ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 13, pp. 2579–2584. © Pleiades Publishing, Ltd., 2013.
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Ion-Exchange and Adsorption Properties of Karelian Schungites in Contact with Water

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Received February 22, 2012

Abstract—The kinetics of leaching of Karelian shungites (I, II, and III types) with distilled water was determined experimentally. The kinetics of the adsorption-catalytic removal of phenol from aqueous solutions in contact with finely dispersed shungite in atmosphere of oxygen or in inert atmosphere (argon) was studied.

Keywords: Karelian shungites, electron microscopy, water leaching, catalytic oxidation.

DOI: 10.1134/S107036321313001X

Shungites are carbon-bearing rocks [1], in which carbon and mineral constituents (such as aluminosilicates and other minerals) occur in the form of a complex. Shungite differs from graphite, coal, and bitume, because it has no crystal lattice, has two-dimensional structure, and the content of volatile constituents in it is low. Schungite rocks are classified on their carbon content: highly carbonaceous shungites-I and -II contain ≥ 98% and 35–75% carbon, respectively, medium carbonaceous shungites-III, or shungites, 10–20%, and low carbonaceous shungites-IV and -V, or shungite-bearing rocks, less than 10%.

Shungite, while brought into contact with water containing organic pollutants (propanol, butanol, toluene, benzene, chloroform, chlorophenol, etc.) for sufficiently long time (hours) in oxygen atmosphere, exhibits the catalytic activity for oxidation of the latter compounds to carbon dioxide [1, 2]. In the last two decades, this property was used as basis for constructing equipment for chemical treatment of wastewaters and exhaustive purification or conditioning of tap water [1, 3, 4]. The ion-exchange, adsorption, and catalytic properties of different types of shungites in their contact with water systems are studied in more detail in [5–8].

Nevertheless, many specific features of the shungite behavior in contact with water systems are unknown. For example, aqueous solutions of organic impurities treated with shungite have the acid pH values (see [2] and Fig. 71 in [1]). This effect is almost evident, because oxidation causes carbon to convert into the carbonate anion and chlorine in the organochlorine compound, into hydrochloric acid. At the same time, the behavior of pure water in contact with shungite has not been studied. The elution kinetics of various elements from shungite-III was determined at quantitative level by the mass spectrometric method [5]. However, the specific chemical form and the valence states of each element in the aqueous phase are controversially reported. Finally, the fundamental question of the mechanism of the shungite effect on the aqueous solutions of organic substances is controversially reported: catalytic oxidation to carbonate anion is proposed in [2] and physical adsorption of organic molecules on the developed shungite surface, in [9, 10].

The interaction of shungites with water. We studied shungites of three types: shungite-I (Shun'ga deposit, carbon content 95–98 wt %), shungite-II (Shun'ga deposit, carbon content 70 wt %), and shungite–III (Zazhoginskoe deposit, carbon content 30–35 wt %).

pH of the water samples was determined with an HI-8314 portable microprocessor-based pH/mV/C-meter (HANNA) to within ±0.03. The time of the measurement was 1 min. As fixanals for calibration of pH-meter, we used potassium tetraoxalate (pH 1.68), potassium phthalate (pH 4.1), and monopotassium phosphate (pH 6.86).

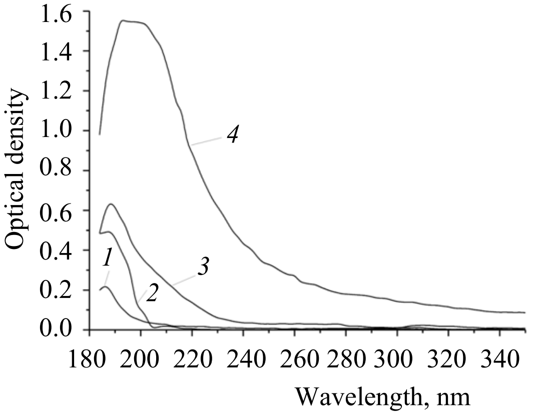

Fig. 1. Absorption spectra of water (*1*) before and (*2*) after grinding with shungites. Shungite: (*2*) I, (*3*) II, and (*4*) III.

