Flame synthesis of superhydrophobic carbon surfaces

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This paper presents the study of soot formation process having superhydrophobic properties by combustion gaseous hydrocarbons and waste oil. It was synthesized soot through flame synthesis on silicon substrate by combustion propan-butan mixture and waste oil.

The hydrophobicity is characterized through the contact angle for water droplets placed on the surface. The surface morphology of the nanoparticles is obtained from SEM images. The morphology and hydrohobicity of the nanostructured surfaces depends upon the deposition, which differs at various flame locations. It was determined the optimum flame location for the synthesis and deposition of surface carbon nanostructures that lead to maximum hydrophobicity. Currently, the construction market needs a quality, durable, and most importantly, available technologies of production of waterproofing materials. Creating highly reliable waterproofing materials with nanostructures will solve the problem of the negative impact of a moist environment and corrosive groundwater. As nanostructured material may be soot with superhydrophobic properties obtained under certain conditions by combustion of hydrocarbon fuels and waste oils. Obtained soot was used to create hydrophobic sand.

Moreover it was determined effect of hydrophobic sand on the growth of amaranth and sunflower.

Introduction

Traditionally understood hydrophobic coating materials, the contact angle with water and which are aqueous solutions of higher than 90^0. A feature of such materials is the instability of the thin layers of water wetting on surfaces thereof. Hydrophobicity a property which is determined not so much in the overall characteristics of the material, structure and properties as a surface layer a few nanometers thick. Therefore, to create hydrophobic coatings and materials primarily requires analysis of the processes take place in nanoscale systems, and it is - a typical nanotehnology.

Practical interest are highly hydrophobic materials with contact angles of water leakage $>120^0$. Notable among such materials occupy superhydrophobic materials and coatings characterized by high contact angles ($>150^0$) and small angle inclination of the surface horizon [1].

Superhydrophobic surfaces have attracted great interest, not only because their design involves exciting multidisciplinary scientifc challenges, but also due to their great potential for industrial applications, exemplified by anti-icing, antifouling, anti-fogging, anti-corrosion and in promotion of dropwise condensation. Significant progress has been achieved in understanding the principles of hydrophobicity, mostly inspired by surface designs found in nature, ranging from plant leaves to the skin of fish or other swimming organisms, the performance of which is tailored by evolution in their natural environments. However, the majority of man-made surfaces employ readily processable albeit sensitive materials, which cannot survive outside a very limited range of well controlled environments, prohibiting their potential usability [2].

There has been prolific research on the applications of the unique features of a superhydrophobic surface. Because water drops on a superhydrophobic surface can roll aroun freely, the drops can detach and remove dust from a surface. This self-cleaning effect could be applied to a surface to keep it dust free, such as on the outer wall of a skyscraper or on soalr cell panels. There are also many applications for drop control on a superhydrophobic surface because complications associated with contact between a liquid drop and solid surface can be avoided on

a superhydrophobic surface. Examples of drop control include open-surface digital microfluidics and a droplet guiding system. Shear stress on the aqueous fluid flow caused by a solid wall can be significantly reduced with a superhydrophobic surface due to the small contact area of the aqueous fluid that is in direct contact with a solid wall. Based on this principle, the drag reduction effect of a superhydrophobic surface has been studied. There has also been work to develop fabrics free from stains or water/oil separation systems that apply a superhydrophobic surface.

To achieve a superhydrophobic surface, two requirements must be satisfied. Firstly, the surface must be very rough. A hierarchical moprhology with micron-to-nanoscale roughness is more desirable. Secondly, the material must have a low surface energy. When these two conditions are satisfied, a water droplet on the surface corresponds to the Cassie wetting state where complete contact between a liquid and solid becomes unstable in terms of energy and micro/nano-sized gaps are formed between the liquid and solid [3].

Superhydrophobic surfaces are generally expressed by the contact angle between a water droplet and the solid surface. Wenzel's early works and later Cassie-Baxter's work defined the importance of surface roughness and heterogeneity, which are now recognized as key parameters in the wettability of hydrophobic surfaces [4, 5].

