ABSTRACT: Despite reducing the consumption of the pesticide (2,4-dichlorophenoxy)acetic acid (2,4-D), it can still be occasionally found in natural waters. The most effective method for its removal is adsorption on a solid surface using carbonaceous sorbents; however, these sorbents are considered highly priced. Therefore, diverse waste products have been increasingly used in recent years. In this study, the sorption possibility of 2,4-D from aqueous solutions with low concentration (1 μg L−1) of carbon- and silicon-containing sorbents of different nature was investigated. It was observed that precipitated silica from rice husk could be used for sorption posttreatment of 2,4-D. There was almost a complete removal of the pesticide with the carbon sorbent by “Sibunit”. Mesoporous sorbents derived from rice husk and straw showed a sorption efficiency of 23%–35%, indicating their use for treatment of natural waters.

KEYWORDS: (2,4-dichlorophenoxy)acetic acid, low-cost sorbents, carbon- and silicon-containing sorbents, rice production wastes, sorption efficiency

Introduction
(2,4-dichlorophenoxy)acetic acid (2,4-D) is a hormonal herbicide of systemic action and is widely used across the world to control weeds. In open water, 2,4-D comes from leaching of soil with waste water from chemical and related industries, as well as from the process of decomposition of other herbicides from the family of chlorophenoxyacetic acids.1

Carbonaceous sorbents are used for removing pesticides from various water sources and types of soil.2, 3 In recent years, sorbents based on nanostructures have been studied.4 Molecularly imprinted polymers are considered to be advanced materials for sorption of pesticides from aqueous solutions. Their advantages include the practically unlimited possibility of constructing sorbents selective to organic compounds of different classes, the relative ease of synthesis, and stability. For the selective sorption of 2,4-D, a molecularly imprinted 2,4-D polymer based on 4-vinylpyridine and methacrylic acid as well as acrilamide was used.5 A new sorbent for the selective sorption of 2,4-D from aqueous solutions—silica gel modified by superbranched poly(methylcholrosilylpropyl) carbosilane with molecular prints of 2,4-D—was synthesized. Analysis of the sorption isotherms showed that the sorbent has the ability of molecular recognition of the given material.6 Various waste products as sorbents for pesticides have been actively investigated. Alam et al7 used tire rubber granules as a sorption material for the removal of 2,4-D and atrazine. It was found that at the initial concentrations of 0.5 and 1 mg g−1, the removal efficiencies were 83.2% and 87% for 2,4-D and 84.2% and 87.6% for atrazine, respectively.

Agricultural wastes are promising low-cost sorbents for the removal of pesticides and other pollutants from aqueous solutions. In this study, activated rice husk was investigated as a sorbent for the removal of Safranin-T from waste water.8 It has been shown that the effectiveness of sorption of organophosphorus pesticide by rice bran or rice husk is associated with the presence of functional groups (aminogen, hydroxyl, carboxylic) and carbon fibers in the polymer-forming structures. Sorption efficiencies of triazophos from samples of surface water and ground water by rice bran were 97 ± 0.5% and 98 ± 0.4% and those by rice husk were 96 ± 0.7% and 96 ± 0.9%, respectively.9

Rice husk, middlings, bagasse fly ash of sugarcane, and Moringa oleifera pods were used to remove methylyparathon from aqueous solutions. Based on the thermodynamic parameters (ΔH, ΔS, ΔG), it was found that the sorption was an exothermic and spontaneous process.10 Studies on the removal of triose phosphate and methylyparathon from the aqueous medium by rice husk and bran showed that the adsorption energy values of the husk and bran were 14 ± 0.1 kJ mol−1 and 11 ± 0.2 kJ mol−1, respectively.
The maximum adsorption capacity of the rice husk modified by methylacrylic acid during adsorption of paraquat was 317.7 mg g\(^{-1}\), which is higher than that of Fuller’s soil (60 mg g\(^{-1}\)) and activated carbon (90 mg g\(^{-1}\)).

