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Adsorption of Glyphosate on Carbon-Containing Materials

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Abstract—A study is performed of the adsorption of glyphosate on carbon-containing materials obtained from pyrolysis products of sugar cane waste and commercial coconut activated carbon. The adsorption capacity of the materials with respect to glyphosate was determined using a variety of experimental models. The obtained data indicate the adsorption of glyphosate on the samples occurs due to chemical interaction with the adsorbent surfaces.

INTRODUCTION

The use of pesticides and herbicides in insect and weed control is a conventional way of increasing crop yields. The demand for herbicides and pesticides in agriculture grows every year. At the same time, the negative effect of modern chemicals for protecting plants should be reduced during their development. An ideal herbicide must meet several requirements: it should be effective in relatively low doses, have a quick effect on weeds, and eventually decompose into relatively simple chemical compounds. Many herbicides (including glyphosate), however, do not meet this standard, so their regular use can contaminate soils and adjacent environments.

Glyphosate is one of the most common and widely used herbicides. Glyphosate (*N*-(phosphonomethyl)-glycine, $C_3H_8NO_5P$) is a derivative of a phosphonic acid and is soluble in water (10.5 g/L). Glyphosate enters water through careless transportation in open containers or improper storage and use. This has a large negative effect on aquatic biota, phytoplankton, and periphyton [1−3]. Glyphosate is a carcinogenic compound (hazard category 2A), according to data from the World Health Organization's International Agency for Research on Cancer (IARC) [4]. Glyphosate products thus require special care and attention.

Ways of removing glyphosate from water can be conditionally divided into physical (straining, settling, filtration (centrifugal and otherwise), and ultraviolet treatment); chemical (neutralization, oxidation, and reduction); physicochemical (flotation, sorption, extraction, ion exchange, electrodialysis, reverse osmosis, and thermal); and biological (biological ponds, filtration fields, biofilters, aeration tanks (oxytanks), and digesters). Each way of removing glyphosphate traces from aqueous media includes many specific options in the purification process and the design of its hardware. It should be noted that water purification is considered a complex process with fundamentally different ways of achieving maximum efficiency to remove harmful compounds. It is known that herbicide can bond with organic matter in the soil or its clay fraction. This lowers the concentration of the herbicide in the soil and thus its toxicity. It is known that glyphosate can lose its herbicidal properties due to adsorption on mineral or organic compounds when it enters the soil. Glyphosate bounds most strongly to the inorganic components of the soil (i.e., clay particles and aluminum and iron oxides) [5−9].

Some studies show that the adsorption of an herbicide correlates negatively with soil pH. This is because an increase in pH can raise the negative charge of both the surface of the soil particles and glyphosate molecule, which weakens adsorption [10, 11].

Despite the vital role of the soil's mineral components, the organic part is also of great importance in the adsorption of glyphosate. Studies of the sorption of glyphosate on seven purified fractions of soil humus showed that their aromatic components (presumably phenolic groups) have a strong effect. The organic part
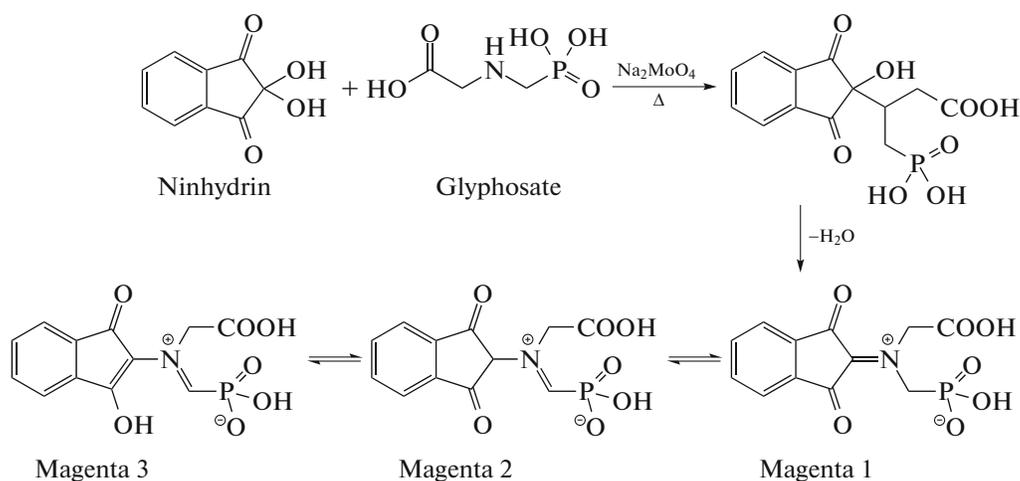
Fig. 1. Reaction between glyphosate and ninhydrin in the presence of sodium molybdate.

plays a more important role in the sorption of glyphosate in sandy soils than in clayey sediments. The desorption of glyphosate from humus, however, proceeds faster than from amorphous iron and aluminum oxides [12]. The preservation of crop residues in a field also reduces the mobility of glyphosate and increases its half-life [13].