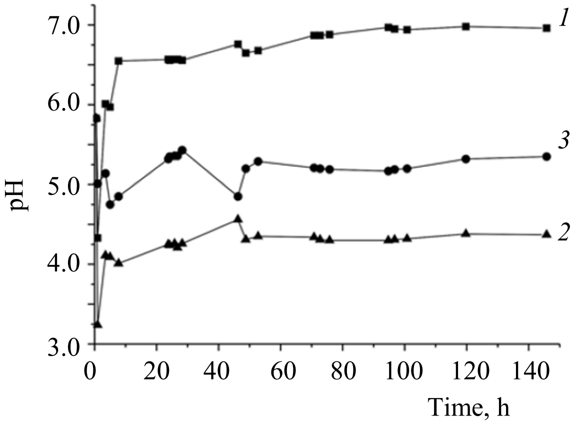

Fig. 2. Change in pH of the water treated with granular shungites in the static mode. Sungite: (*1*) I, (*2*) II, and (*3*) III.

The water was filtered through a track membrane, which, contrary to conventional filter paper, does not contain foreign impurities. The membrane (pore size 0.4 μm, thickness 20 μm) was made at the Flerov Laboratory of Nuclear Reactions (Joint Institute for Nuclear Research, Dubna). The spectra were recorded on an SF-46 spectrophotometer in the wavelength range 184–350 nm. The absorption maxima in the ranges 190–195, 200–210, 240, and 260–290 nm were assigned to $[SO_4]^{2-}$complex, Cl^- anion, and products formed in Fe(III) hydrolysis [11]. In the experiments, we used twice-distilled water (pH 5.83).

In 10 mL of distilled water, 1 g of shungite was ground for 10 min and the absorption spectrum of the water passed through a track membrane was measured. The results of the measurement are demonstrated in Fig. 1. In the case of shungite-III, a majority of the sulfate anions (band 190-195 nm) and considerable amount of the Cl^- anions (band 200–210 nm) and products formed in Fe(III) hydrolysis (band 215–220 nm) passed to the water, in good agreement with the data of [5]. The absorption spectrum of distilled water has a low intensity absorption band within 188–190 nm attributable to OH^- anion.

Into distilled water (two samples, each 10-mL volume) a granular shungite-I was introduced (1 g into each sample). Shungite–II and shungite-III were introduced by the same manner (two samples for each substance). Then, half of the samples was kept in the static mode and the other half, in the dynamic mode; in the latter case, schungite powder (particle size 0.5–2.0 mm) was stirred in water with an electromechanical stirrer. pH of the aqueous phase on the interface with the shungite deposit was measured at regular intervals for all six samples. For samples kept in the dynamic mode the stirring was stopped prior to the measurement and resumed after the measurement was complete. The results of the measurements are shown in Figs. 2, 3.

The shungites, as solid acids [12], in contact with water considerably increase its acidity during the first minutes and hours (see Figs. 2, 3). However, after several hours and tens of hours, the acidity of the water decreases owing to gradual passage of the K^+ and Na^+ ions into solution [5]. The pH decrease is considerably larger (approximately by a unity) in the presence of trace amounts of organic impurities, especially

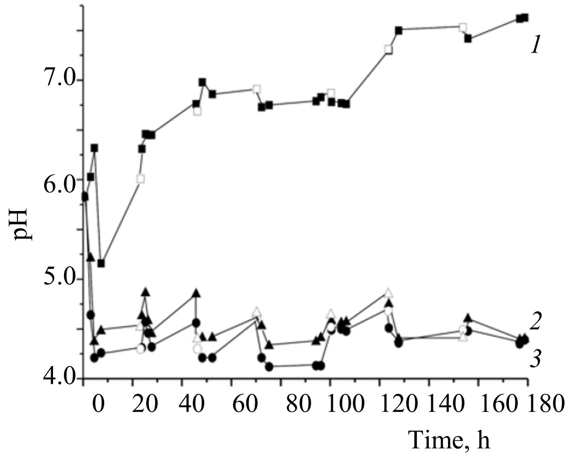

Fig. 3. Change in pH of the water treated with shungites in the dynamic mode. Shungite: (*1*) I, (*2*) II, and (*3*) III. Light icons correspond to the final moments of time intervals of the static mode.