Previous studies\(^{12,13}\) have shown that rice husk ash (RHA) is a good sorbent for the removal of 2,4-D from aqueous solutions. Compared with granulated activated carbon, RHA gave 10,000 times higher rate constant. RHA adsorbs 2,4-D instantly and stops its further transport through soil.\(^{13}\) Packed-bed adsorption capacity (mg/m\(^2\)) for RHA is 2.7 times higher than that of synthetic activated carbon.\(^{13}\)

Thus, the problem of finding an effective low-cost sorbent for the removal of 2,4-D from the environment remains relevant today. In this study, we investigated the sorption of 2,4-D from aqueous solutions by carbon- and silicon-containing sorbents of different nature.

**Methods**

Reagent solutions and materials. All the reagents were of analytical grade and obtained from Sigma Aldrich Co. Stock solution of the pesticide was prepared by dissolving 2.52 mg of 2,4-D in 25 mL of ethanol. Working solution of 2,4-D with a concentration of 1 ppm was prepared by diluting ethanol in the feed solution one hundred times. The required concentrations were prepared by subsequent dilutions of the work solution.

Development of sorbents. Sorbents of different nature were used to remove 2,4-D from aqueous solutions, such as silicon- and carbon-containing products derived from rice husk and straw (rice husk; samples of amorphous silica, obtained by precipitation and thermal method; pulp obtained after alkaline hydrolysis; RHA; potassium aluminosilicate, precipitated from alkaline waste water of rice husk; a synthetic sample nSiO\(_2\)·mSbO\(_3\)·kH\(_2\)O, and commercial products (reagent "silicic acid," the carbon sorbent of "Sibunit" brand, and the natural silicate—Koksharovskiy deposit vermiculite, Primorsky Krai, Russia) (Table 1).

Rice husks were procured from a local rice milling plant at Krasnodar (Russia). The silica specimens were prepared by the schemes described earlier (Table 2).\(^{14,15}\) A synthetic sample nSiO\(_2\)·mSbO\(_3\)·kH\(_2\)O was prepared by the technique described by Zemmukhova and Panasenko.\(^{16}\) The pulp was prepared by the Scheme V described by Zemmukhova et al.\(^{17}\)

**Instrumentation.** 2,4-D detection was carried out by gas–liquid chromatography. Analysis of 2,4-D was performed by GLC–MS using chromate-mass spectrometer GCMS-QP 2010 Ultra in an electron-impact ionization mode with an electron energy of 70 eV and ion source temperature of 200°C. The defined range of m/z values was 50–500. The separation was carried out using an HP-5MS column (30 m; 0.25 mm i.d.; 0.25 µm film thickness, Agilent) in a temperature gradient mode from 70°C to 130°C at 20°C minute\(^{-1}\) and 130°C to 270°C at 3°C minute\(^{-1}\). The injector temperature was 270°C, and the interface temperature was 270°C. Helium was used as the carrier gas, with a volume velocity of 1.19 mL minute\(^{-1}\), linear gas velocity of 40 cm second\(^{-1}\), and split ratio of 1:5.

All chromatographic responses were detected in a selected ion monitoring mode. 2,4-D identification was carried out on the basis of retention time match and mass spectrum of the analyte and a reference external standard of 2,4-D.