Carbon nanostructure deposition from flames can be used to modify hydrophilic surfaces so that they become superhydrophobic. When carbon nanostructures are deposited upon a surface, they create a superhydrophobic topology that facilitates a water droplet to sit on the asperities of the roughness while air is entrapped in the structure below.

The resulting coating with hydrophobic properties is relevant area of research. To change the wetting of the surface is often used amorphous carbon [6]. The technique of rapid deposition of the carbon layer is proposed I.K. Puri [7]. This method allows to obtain the synthesis of large aggregates of individual particles (nanobeads) with sizes ranging from 20 nm to 50 [8], but the synthesis is possible, and larger particles. This method was used burning acetylene flame (700^0 C) and the catalyst - Nickel [9]. As the substrate to create a layer of carbon used silicon plate. The silicon substrate was exposed to flame at a distance of 10 mm at different exposures of time. Irrespective of the method of processing the surface facing the flame synthesized on carbon nanostructures are identical to [7].

Pozzato and others [10] found that when water drops form a very large contact angle (150^0), allows the hydrophobicity of the particles to slide easily drop from the surface. TEM image of Si substrate subjected to treatment for 5 minutes, shows that the carbon nanoparticles (nanobeads) are connected with each other. Since the deposition process for the catalytic nanobeads not been suggested that growth is the result of fuel pyrolysis in gas phase. The pyrolysis products are transported in the layer adjacent to the relatively cool surface Si, where they condense and form nanobeads. Pyrolysis is a determining factor in the formation of carbon, while is flame oxidation occurs.

Sharon, etc. [11], which are among the first synthesis of carbon nanoparticles researchers have shown that it is desirable to have a source of carbon, which contains a combination of the sp^2 and sp^3 communication structure. They showed that the sources with sp^2 orbital, such as graphite, hinders the formation of spherical structures. Camphor pyrolysis vapors in 1000^0C under argon were synthesized spongy carbon nanostructure. As catalist it was used ferrocene. Thus were obtained the solid and hollow carbon particles of two sizes of ≈ 250 nm and 500-800 nm. They consisted of amorphous layers that have been coated with graphite shells. Spectral analysis of electron energy loss (EEL) has shown that the interior of the particles (beads) was amorphous. X-ray analysis of the different spectra shows that peripheral part nanobeads contains 98.1% by volume of carbon [11].

One of the materials with low surface energy, which is often used to modify and control surface wettability are amorphous carbon films (AC) [6]. In [12] to obtain superhydrophobic layer consisting of a homogeneous nanobeads carbon, the method of rapid deposition on Si substrate placed in ethylene-air diffusion flame. The resulting carbon particles are

morphologically similar nanobeads carbon synthesized Levesque and his co-workers [8] with the dissociation of acetylene at 700^0C over nickel catalyst nanoclusters.

In [13] were determined the optimal conditions for the formation of hydrophobic surface on a silicon substrate coated on the surface of the ferromagnetic fluid, as well as a foil or mesh of stainless steel, depending on their location in the flame.

Synthesis of hydrophobic soot in flame

For the synthesis of hydrophobic soot in [7, 14-16] applied burner device, the image of which is shown in Fig. 1.
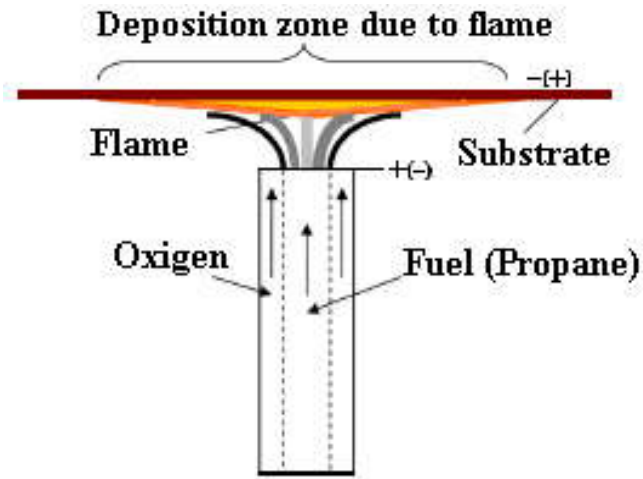

Fig. 1. The scheme for the synthesis hydrophobic soot on a substrate [7, 14-16].