The concentration (mg L^{-1}) of ions in water in contact with shungite

Ion	Shungite–I	Shungite–II	Shungite –III	
			this study	data of [5][a]
$[SO_4]^{2-}$	23.0	130	52.5	150±50
Cl^-	39.3	38.4	90.8	1±0.5

[a] Shungite III-A contained (27±7)% carbon [5].

organochlorine compounds [2]. The static experiments were also performed with shungites (1 g samples) ground in 10 mL of water. The measured pH values were similar to those for granular shungite fractions (see Fig. 2).

In the dynamic experiments (Fig. 3), the water pH over shungites-II and -III is at a level of ≤ 4.5 for tens hours, since these shungites, unlike shungite-I, have a layered texture. In this case, passage of the alkali ions into the solution is compensated by a continuous opening of new planes. For shungite-II containing the largest amount of the $[SO_4]^{2-}$ ions [1] pH was always the lowest.

The concentration of $[SO_4]^{2-}$ and Cl^- ions in water in contact with schungites was determined by titration [13]. In the case of Cl^-, to 0.5 mL of 1.4 N HNO_3, 10 mL of water in contact with shungite was added, the solution was titrated with $AgNO_3$ (2% solution), and the Cl^- concentration was determined from the formation of AgCl precipitate. In the case of $[SO_4]^{2-}$, the same water volume (10 mL) was added to 0.5 mL of 1.2N HCl, the solution was titrated with $BaCl_2$ (5% solution), and the $[SO_4]^{2-}$ concentration was determined from the formation of $BaSO_4$ precipitate. The results obtained are collected in table.

Because shungite-IIIA used in [5] and shungite-III used in this study differ markedly, we may conclude that the data obtained in these two studies for the washout of sulfate anion coincide well. At the same time, data on the chlorine anion are clearly inconsistent, and preference should be given to this study, because in [5], we might lose the bulk of chlorine during preparing samples for mass spectrometric analysis.

Electron microscopic analysis of shungites treated with water. Samples of initial and water-treated schungites were studied with a GSM-35C scanning electron microscope (Japan-Jeols) at a voltage of 10 kV. It is seen at a very high magnification (from 6,000 to 40,000) that some areas on the sample surface are changed (Figs. 4–7).

The water treatment of shungite-I increases the surface porosity and makes surface relief more broken (see Figs. 4, 5). In both figures, shungite-I has the globular structure. The surface of the water-treated shungite-III (Figs. 6, 7) is changed drastically: the pore size is increased by an order of magnitude, the carbon constituent is dispersed, the surface relief is more pronounced, with separation of the silicate constituent on it noticeable (white color in Fig. 7). In the regions

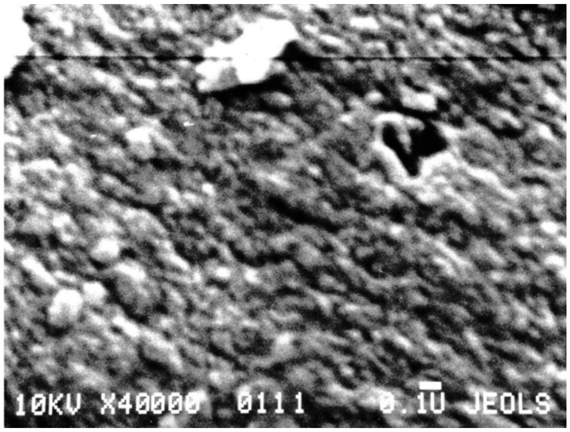

Fig. 4. Micrograph of the surface of the initial shungite-I (Magnification 40 000).