**Table 1.** Physical–chemical characterization of sorbents.

<table>
<thead>
<tr>
<th>SORBENT</th>
<th>COMPOSITION</th>
<th>PREPARATION SCHEME</th>
<th>CONTENTS (%)</th>
<th>S(_{sp}) (m(^2)g(^{-1}))</th>
<th>d (nm)</th>
<th>% SORPTION(^c)</th>
<th>pH</th>
<th>X-RAY PHASE ANALYSIS(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>SiO(_2)·nH(_2)O from RH</td>
<td>Scheme III</td>
<td>88.4</td>
<td>7.8</td>
<td>11.0</td>
<td>52.7</td>
<td>32 ± 10</td>
<td>8.24</td>
</tr>
<tr>
<td>S2</td>
<td>SiO(_2)·nH(_2)O from RS</td>
<td>Scheme III</td>
<td>91.0</td>
<td>−</td>
<td>8.9</td>
<td>30.6</td>
<td>20.1</td>
<td>23 ± 13</td>
</tr>
<tr>
<td>S3</td>
<td>SiO(_2)·nH(_2)O</td>
<td>Commercial product</td>
<td>88.4</td>
<td>−</td>
<td>11.6</td>
<td>73.0</td>
<td>34.5</td>
<td>23 ± 6</td>
</tr>
<tr>
<td>S4</td>
<td>SiO(_2) from RH</td>
<td>Scheme II</td>
<td>99.4</td>
<td>0.5</td>
<td>231.0</td>
<td>4.4</td>
<td>13 ± 3</td>
<td>7.79</td>
</tr>
<tr>
<td>S5</td>
<td>nSiO(_2)·mSbO(_3)·kH(_2)O</td>
<td>Synthetic product</td>
<td>27.8</td>
<td>8.0</td>
<td>37.8</td>
<td>16.0</td>
<td>35 ± 9</td>
<td>8.00</td>
</tr>
<tr>
<td>S6</td>
<td>KAlSi(_3)O(_8)·nH(_2)O from RH</td>
<td>Scheme IV</td>
<td>37.4</td>
<td>−</td>
<td>11.5</td>
<td>105.7</td>
<td>13.2</td>
<td>27 ± 6</td>
</tr>
<tr>
<td>S7</td>
<td>(Mg, Fe)(_2)[(AlSi(_2)]O(_3)]</td>
<td>Commercial product</td>
<td>38.0–43.0</td>
<td>2.0</td>
<td>5.9</td>
<td>205.1</td>
<td>12 ± 3</td>
<td>8.21</td>
</tr>
<tr>
<td>S8</td>
<td>Pulp from RH</td>
<td>Scheme V</td>
<td>n/d(^a)</td>
<td>95.3(^b)</td>
<td>0.5</td>
<td>5.4</td>
<td>13.2</td>
<td>25 ± 9</td>
</tr>
<tr>
<td>S9</td>
<td>RH</td>
<td>Scheme V</td>
<td>15.0</td>
<td>82.3(^b)</td>
<td>5.0</td>
<td>2.0</td>
<td>83.6</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>S10</td>
<td>(SiO(_2) + nC) from RH</td>
<td>Scheme I</td>
<td>47.5</td>
<td>52.0</td>
<td>0.5</td>
<td>260.0</td>
<td>4.2</td>
<td>17 ± 3</td>
</tr>
<tr>
<td>S11</td>
<td>Activated charcoal</td>
<td>Commercial product</td>
<td>−</td>
<td>99.5(^b)</td>
<td>n/d</td>
<td>267.1</td>
<td>34.2</td>
<td>−100</td>
</tr>
<tr>
<td>S12</td>
<td>Chitosan</td>
<td>Commercial product</td>
<td>−</td>
<td>n/d</td>
<td>n/d</td>
<td>2.3</td>
<td>9.4</td>
<td>8 ± 3</td>
</tr>
</tbody>
</table>

Notes: \(^a\)indicator not defined; \(^b\)content determined by ash; \(^c\)mean values and standard deviations shown; \(^a\)—amorphous, \(^c\)—crystalline.
using simultaneous recording signals with ion values m/z 220, 175, and 162. The analysis was performed using the GC-MS Solution software. Quantitative analysis was performed using external calibration standard on 2,4-D.

The pH measurements were made on a digital pH-meter 150 M (“Anteks” Ltd.).

