

## Investigation of Hydrolysis Lignin for the Purpose of Its Possible Use as a Land Reclamation Sorbent for Rehabilitation of Soil Polluted with Radionuclides

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### Abstract

Sorption properties of various kinds of hydrolytic lignin – neutralized, acid, lignin from dumps – toward  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  radionuclides are investigated. It is shown that neutralized lignin and lignin from dumps much better sorb  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  than the acid lignin does. The major part of sorbed ions (40–58 %) does not desorb and is present in non-exchangeable fixed form. Lignin from dumps is characterized by the maximal distribution coefficient, which allows one to consider this material as the most promising material for use as a land reclamation sorbent.

### INTRODUCTION

Hydrolytic lignin (HL), a large-scale waste product of hydrolysis yeast production, occupies an essential place in the total amount of the industrial wastes in a number of the FSU countries. For instance, in the Republic of Belarus alone the amount of HL wastes accumulated in dumps by present is more than 6 million tons.

The problem of using HL arose simultaneously with the establishment of hydrolysis production and still remains urgent, because only insignificant part of lignin finds practical application. A large number of scientific works and reviews deal with the problem; many proposals concerning the application of HL in various areas of national economy have been made [1, 2, etc.]. The most important industrial area in which a broad practical use of HL may be possible is agriculture.

At present, the main problem of agricultural land tenure is a decrease in the resources of humus in soil and the lack of high-quality organic fertilizers. In some regions of Belarus, where humus-lean sod-podzol soil prevails, 15

to 20 t/ha of organic fertilizers are to be introduced into soil in order to maintain self-supporting humus balance of soil [3]. Conventional organic fertilizers used for this purpose (manure, bird dung, peat) cannot essentially fill up the deficit of humus in soil, so it is necessary to use also other sources of organic raw material, including the secondary material resources. Large-scale HL wastes can be considered as belonging to these resources.

Substantial experience has been accumulated by present in the use of HL as a component of organic fertilizers and organomineral mixtures. Many works reviewed in [4–6] demonstrated the participation of HL in humus formation, the effect of its complex-forming properties on the regime of plant nourishment, on the soil microflora. The introduction of HL into soil improves its structure, increases its absorption capacity and therefore increases its fertility. It is known that humification of HL in soil occurs much slower in comparison with usual organic fertilizers, so its use can give a prolonged positive effect [7].

The main problem of the use of HL as an organic fertilizer is connected with its increased acidity and low content of nutrients. The introduction of a large amount of acid lignin results in a sharp decrease in the concentration of nitrates in soil, which has a negative effect on the development of plants and on the crop capacity of agricultural plants, so it is better to use lignin after preliminary neutralization and enrichment with nutrients.

At present there is a number of suggestions and technological decisions concerning neutralization of the increased acidity of lignin. It is proposed to neutralize HL with dolomite powder [1, 8], lime milk [9], wood ash [10], ammonia [11, 12]. It should be noted that, according to the data of [13], the acidity of HL somewhat decreases after storage in dumps for a long time, which allows one to use it as an organic fertilizer without additional treatment.

There are different methods to obtain organic fertilizers and organomineral mixtures based on HL. The nutrient value of these fertilizers may be increased by adding organic and mineral substances and such components as, for example, phosphorite powder, calcium-containing salts, ammophos, potassium chloride, defecation mud (a waste product of sugar production from white beet) [14–17], *etc.*

The simplest way to obtain fertilizers from HL is its preliminary composting reproducing the natural process of decomposition and humification of wood. There are many suggestions to compost HL with bird dung, manure and peat [1, 4, 5, 9, *etc.*]. The duration of compost maturing is from several months to a year or more. As a result of processes taking place during the storage of HL in heaps, humus substances are formed; they promote improvement of the physicochemical properties of soil. It is also stressed that these fertilizers are similar in efficiency to the peat-manure compost.

However, in spite of a definite positive experience in the use of lignin-containing fertilizers and composts based on HL, the low technological and economical efficiency of their application should be pointed out, along with essential transportation and labour expenses, and the primitive character of the technology of obtaining HL-based fertilizers.

The use of HL to solve ecological problems and first of all to carry out a set of works aimed at rehabilitation of the soils of Belarus polluted with radionuclides [18] becomes more and more important nowadays. The high content of organic matter, large specific surface and the capillary porous structure of HL allow assuming its high sorption capacity with respect to radionuclides and the possibility of using HL as components of land reclamation sorbents for the rehabilitation of soil polluted with radionuclides. For this purpose, we carried out investigations of the physicochemical and sorption properties of HL with respect to cesium and strontium radioactive isotopes.

## EXPERIMENTAL

The subjects of investigation were HL samples, from the Bobruysk and Rechitsa hydrolysis plants, of different kinds: acid (after hydrolysis), neutralized, and directly from dumps.

The physicochemical properties of HL were determined in agreement with the technical requirements of the Republic of Belarus (TU 00479190.005–98 and TU 00479190.001–96). Investigation of the sorption characteristics of HL samples with respect to  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  isotopes was carried out according to the procedure known in radiation chemistry [19] under static and dynamic conditions.

To study sorption of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  under static conditions, weighed portions of the samples were saturated with radioactive chloride solutions of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  with the activity of 376.41 and 382.33 Bq/ml, respectively, for 2 and 30 days of interaction at the solid to liquid phase ratio equal to 1 : 4. Desorption of the absorbed ions under the dynamic conditions was carried out by consecutive washing with the portions of 0.1 M KCl solution (for  $^{137}\text{Cs}$ ) and 0.05 M  $\text{CaCl}_2$  (for  $^{90}\text{Sr}$ ). Additionally, desorption of the residual radionuclides from the samples was carried out under static conditions with 0.5 M KCl and 0.25 M  $\text{CaCl}_2$  solutions, respectively, and similarly with 0.1 M  $\text{HNO}_3$  solution.