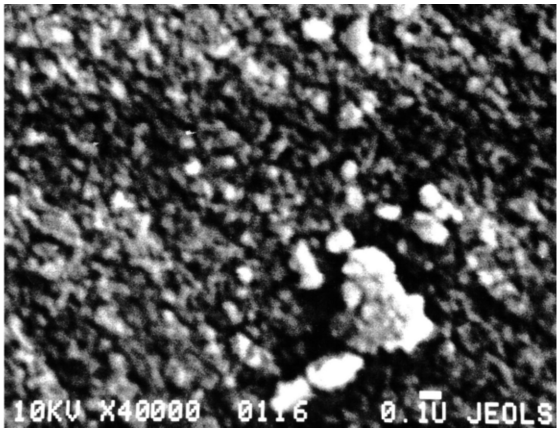

Fig. 5. Micrograph of the surface of the shungite-I treated with distilled water (Magnification 40 000).

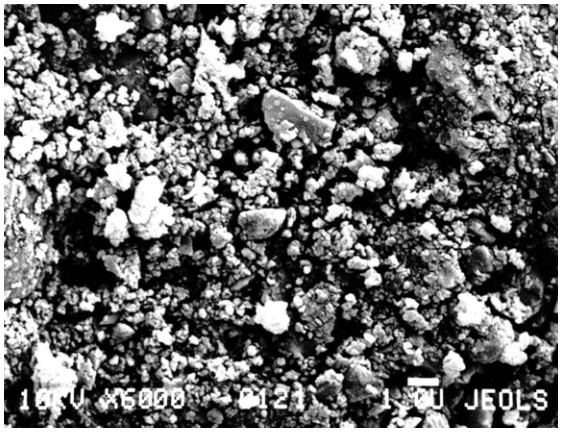

Fig. 6. Micrograph of the surface of the initial shungite-III (Magnification 6 000).

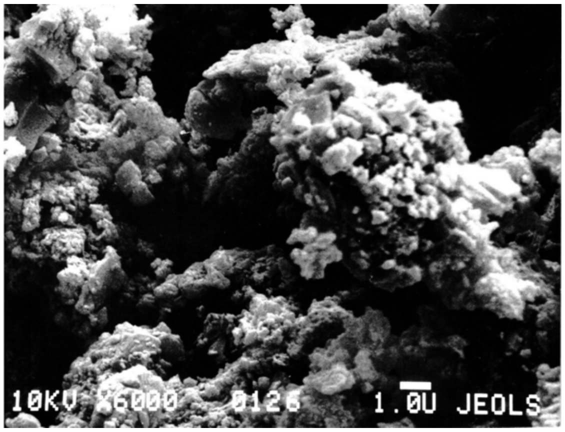

Fig. 7. Micrograph of the surface shungite-III after treatment with distilled water (Magnification 6 000).

penetrated with water, wherein deprotonation takes place, the adhesive force between the particles decreases, which causes particles to disperse and disintegrate onto less than <0.4-μm fractions capable to pass through a track filter, which decreases the content of carbon material.

Adsorption and catalytic properties of shungites in contact with water. Previously, the high effectiveness of finely-dispersed shungite-III in oxidation of organic impurities in liquid water has been demonstrated in [2, 6]. Shungite ground 24 h before the experiment decreases the concentration of phenol from 30 to 6 mg L^{-1} after 8 hours of contact [6] and that activated with hydrogen peroxide decreases the concentration of p-chlorophenol from 1.5 to 0.15 mg L^{-1} after 7 h of contact [6]. At the same time, in water containing 25 mg L^{-1} benzene or toluene, only no more than 3% of the initial concentration of the organic impurity is present after 7 h of contact, with 90% of impurity oxidized to CO_3^{2-} anion [2]. In these studies, however, there is no evidence that shungite in water acts indeed as oxidant of organic microimpurities onto simpler substances (up to CO_3^{2-}) rather than only a sorbent. Therefore, in this study we have reproduced the experiments [2, 6], but with the difference that the half of the experiments was performed in oxygen and another half, in pure argon.

