removal from aqueous solution. The biggest amount (110.1 mg/g) of hydrocarbons was absorbed by the G material and the lowest one (94.4 mg/g) by the H material. Probably the high sorption effectiveness of G type was caused by microorganisms which grown on the aspen seeds during 15 d drenching in water. Sorption in the unmodified S material flew in a similar way to the modified one, which means submitted for various mercerization types (Figs. 1(a)–(f)). In case of all the tested seed types, the benzene sorption was flowing most powerfully and toluene was on the second place here. The sorption isotherms for ethylbenzene, *o*-xylene, and *p*-xylene were very similar—especially when the S, W, and H materials were taken into account, which proves a little influence of the hot water mercerization in times of 60 and 240 min. Cumene appeared to be the slowest compound absorbed. The intensity of sorption was proportional to the concentration of the compounds present in the adsorbate. Even after 360 min, no desorption was noted down in any of the analyzed cases. All the materials submitted for the research (independently on the mercerization method) absorbed *o*-xylene and benzene in the least intensive way. A low amount of the absorbed benzene (even below 50% and a longer contact time—e.g., 24 h) is a natural casus, however a little *o*-xylene sorption results probably from a poor affinity of a compound to the seeds surface [22]. The amount of the compounds absorbed from a solution was increasing within a decrease in their dissolubility in water (Table 5). *o*-Xylene constitutes an exception here, which was absorbed on the level of 49.8%–58.8%, despite of its poor dissolubility.

The G material was absorbing benzene a little less intensively than raw seeds, however each next hydrocarbon was absorbed more intensively and finally this mercerization type occurred to be the most effective method when talking about the sorption capacity increase. An essential number of the hydrocarbons absorbed from a water solution by means of tested seeds can be explained by one of the lowest fibers diameter (about 9 μm) as well as by their built in the form of a nanotube [7]. In a similar experiment, conducted with montmorillonite as a sorbent [23], a sorption of the BTEX mixture was extracted on a level of 19 mg/g, which stands for only 20% of the amount extracted in the own studies. The optimal sorption time should be prolonged in view of the sorptive abilities of the tested seeds, both the mercerized and the raw ones. Their significant hydrophobicity level is a kind of problem here however, what makes the contact between a sorbent and an adsorbate quite a difficult one. The tested hydrocarbons were absorbed in considerable amounts, exceeding even the effects attained from other authors in the usage of a ground peat, organo-silicate, and polymer and montmorillonite [11,22,23]. The regression analysis, that was conducted, has shown a high correlation ($p < 0.01$) between the BTEX sorption isotherms noted down for differently mercerized aspen poplar seeds. It is actually the certification of minor changes in the sorption of monoaromatic hydrocarbons dissolved in water by means of seeds, submitted for mercerization of differential methods.

Table 3
Pseudo-first-order rate constant k1 for sorption of BTEX on aspen poplar seeds

	S	H	W	N	Na	G
Benzene	0.0294	0.0263	0.0262	0.0280	0.0250	0.0287
Toluene	0.0257	0.0248	0.0262	0.0250	0.0240	0.0248
Ethylbenzene	0.0267	0.0251	0.0256	0.0311	0.0236	0.0230
p-Xylene	0.0222	0.0219	0.0331	0.0220	0.0220	0.0234
o-Xylene	0.0219	0.0215	0.0222	0.0225	0.0220	0.0258
Cumene	0.0217	0.0223	0.0194	0.0239	0.0195	0.0205

Table 5
Capacity of BTEX hydrocarbons removed from solution on time $t = 360$ (%)

	S	H	W	N	Na	G
Benzene	60.9	59.7	61.0	54.8	56.8	59.2
Toluene	62.5	61.7	62.6	53.6	56.2	62.9
Ethylbenzene	66.4	66.2	66.7	60.8	63.1	66.9
p-Xylene	65.0	64.6	64.9	59.3	61.8	65.8
o-Xylene	57.4	56.9	58.2	49.8	53.0	58.8
Cumene	72.9	73.3	73.3	72.3	75.3	76.4

Table 4
Pseudo-second-order rate constant k2 for sorption of BTEX on aspen poplar seeds

	S	H	W	N	Na	G
Benzene	3.20E-04	2.00E-06	1.50E-06	1.30E-06	1.10E-06	1.50E-06
Toluene	1.50E-04	3.30E-06	2.80E-06	3.60E-06	1.90E-06	2.50E-06
Ethylbenzene	1.29E-05	1.29E-05	1.05E-05	8.30E-06	6.70E-06	7.70E-06
p-Xylene	1.18E-05	1.29E-05	1.08E-05	7.10E-06	6.70E-06	6.70E-06
o-Xylene	1.18E-05	1.25E-05	1.03E-05	8.30E-06	5.30E-06	7.10E-06
Cumene	2.35E-05	2.91E-05	2.42E-05	4.50E-05	3.60E-05	4.09E-05