Describing in detail the adsorption of a herbicide in water and soil is a necessary stage of studying its behavior in the environment, since the bonding of a herbicide largely determines its ability to spread and decompose. Experiments are performed in which a certain mass of an adsorbent is in equilibrium with a known volume of a solution with a certain concentration of adsorbate. The equilibrium concentration of adsorbate thus describes the adsorption process. The time required to attain equilibration can be from 2 to 48 h. The soil (adsorbent)−solution ratio is usually 1 : 0.3 to 1 : 20. Such studies are performed on 4−6 different initial herbicide concentrations.

Numerous studies indicate that the degradation of glyphosate in the soil can be described with a two-phase model of first-order kinetics [14−17]. The amount of the substance adsorbed in the soil is found from the difference between the initial and equilibrium concentrations. The experimental results are represented in the form of an adsorption isotherm showing the ratio between the amount of the substance adsorbed per unit mass of the adsorbent and the equilibrium concentration of the adsorbate.

There are several types of adsorption isotherms. An S-type is observed when the molecules of a solute are monofunctional, and there is competition between the adsorbent and the solvent for the bonding sites. An L-type isotherm corresponds to sorption in the form of a monomolecular layer, and sorption becomes more difficult as the sorption sites are filled. The H-type corresponds to strong affinity of a sorbent for a sorbate, and the solute is almost completely sorbed from the solution. Finally, the C-type characterizes a linear or near linear adsorption isotherm and is observed when the substance easily penetrates into the sorbent.

L- and C-type isotherms are often observed during the adsorption of herbicides. The Langmuir equation is used to describe isotherms in the first case; the Freundlich one, in the second.

The bonding of glyphosate to clay soil has been thoroughly studied. The adsorption of glyphosate in an aqueous environment, however, requires additional studies for the development of new adsorbents and more modern procedures. In this work, we develop carbon-containing materials obtained via the pyrolysis of sugar cane waste, and study the adsorption of glyphosate in a model aqueous solution. The pyrolysis of sugar cane was described thoroughly in [18]. Sugar cane bagasse carbonizate (BC) and chemically activated (ABC) samples obtained under identical conditions are used to study the adsorption characteristics. The waste was impregnated earlier with a 1 M potassium hydroxide solution. Commercial coconut activated carbon CAC-A (CAC) was used as a standard.

EXPERIMENTAL

The sorption capacity of experimental materials with respect to glyphosate was found using model monocomponent solutions. The initial concentration of glyphosate was 2−16 mmol/L (0.338−2.704 g/L). The concentration of glyphosate was determined via spectrophotometry with a ninhydrin solution at wavelength $\lambda = 570$ nm [19−23]. Figure 1 shows the reaction between glyphosate and ninhydrin in the presence of sodium molybdate.
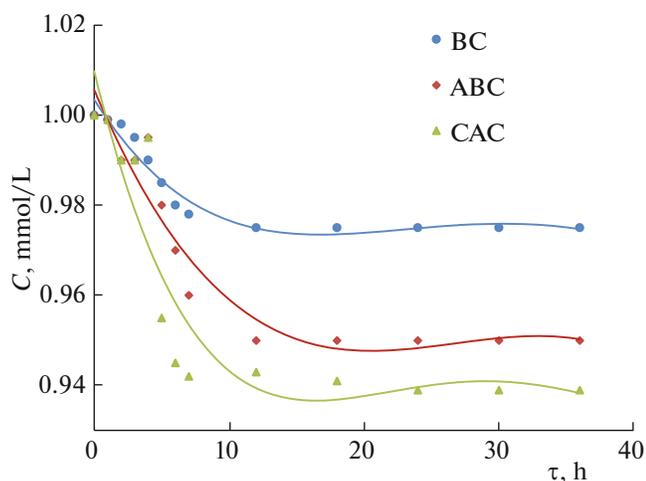
Fig. 2. Dependences of the residual concentration of glyphosate in a solution (C) and the contact time (τ) for BC, ABC, and CAC adsorbents.

RESULTS AND DISCUSSION

Figure 2 shows the ratios between the residual concentration of glyphosate in the solutions and the contact time for three sorbents: BC, ABC, and CAC.

The data show that the equilibrium in the adsorbent–adsorbate–solvent system was reached within 6 h for all of the experimental samples. The parameters of the adsorption for the resulting sugar cane bagasse carbonizate are comparable to those of commercial coconut activated carbon CAC-A (0.942 mmol/L). When it was impregnated with a 1 M potassium hydroxide solution, adsorption reached 0.956 mmol/L.

Figure 3 shows the isotherms of glyphosate adsorption on the test materials. The shape of the isotherms suggests that the sorption of glyphosate on these samples was limited to the formation of a monolayer.

Table 1 shows the isotherm parameters obtained upon approximation of the experimental data with the Langmuir, Freundlich, and Dubinin–Radushkevich models.

The correlation coefficients (Table 1) show that the adsorption of glyphosate on the samples is best described by the Langmuir equation (the correlation coefficients are the highest) and (to a lesser extent) the Dubinin–Radushkevich model. The empirical Freundlich equation is the least applicable to describe the experimental adsorption data (the correlation coefficients are the lowest).