As shungite sorbent-catalyst (SSC) we used shungite-III (0.5–2.5 mm fraction). Smaller fractions were removed by the resuspension – decantation method. 24 hours before the experiment the SSC powder was washed in strong hydrochloric acid and then in distilled water to pH 5. The concentration of phenol and products formed in its conversion, which have not lost phenolic properties, were determined spectrophotometrically at the wavelength 500 nm (color reaction with 4-AAP**)** [13]. To avoid distortion of kinetic curve, the volume of the analyzed solution does not always exceed 2% of the total volume. Adsorption of phenol and its oxidation products on the filter paper was precluded by centrifugation of the analyzed solution to remove SSC particles.

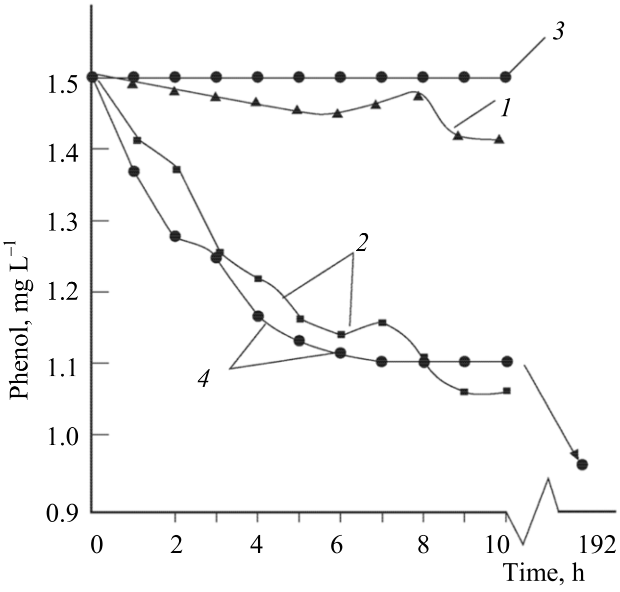

Fig. 8. Variations of apparent phenol concentration with time for different water systems treated in the static mode. System: (*1*) pure water purged with oxygen, (*2*) aqueous shungite suspension made turbid by oxygen bubbling, (*3*) pure water purged with argon, and (*4*) aqueous shungite suspension made turbid by argon bubbling.

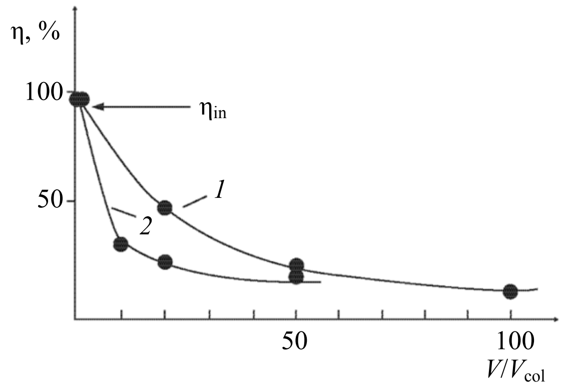

Fig. 9. Efficiency η (%) of (*1*) phenol and (*2*) chloroform sorption in aqueous solution passed through a column (V_{col}) with granular shungite-III vs. the solution volume (V) passed through a column. Size of shungite particles is from 0.12 to 0.25 mm, package height, 10 cm, and solution flow velocity, 1 mm min^{-1}; the same for Fig. 10.

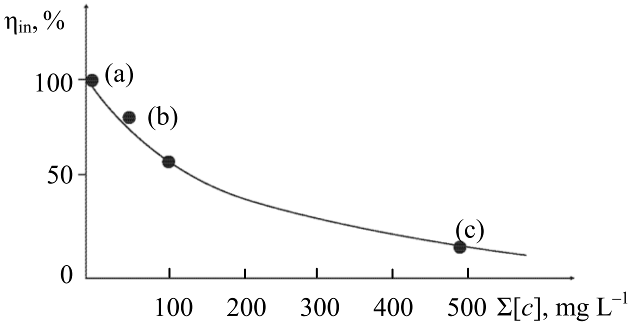

Fig. 10. Initial efficiency (η_{in}) of phenol sorption from aqueous solution passed through a column with granular shungite–III vs. the total concentration of the Ca^{2+} and Mg^{2+} cations (ratio 1 : 1). Water: (a) distilled water, (b) water of the river Neva, and (c) water of the river Moskva.