The processes of hydrophobic soot in diffusion combustion of propane-oxygen mixture. Substrates - 7 cm diameter discs and 1-0,5 mm thick, made of different materials (silicon, nickel and stainless steel) were installed in the flame at a height of 2-3 cm from the matrix burner and the soot deposited upon them. The exposure time was varied in the range 2-10 minutes. A study was conducted of the electric field influence on the formation and properties of the resulting soot surface.

The figure shows the soot deposition process on a substrate (2a) and shows the temperature profile (2b) in the middle part of adjustment of propane-oxygen flame at a rate of diffusion propane - 150 cm^3 / min, and oxygen - 260 cm^3 / min.

a
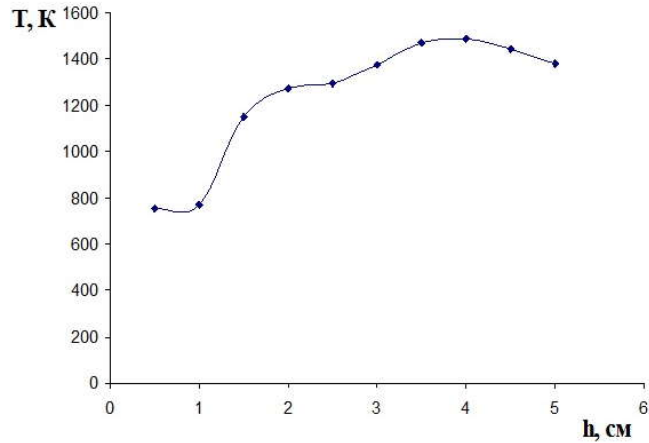
b

Fig. 2. Photography soot deposition process on a substrate (a) and the temperature profile along the height of the middle part of the flame C_3H_8/O_2 (b) [14].

Flame visually can be divided into two zones (Fig. 2b). First - the blue area, which is gradually moving into the red zone. The height of the blue zone is about 1 cm. In this zone the temperature is 770 K. At a distance of 1 to 2 cm from the burner matrix is a sharp rise in temperature, and in the range of 2 to 2.5 cm in its stabilization occurs. Since 2.5 cm temperature rises to the maximum value of 1470 K at a distance of 4 cm from the burner matrix. Above there is a gradual decline in temperature.

It was found that the exposure time of less than 4 minutes on the substrate deposited usual black. The exposure time of more than 4 minutes, resulting in the formation of soot to hydrophobic properties and increase the exposure time of more than 10 minutes has no effect on the improvement of these properties.

On the surface of the substrate is the deposition of soot with an average thickness of 1-1.5 mm. Figure 3 shows a pattern obtained by using a silicon substrate.