The results agree with one another comparatively well, despite the ambiguous description of experimental data by the different models of adsorption. The Langmuir model data show that the CAC sample (0.2714 mmol/g) had the greatest sorption capacity with respect to glyphosate (Q_L), while the BC sample (0.2330 mmol/g) had the poorest one. The same sorption capacities were obtained using the Dubinin–Radushkevich equation (Q_{DR} value). We obtained the same result with the Freundlich equation: the activated carbon CAC-A had the greatest sorption capacity, and BC had the poorest.

The Langmuir and Freundlich models are widely used to describe processes of adsorption. At the same time, however, they have a considerable shortcoming: they lack any data on a mechanism of the adsorption process. On the other hand, the K_{DR} parameter is introduced in the Dubinin–Radushkevich model (equation), allowing us to study the forces of sorbent–sorbate interaction, since constant K_{DR} and the energy of adsorption are associated by the equation
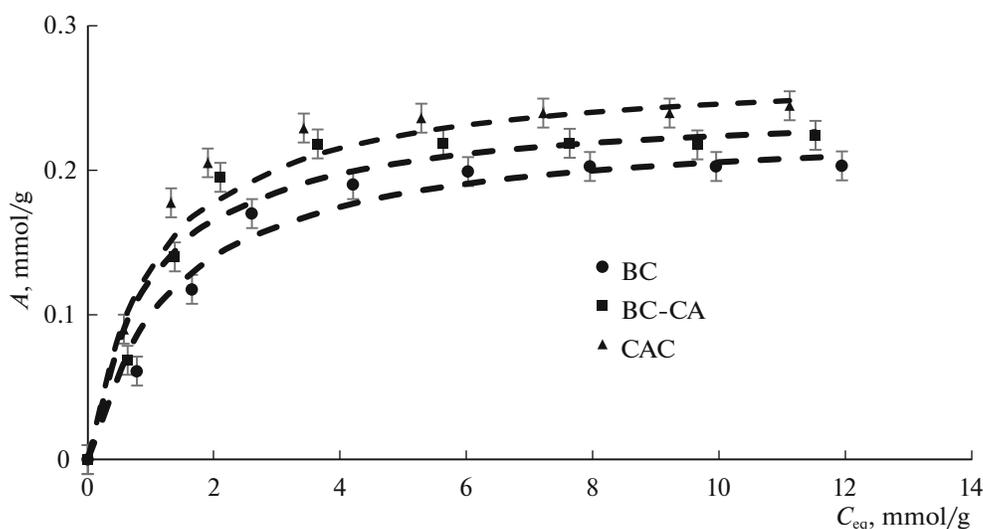

Fig. 3. Adsorption isotherms of glyphosate on experimental materials: (*1*) BC, (*2*) BC-CA, and (*3*) CAC. A is a specific adsorption and C_{eq} is the equilibrium concentration.

Table 1. Parameters of Langmuir, Freundlich, and Dubinin−Radushkevich adsorption equations

Sample	Langmuir model			Freundlich model			Dubinin−Radushkevich model			
	K_L	Q_L	R^2	K_F	$1/n$	R^2	K_{DR}	Q_{DR}	E_{ad}	R^2
BC	0.7504	0.2330	0.9829	0.0904	0.4056	0.7891	6×10^{-9}	0.4891	9.13	0.8423
ABC	1.0278	0.2453	0.9904	0.1102	0.3577	0.7629	5×10^{-9}	0.4978	10.0	0.8133
CAC	0.9531	0.2714	0.9917	0.1179	0.3739	0.7942	5×10^{-9}	0.5514	10.0	0.8464

K_L in L/mmol; Q_L in mmol/g; K_F in $mmol^{1-1/n}L^{1/n}/g$; K_{DR} in mol^2/J^2; Q_{DR} in mmol/g; and E_{ad} in kJ/mol.

$$E_{ad} = (2K_{DR})^{-0.5}. \quad (1)$$

If the energy of adsorption is 8−16 kJ/mol, we must assume that adsorption proceeds via chemical interaction with the adsorbent (chemisorption). If the energy is less than 8 kJ/mol, we may assume that adsorption is predominantly physical [24]. The adsorption energies E_{ad} calculated for the Dubinin−Radushkevich model (Table 1) are more than 9 kJ/mol. We may conclude that the adsorption of glyphosate on the carbon-containing materials was due to chemical interaction with the adsorbent.

CONCLUSIONS

Studies show that carbon-containing materials obtained from plant raw materials have comparatively high adsorption capacity with respect to glyphosate. The material obtained via joint pyrolysis of sugar cane bagasse waste with crushed clay appears to be a fairly effective adsorbent of glyphosate from water. When the carbonizate is impregnated with a 1 M potassium hydroxide solution, we can achieve adsorption characteristics (0.956 mmol/L) comparable to that of commercial coconut activated carbon CAC-A (0.942 mmol/L). According to our data, the time required to reach equilibrium in the glyphosate−solvent−adsorbent system is no more than 6 h.

FUNDING

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