The results of the experiments are demonstrated in Fig. 8. The kinetic curves show that the phenol removal from water in the presence of oxygen occurs faster and to a larger extent than in Ar. Consequently, SSC is the active catalyst for oxidation of organic substances dissolved in water. Under the action of SSC in argon, phenols also disappear. In this case, however, SSC was crushed, stored, and washed with hydrochloric acid in the air atmosphere and, therefore, active oxygen was certainly present on the surface of grains.

The kinetic curves (Fig. 8, curves *2, 4*) are irregular, as was also observed previously [6]. This is not the result of measurement errors, but an objective fact, since hydroquinone and other di-and tri-hydroxybenzenes formed in phenol oxidation also enter into the color reaction with 4-AAP, with the extinction coefficient higher than that of phenol. In this case, a part of products formed in phenol oxidation desorbs from the shungite surface and enters the aqueous phase, in accordance with its adsorption isotherm. As a result, the kinetic curves describe the time behavior of the sum of extinctions of all hydroxybenzenes, which can enter into the color reaction with 4-AAP and are in the aqueous phase (Fig. 8, curves *2, 4*). The color reaction with 4-AAP ceases only after the series of non-aromatic oxy and hydroxy acids, the latest of which is oxalic acid, is formed after opening of benzene ring.

Thus, the main mechanism of the treatment of water in contact with the SSC powder to remove organic contaminants is the oxidation of organic molecules in the presence of the SSC catalyst. On the other hand, it was clearly demonstrated [9, 10] that in the presence of the shungite powder phenol is removed in aqueous solution by the physical adsorption mechanism. However, our data are not in variance with the data of [9, 10] obtained at the very high phenol concentration (1 g L^{-1}). At this concentration the active centers of shungite are blocked or simply have no time to compete in speed with physical adsorption.

To verify this hypothesis, we used in the experiments the intermediate values of the initial concentrations (100 mg L^{-1} for phenol and 100 mg L^{-1} for chloroform). The concentration of phenol at the inlet and outlet of the schungite column was measured on an ion chromatograph and the chloroform concentration, on a gas chromatograph. In the latter case, salting out with sodium sulfate and subsequent extraction with diethyl ether were used. The results of the experiments are demonstrated in Figs. 9, 10.

Adsorption of the shungite-packed column with respect to the component X may be characterized by sorption efficiency [Eq. (1)]:

$$\eta = \frac{[X]_{in} - [X]_{fin}}{[X]_{in}} \quad (1)$$

or purification coefficient [Eq. (2)]:

$$K_{pur} = \frac{[X]_{in}}{[X]_{fin}}\,. \quad (2)$$

Here [X_{in}] and [X_{fin}] are the concentrations before and after the purification, respectively. From the Eqs. (1) and (2), we obtain

$$K_{pur} = \frac{1}{1 - \eta}, \quad (3)$$

where K_{pur} increases with increasing η. The η value varies in the range from 0 to 1, with K_{pur} varying from 1 to ∞.

After the solution volume (V) equal to 100 volumes of the column is purified, the sorption efficiency (η) and purification coefficient (K_{pur}) of shungite are decreased by an order of magnitude, which is a characteristic of physical adsorption. However, the purification efficiency remains constant up to volumes $V = 1000 \times V_{col}$ owing to the beginning of a slower process, a catalytic oxidation of adsorbed organic compounds. However, this mechanism is noticeable only at their concentrations not higher than 100 mg L^{-1}. At concentrations below 10 mg L^{-1} catalytic oxidation is prevalent.

Shungite losses ability to remove organic impurities, at least phenol and chloroform, at the concentration of the inorganic salts in the water above 200–300 mg L^{-1} (see Fig. 10).

ACKNOWLEDGMENTS

The authors thank E.Zh. Batrakova, who took part in a some of the experiments.

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