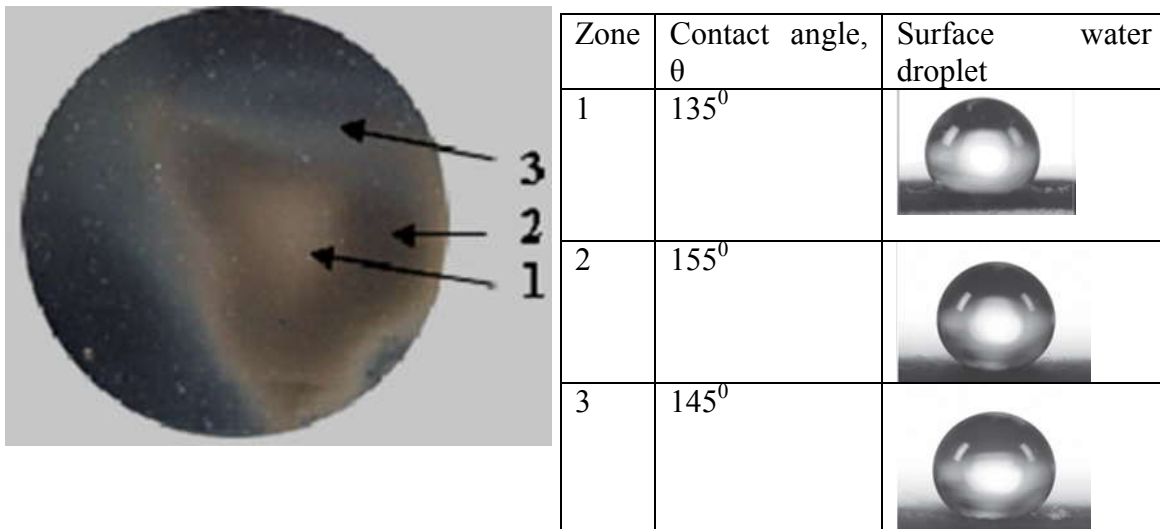| Zone	Contact angle, θ	Surface water droplet
1	135^0	
2	155^0	
3	145^0	

Fig. 3. Sample of soot on the surface of silicon substrate produced by burning of propane-oxygen flame [14]: 1 - the central gray area; 2 – brown zone; 3 - black sooty outer zone

On the surface of the substrate can be visually observed separation of soot deposited on the three zones. It can be seen that the central gray area (1) is surrounded by a brown band (2), which in turn was covered by black sooty outer zone (3). Zonal soot deposits on said surface of the silicon substrate that different regions of the flame soot particles are formed with differing properties. The main cause of this phenomenon is the unevenness of the temperature gradient in the volume of the flame. Also, this dependence can be explained by limiting diffusion of oxidant into the flame: in the middle of the flame richer fuel compared to the edges.

For obtaining large quantities of soot was created a new experimental setup represented in Figure 3. Soot formed in the flame for a certain time (about 6 seconds) was together with the gaseous products of the process in the high-temperature zone. Thereafter, the mixture was cooled gases and soot was separated from the gases in special apparatuses. By the second method, raw materials are burned with burners using a narrow slit, mounted in metal casings. Flat flame was connected with the moving metal surfaces. The time of contact of the flame with the surface is slightly. The precipitated on a metal surface black quickly removed from the area of soot formation. The formation of soot particles can be suspended at a certain level, interrupting the process of its formation. Superhydrophobic properties of soot having applications to create a hydrophobic sand were prepared using the above principle by the deposition of soot particles on a cold surface, placing it at a certain height of the flame. The photo of experimental setup is shown in Figure 4.

Fig. 4. The photo of the experimental setup

The principle of the device is based on the deposition of soot particles from the flame on the surface of iron spinning cylinder. A cylinder made from stainless steel, 12.5 cm diameter 13.5 cm height, the speed of 1/sec, the number of nozzles at the burner is 7 with 2 mm diameter, the flow rate of gaseous feed carbon was 425 - 500 cm^3/min [15].

Figure 5 represents electron micrographs of soot samples obtained by combustion propan-oxygene flame with application and without application electric field.