**Sorbent characterization.** X-ray phase sorbent analysis was performed by the Bragg-Brentano method in Cu Kα radiation using a diffractometer D8 Advance. Phase identification in the experimental X-ray patterns was done by using the program EVA (EVA Software defines a new benchmark for phase analysis) database of powder diffraction patterns PDF-2 (The Powder Diffraction File).

Specific surface area of sorbents was determined by BET (Brunauer, Emmett, and Teller) method using nitrogen as a standard and employing surface area analyzer (ASAP 2020, Micromeritics Instrument Corporation). The silicon content was determined gravimetrically. Free carbon content was detected by a previously described method. The water content was determined by thermal gravimetric analysis (derivatograph system Q-1000 from IOM). The characteristics of sorbents including the surface area, chemical composition, and % sorption are presented in Table 1.

**Sorption method.** Sorption study of 2,4-D was carried out in an aqueous solution in static conditions at a temperature of 18–20°C.

Appropriately weighed sorbents (0.1 g) were added to dry glass-stoppered conical flasks into which 100 mL of varying concentrations of 2,4-D solution (ie, 0.5–3.5 ppb) were added. Then, the contents of the flasks were mixed using LAB-PU-01 shaker for 1 hour for equilibration. A control blank sample was simultaneously placed on the same shaker to estimate the evaporation losses of pesticide. The samples were filtered using a filter paper to remove the sorbents. Similar results between control and treated samples suggested no losses due to evaporation.

The sorbed concentration of 2,4-D onto the sorbents was evaluated using the following equation:

\[
\text{% sorption} = \frac{C_e - C_i}{C_i} \times 100\% \tag{1}
\]

where \(C_i\) and \(C_e\) are the initial concentration and equilibrium concentration, respectively, ppb.

The equilibrium time was determined by independent experiments. Sorbents S4 and S10 were poured into 2,4-D solution (\(C = 1\) ppb). Analysis of 2,4-D content in the equilibrium solutions was performed every 1st, 3rd, 6th, and 24th hours.

All experiments were performed at least in triplicate. The results are the average of three independent measurements.
along with standard deviation showing 95% confidence level with a precision of ±2% in most cases.

**Sorption isotherms.** The equilibrium sorption isotherm expresses the specific relation between the concentration of sorbate and its degree of accumulation onto the sorbent surface at a constant temperature.

Sorption isotherms were obtained by the approximated Henry (2) and Freundlich (3) equations:  

\[ C_{ads} = K_H \cdot C_e \]  \hspace{1cm} (2)  
\[ C_{ads} = C_m \cdot C_e^n \]  \hspace{1cm} (3)

where \( C_{ads} \) is the sorbed concentration onto the sorbent surface, \( \mu g \cdot g^{-1} \); \( C_e \) is the equilibrium concentration in the solution at equilibrium, ppb; \( K_H \) is the sorption capacity, Henry; \( C_m \) is the multilayer sorption capacity; and \( n \) is a constant.

Logarithmic plot of Freundlich isotherm gives straight lines. The slope of the linear plots gives the value of \( 1/n \), which is a measure of the intensity of sorption, and the intercept yields the value of \( C_m \), indicating multilayer sorption capacity. The slope of Henry’s isotherm is a measurement of Henry sorption capacity.

Gibbs free energy \( \Delta G \) (kJ mol\(^{-1}\)) was estimated using the following equation:

\[ \Delta G = -R \cdot T \cdot \ln \cdot K \]  \hspace{1cm} (4)

where \( R \) is the gas constant, \( T \) is the temperature in Kelvin, and \( K \) is a constant.

In addition to determining the conditions of the static adsorption, filtration of the 2,4-D solution was carried out through the sorbent bed. The water contaminated with 3 ppb concentration of 2,4-D was passed in a graduated cylinder containing the sorbent S1 of mass \( \sim 0.51 \) g and bed height 14.5 mm. The volumes of individual portions of the sorbate solution were 100, 200, 250, 300, and 350 mL. For each volume of the sorbate solution, a new sorbent sample weight was used.