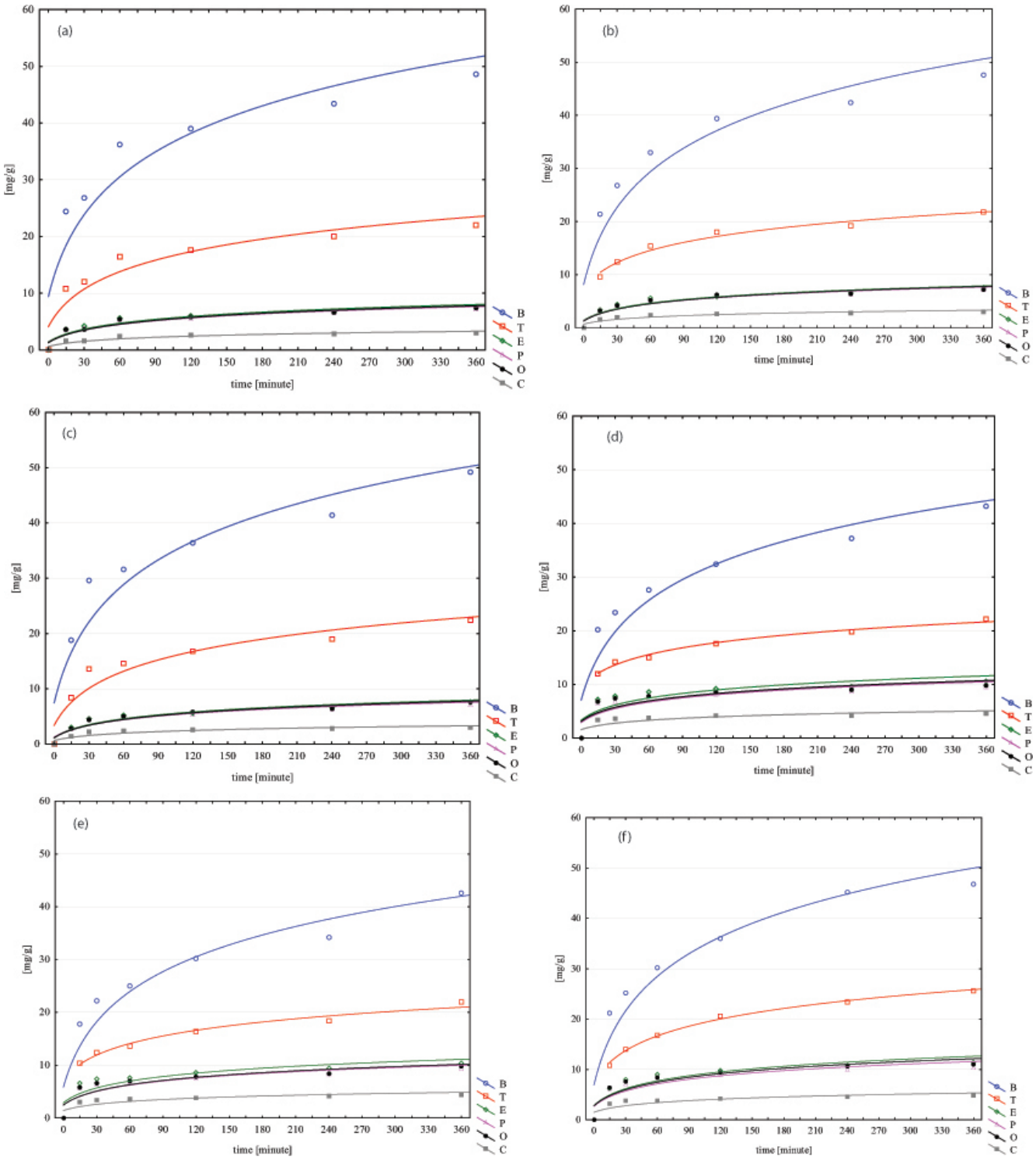

Fig. 1. (a) BTEX sorption on S weeds, (b) BTEX sorption on H weeds, (c) BTEX sorption on W weeds, (d) BTEX sorption on N weeds, (e) BTEX sorption on Na weeds, and (f) BTEX sorption on G weeds.

4. Conclusions

As a result of the conducted laboratory experiment, mixed sorption features of mercerized aspen poplar seeds (*Populus tremula* L.) have been verified. The sorbents which underwent the research were leading to a significant decline of the aliphatic hydrocarbons dissolved in water, which can stand for their usage, as means of limiting the effects of penetration of the oil-related pollutions into environment. In dependence on the mercerization method applied, from 98.5% to 114.9% have been attained, in proportion to the sorption amount of seeds, which were not submitted for

mercerization. The weakest sorption features were shown by the W material and the best ones by the G material, which points at the possibility of low cost of seeds mercerization, through drenching them in water in the oxygen-free conditions. An additional advantage, supporting the idea of applying the analyzed material G as a sorbent, is a low price of mercerization, as well as the possibility of using a cheap source of fibrous organic matter. After 6 h contact with the G material, nearly 60% of easily dissoluble benzene and over 76% of cumene were removed. The amount of the absorbed substances can be ranged in the following way: benzene > toluene > ethylbenzene > *o*-xylene > *p*-xylene > cumene. Nevertheless, a relevant level of hydrophobicity of the analyzed materials inhibits the contact of the seeds surface with an adsorbate, extending time of the process in this way.

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