<div align="center">a   b</div>
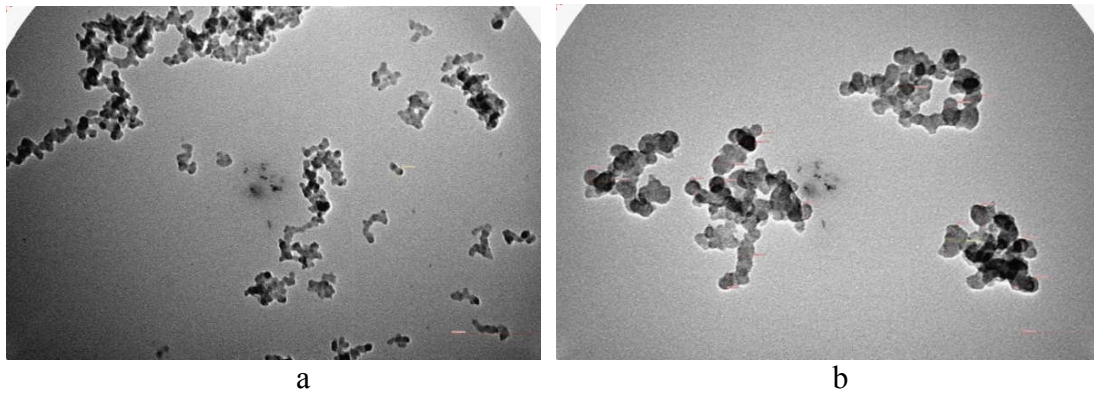
a - with application electric field; b - with application electric field

Fig. 5. SEM images of soot obtained by combustion propan-oxygene flame

The soot particles have spherical shapes with 18-20 nm sizes (with application electric field) chain structures and soot particles have spherical shapes with 20-30 nm sizes (without application electric field) which prove of hydrophobicity of the surface of soot samples.

Synthesis of superhydrophobic soot by combustion waste oil

A number of experimental studies to determine effective soot by burning waste oils were carried out. The raw materials used waste oil from service stations to replace oil cars. Used oil burned using a conventional wick, by impregnating carbon and glass fiber fabric. A silicon (Si) disk is placed 2-4 cm above the burner and exposed to a flame for 4, 6 minutes.

To check the resulting hydrophobic soot was soaked in an ethanol solution and after drying was tested for hydrophobic properties by the method of sitting drop. The results showed that obtained soot by combustion waste oil has a hydrophobic property with contact angle 145-150^0. The experimental research on the production of soot by combustion waste oils showed that the combustion of 100 grams of oil, depending on the conditions can be obtained from 0.5 to 1.5 grams of soot. Extraction of the resulting soot shows a benzene soluble content of the small parts, which indicates non-toxicity of the obtained product.

Figure 4 shows a schematic representation of the experimental setup for the combustion of waste oil, which consists of a burner and a metal substrate.
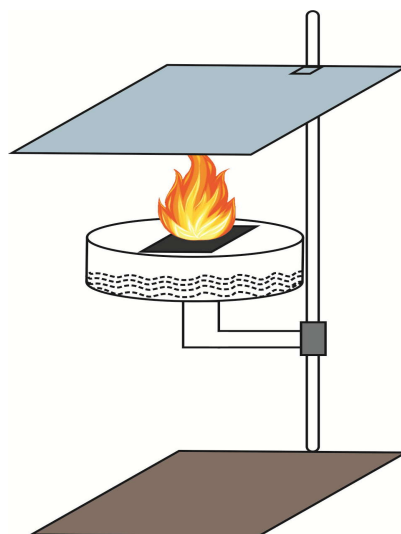

Fig. 4. Scheme of the experimental setup for the combustion of waste oils

The hydrophobic properties of soot depend on the size, shape, granularity and size distribution of individual soot particles. To determine these parameters, the samples are examined using electron microscopy. When an electric field is applied, soot particles have a small diameter spread in the range 10-20 nm. Soot formed from smaller soot particles produce chain structure while larger soot aggregates into irregular shape soot particles. An important parameter influencing the hydrophobicity of a sooty surface is the distance at which the soot is collected from the flame front. The most soot is produced in a propane flame when the substrate is placed 1.8-2.2 cm from the burner.