**Results and Discussion**

**Study of the physical–chemical properties of the sorbents.** The sorbents that we investigated can be divided into three groups based on their chemical composition: silicon (S1, S2, S3, S4), metal–silicon (S5, S6, S7), and silicon–carbon (S8, S9, S10). Samples S11 and S12, with a maximum and a minimum efficiency of the sorption, are not included in these groups.

As shown in Table 1, the selected sorbents were amorphous substances, except the vermiculite. Samples S2, S5, and S12 contain some crystal structures. The sorbents differed from each other by the content of silicon dioxide, carbon, and water. Specific surface area of the samples, measured according to Brunauer et al., ranged from 2 to 260 m\(^2\) g\(^{-1}\), and the pore diameter ranged from 4.2 to 205.1 nm. All the sorbents had a mixed void structure and low values of specific surface area.

**Investigation of sorption of 2,4-D from an aqueous solution.** One of the characteristics of the sorption process is that the sorption time reaches equilibrium, which is set by the dependence of the sorption on the agitation time of the sorbent with a solution. The two sorbents, S4 and S5, were selected to determine their characteristics. The dependency of 2,4-D sorption on the agitation time in the aqueous solution–sorbent is shown in Figure 1, which shows that the sorption equilibrium reached 90% 1 hour after the sorption began.

Therefore, all the subsequent experiments on the sorption of 2,4-D by silicon and carbon sorbents, were carried out for 1 hour (Table 1).

Removal efficiency from the aqueous solutions depends on several factors such as size of the surface area, pore radius, surface chemistry, and the concentration of sorbate and its nature. For a practical use of the sorption method, the sorption isotherm is the main characteristic of the sorbent, which determines the choice of the optimal process conditions. Sorption isotherm of 2,4-D on the precipitated silicon dioxide (S1) was determined at low concentrations that occur in natural waters (from 0.5 to 3 ppb; Fig. 2).

Sorption isotherm was linearized from Henry (3) and Freundlich (4) equations and calculated using adsorption constants and free energy change (Table 3). \( R \)-squared—both were high according to Henry and Freundlich equations.

**Figure 1.** The dependency of sorption of (2,4-dichlorophenoxy)acetic acid on the agitation time with the sorbent.

**Figure 2.** Experimental sorption isotherm (2,4-dichlorophenoxy)acetic acid by the precipitated silica from rice husk: \( x \)-average experimental values.
Gibbs free energy (\(\Delta G\)) calculated by Henry and Freundlich equations did not differ significantly. Given that 2,4-D is a derivative of benzene, for comparison there were Gibbs free energy values of aromatic compounds on the carbon surface. It is known that this value lies between the range 20,000–25,000 J mol\(^{-1}\),\(^{22}\) which is an order of magnitude faster than the value obtained with 2,4-D sorption on the precipitated silica. These values indicate the \(\Delta G\) weak interaction of sorbate molecules with the surface of the precipitated silica.

During the filtration of 2,4-D with a concentration of 3 ppb via a layer of the precipitated silica at different ratios of S:L, the equilibrium concentrations of 2,4-D in the eluate did not exceed 1 ppb (Fig. 3).

Removal efficiency of 2,4-D by different sorbents can be seen in the histogram depicted in Figure 4.

As shown in Table 1, the investigated sorbents have a mixed void structure (\(d_{\text{pores}} = 4–200\,\text{nm}\)) with a predominance of mesopores (\(d_{\text{mesopores}} = 3\) to 200–400 nm) and a small proportion of micropores (\(d_{\text{micropores}} = 1.4–3\,\text{nm}\)). Considering the ratio of the pore diameter and the effective diameter of the hydrated molecule 2,4-D (\(d = 1\,\text{nm}\)), calculated by the geometric dimensions of the molecule,)\(^{23}\) we assumed that part of the sorbent surface is not available for the sorbed substance. It was found that the effectiveness of 2,4-D sorption from the aqueous solutions by siliceous sorbents was inversely proportional to the specific surface area of the studied samples (Table 1). However, in the silicon–metal and silicon–carbon sorbent groups, the dependency on the specific surface area was missing, which was apparently due to the different nature of the sorbent material in these groups.