Also, the resulting samples of hydrophobic soot were investigated by a scanning electron microscope. Figure 5 shows SEM image obtained soot by combustion waste oils.
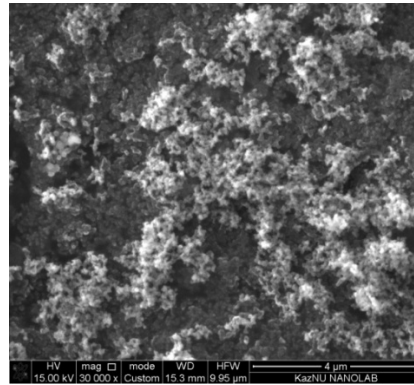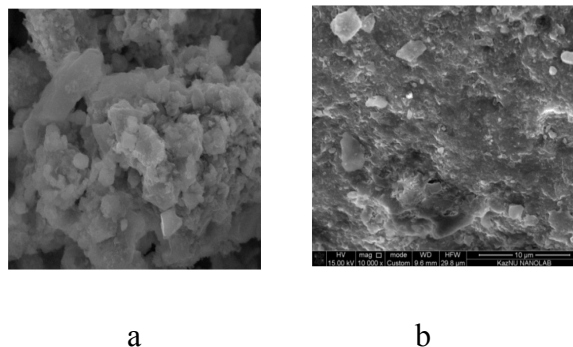

Fig. 5. SEM image of soot obtained by combustion waste oils

Thus, studies have shown that the burning method from the surface of the impregnated carbon cloth or glass cloth allows to obtain soot having high hydrophobic property. In continuation of these works synthesized soot from waste oil was used to create the hydrophobic sand fine and coarse fraction.

Obtained hydrophobic sand was investigated with a scanning electron microscope and element analysis.

Figure 6 shows SEM images of ordinary river sand (a) and the obtained hydrophobic sand based on soot having hydrophobic properties (b).

a   b

a - clean river sand, b - hydrophobic sand obtained on the basis of soot by combustion waste oils

Fig. 6. SEM images of the samples from the coarse fraction of sand

7

Results and Discussion

The results showed that the surface of the soot produced by burning waste oil has a hydrophobic property to the wetting angle 145-150^0, figure 7.

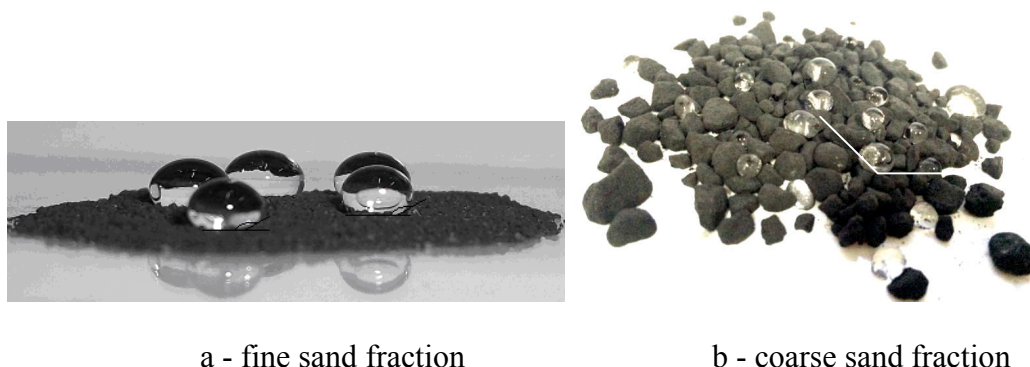a - fine sand fraction   b - coarse sand fraction

Fig. 7. Water droplets on the sooting surface obtained by burning of waste oils

Initial river sand absorbs water instantly until complete wetting. Applied to the surface of the resulting hydrophobic sand water is distributed on the surface in the form of droplets and not absorbed hydrophobic sand until complete evaporation.

Figure 8 shows the results of analysis EDAX hydrophobic sand coated with a polyurethane coating and the hydrophobic soot.

A qualitative assessment of the presence of functional groups on the surface of hydrophobic sand obtained based on hydrophobic soot formed during combustion of waste oils were examined by IR spectroscopy. At the IR spectra of the samples are observed characteristic absorption bands in the frequency range of 463.13; 532.48; 587.60 cm^{-1} correspond to the stretching vibrations of Si-O group. Antisymmetric stretching vibrations ≡S-H contributed to the appearance of the peak at 648.23 cm^{-1} band at 695.10 cm^{-1} corresponds to the Si-C vibrations. Acquisitions at 797.15; 778.71; 725.61 cm^{-1} due to vibrations deferential Si-H groups.
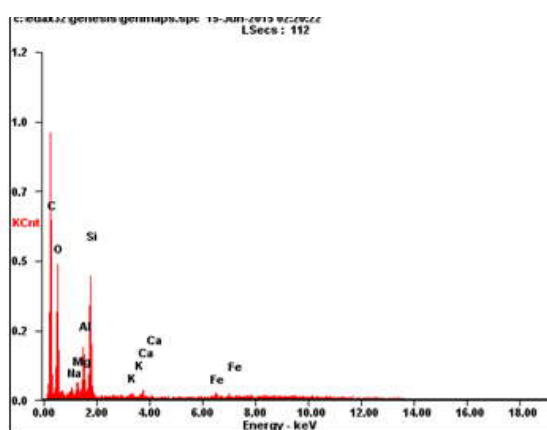
Element	Wt%	At%
CK	58.89	70.20
OK	24.91	22.29
NaK	0.51	0.32
MgK	0.70	0.41
AlK	2.67	1.42
SiK	7.86	4.01
KK	0.70	0.26
CaK	1.38	0.49
FeK	2.36	0.61
Matrix	Correction	ZAF

Fig. 8. EDAX microanalysis of hydrophobic sand

In analyzing the infrared spectrum of the hydrophobic sand was also noted the occurrence of an absorption peak at 1875.05 cm^{-1}, characteristic fluctuations -C = O group and stripes on 2346.67 cm^{-1}, P-H group. The IR spectra of the samples are observed characteristic absorption bands C–H (2850,71 cm^{-1}), и -OH (2919,45 cm^{-1}, 3428,36 cm^{-1}).

The effect of hydrophobic sand on the growth of amaranth and sunflower was determined in the following experiments. The pots for growing the plants were filled by the mixture of vermiculite / river sand (1:1) / hydrophobic sand (10%) by weight. Settled water without chlorine was poured into the pots in the usual mode. Germination of seeds, height and habitus of plants were analyzed.

To get a full picture of the effect of hydrophobic sand on the growth of plants it was used plants grown under conditions maximum to the experiment. For this, 1/3 layer of hydrophobic sand was loaded into pots and ground for growing plants was placed onto it. In this case, consumption of irrigation water and the effect of sand on the growth of plants were considered.

As a result hydrophobic sand slightly decreases the intensity of sunflower growth at the first stages of plants development. To the end of the experiment the difference in growth was levelled.

The obtained results allow concluding that hydrophobic sand in small doses (10%), when being mixed with soil ground, does not practically exert a negative effect on the growth of sunflower sprouts. However, when using a support from hydrophobic sand, a slight delay in the growth of plants was observed. These facts were taken into account when analyzing the results obtained using an insulating layer of hydrophobic sand in the experiments with heavy metals (Zn, Cd, Cu) on evaluation of migration and accumulation of heavy metals by amaranth and sunflower. Figure 9 presents examples of experiments with heavy metals and the insulating layer of hydrophobic sand on the example with Cd.

1   2

1 - control contains 50 mg/kg of Cd, 2- the experiment the lower layer contains 50 mg/kg of Cd^{2+} and a layer of hydrophobic sand. The upper arrow points at a layer of hydrophobic sand. The lower arrow – soil ground with Cd^{2+}

Fig. 9. The experiment with the use of an insulating layer of hydrophobic sand

Conclusion

Thus, as part of the technique perfected the synthesis experiment having superhydrophobic properties of soot during combustion of propane-butane mixture and oil waste. With the use of the resulting soot created hydrophobic sand. The resulting hydrophobic sand is recommended to use as a filler in building materials for exterior decoration and agriculture to prevent seepage of irrigation water in the lower layers of soil or evaporation.

Hydrophobic sand can also be used for isolation of soil around the plants and soil salinity saline groundwater, leading to the destruction of the root system of plants.

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