As shown in Table 1, the sorption ability of the samples depends on the pore diameter. For micro- and macroporous samples, the sorbent capacity is low. For example, S10 and S4 with pore diameters 4.2 and 4.4 nm showed sorption efficiency values of 17% and 13%, respectively, which is probably determined by the ratio of the pore diameter and the size of the sorbate molecules. Macroporous sorbents, such as vermiculite (\(d_{\text{pores}} = 205.1\,\text{nm}\), \(S_{\text{sp}} = 5.9\,\text{m}^2\,\text{g}^{-1}\), % sorption = 12%), have a small specific surface area and correspondingly low sorbing capacity. Mesoporous sorbents showed high sorption properties (S1, S2, S3, S5, S6). Similarly, fibrous structure samples (S9 and S8) sorbed well. This can be explained by the porous structure lability similar to carbon fiber sorbents.\(^{24}\)

Thus, it was found that the most effective and low cost method of treating water solutions containing 2,4-D is using mesoporous sorbents derived from rice processed products.

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**Table 3. Results of the sorption isotherm equations by Henry and Freundlich approximations.**

<table>
<thead>
<tr>
<th>EQUATION</th>
<th>LINEARIZED FORM</th>
<th>(K_m/C_m)</th>
<th>(\Delta G) (J mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Henry</td>
<td>(y = 0.4019,x)</td>
<td>0.4019</td>
<td>2220</td>
</tr>
<tr>
<td>Freundlich</td>
<td>(y = 0.9141,x – 0.8575)</td>
<td>0.4242</td>
<td>2089</td>
</tr>
</tbody>
</table>

---

**Figure 3.** Residual concentrations of (2,4-dichlorophenoxy)acetic acid at different ratios S:L.

**Figure 4.** Removal efficiency of (2,4-dichlorophenoxy)acetic acid.
Table 4 shows the comparative characteristics and the conditions for obtaining sorbents and the parameters of 2,4-D sorption by the sorbents from rice production wastes used in this study and other studies. It is difficult to compare our results with those of previous studies due to various reasons.\(^\text{12,13}\) First, the sorption studies were carried out at different concentrations of 2,4-D aqueous solutions. Second, the control methods of pesticide content were different. Third, the sorbents were prepared by different methods.

**Conclusion**

The sorption efficiency of 2,4-D from model aqueous solutions at 1 \(\mu\)g \(\text{L}^{-1}\) concentration of carbon- and silicon-containing sorbents of different nature was defined. It was observed that the most effective sorbent is a carbon sorbent of “Sibunit” brand. Sorbents based on rice production wastes (husk and straw) removed 2,4-D with an efficiency of 23%–35% and can be used for posttreatment sorption of natural waters.

The sorption efficiency of 2,4-D in all groups of the sorbents depends on the pore diameter, which varies in the range of 4.2–205.1 nm. The most effective sorbents have a mesoporous structure, including precipitated silicon dioxide from rice husk and straw, potassium aluminum silicate from rice husk, pulp from rice husk, and rice husk itself.

It was found that interaction of the sorbate with the surface of the precipitated silicon dioxide from rice husk was dispersive in the investigated concentration range.

**Author Contributions**

Conceived and designed the experiments: ODA and LAZ. Analyzed the data: NPM and VGR. Wrote the first draft of the manuscript: ODA. Contributed to the writing of the manuscript: MAT. Agree with manuscript results and conclusions: ODA, NPM, and VGR. Jointly developed the structure and arguments for the paper: AAK and AEP. Made critical revisions and approved final version: LAZ. All the authors reviewed and approved the final manuscript.

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