In order to characterize sorption of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in the samples under investigation, we used

TABLE 1

Concentrations of water-soluble and exchangeable cations in HL samples

Sample (sampling site)	pH <sub>KCl</sub>	Cation concentration*			
		K <sup>+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>
Acid (Bobruysk)	3.9	0.08/0.09	3.4/3.08	28.94/32.63	0.26/0.49
Neutralized (Bobruysk)	7.8	0.09/0.09	6.96/4.15	66.17/138.52	0.65/0.61
Acid (Rechitsa)	2.4	0.09/0.2	0.18/0.18	4.42/11.73	0/0.22
Neutralized (Rechitsa)	7.0	0.09/0.79	0.26/0.04	16.82/72.36	0.32/0.26
From dumps (Rechitsa)	4.5	0.13/0.15	0.37/0.08	2.59/6.54	0.11/0.12

\*The first value is the concentration of water-soluble cations, mol/l; the second – of exchangeable cations, mg-eq/100 g.

the distribution coefficient  $K_d$  between the solid and liquid phases, which was calculated on the basis of a decrease in the activity of the initial solution of an isotope:

$$K_d = ((a_0 - a_1)/a_1)(V/d) \quad (1)$$

where  $a_0$ ,  $a_1$  are the activities of solution before and after sorption;  $V$  is solution volume;  $d$  is the weighed portion of adsorbent.

## RESULTS AND DISCUSSION

The main indices of suitability and value of the raw material for use as a component of organomineral mixtures and sorbents are the content of nutrient elements (N, P, K) and C : N ratio. An important role in cation-exchange processes in obtaining land reclamation sorbents is played also by such elements as K and Na, Ca and Mg – the exchange analogues of <sup>137</sup>Cs and <sup>90</sup>Sr radionuclides.

Hydrolysis lignin contains up to 95 % of the organic matter, but nitrogen and phosphorus are almost completely absent from it; the ratio C : N > 100, which is also an evidence of the lack of nitrogen. The content of water-soluble and exchangeable cations in different kinds of HL from the Rechitsa and Bobruysk plants is shown in Table 1.

One can see that the concentration of water-soluble K<sup>+</sup> in the samples under investigation is low (0.08–0.13 mol/l) and does not depend on the kind of HL. The samples of HL from the Bobruysk Hydrolysis Plant substantially exceed those from the Rechitsa Hydrolysis Plant in the concentrations of other water-soluble cations. As one should expect, the highest concentration of water-soluble Ca<sup>2+</sup> (66.2 mol/l) is characteristic of the HL samples neutralized with lime materials. The amount of K<sup>+</sup> is higher in the HL samples from the Rechitsa Plant; the maximal amount is observed in neutralized lignin (0.79 mg-eq/l).

TABLE 2

 Sorption-desorption of <sup>137</sup>Cs and <sup>90</sup>Sr radionuclides by HL samples

Sample (sampling site)	Radionuclide	Sorbed, %		Desorbed*, %		Fixed, %	
		2 days	30 days	2 days	30 days	2 days	30 days
Acid (Bobruysk)	<sup>137</sup> Cs	62	67	38/9	28/12	33	40
	<sup>90</sup> Sr	42	34	65/7	78/20	19	0
Neutralized (Bobruysk)	<sup>137</sup> Cs	75	68	31/2	27/4	47	49
	<sup>90</sup> Sr	58	74	22/12	14/18	53	58
Acid (Rechitsa)	<sup>137</sup> Cs	28	51	61/12	33/15	7	32
	<sup>90</sup> Sr	–	–	–/–	–/–	–	–
Neutralized (Rechitsa)	<sup>137</sup> Cs	69	73	36/5	34/2	39	44
	<sup>90</sup> Sr	68	70	22/11	30/15	38	44
From dumps (Rechitsa)	<sup>137</sup> Cs	76	76	34/5	38/2	41	39
	<sup>90</sup> Sr	76	78	38/14	37/11	38	42

\*The first value is for dynamic conditions; the second – for static ones.

As far as the concentrations of other exchangeable cations are concerned, a regularity is observed which is similar to that describing the concentration of water-soluble forms of these elements. The data on the concentrations of  $\text{Na}^+$ , an undesirable component from the viewpoint of agricultural chemistry, showed that the HL from the Rechitsa Plant is preferable for use as an additive to land reclamation sorbents. The capacity of cation exchange in HL, determined in dependence on the equilibrium concentrations of stable isotopes of cesium and strontium in solution, varies within the range 123–1434 mg-eq/l; the minimal values are characteristic of the samples of acid HL, while the maximal ones are exhibited by the neutralized HL from the Bobruysk Plant.

The results of determination of the sorption capacity of HL with respect to  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$

after the interaction with radioactive solutions for 2 and 30 days are shown in Table 2.

It follows from Table 2 that HL (except the samples of acid HL) sorbs both cesium and strontium radionuclides almost equally. Sorption after the establishment of sorption equilibrium is 68–78 %, among this amount 31–48 % of the sorbed ions were desorbed under dynamic and static conditions, and 39–58 % are present in non-exchangeable fixed state.

The samples of acid HL from the Rechitsa Plant are characterized by the least sorption and fixing ability with respect to  $^{137}\text{Cs}$ . For  $^{90}\text{Sr}$ , poorly reproducible results were obtained, which is likely to be due to the high acidity of these samples (pH 2.4). Investigation of desorption of  $^{90}\text{Sr}$  from the acid HL from the Bobruysk Hydrolysis Plant showed that almost the whole amount of sorbed strontium

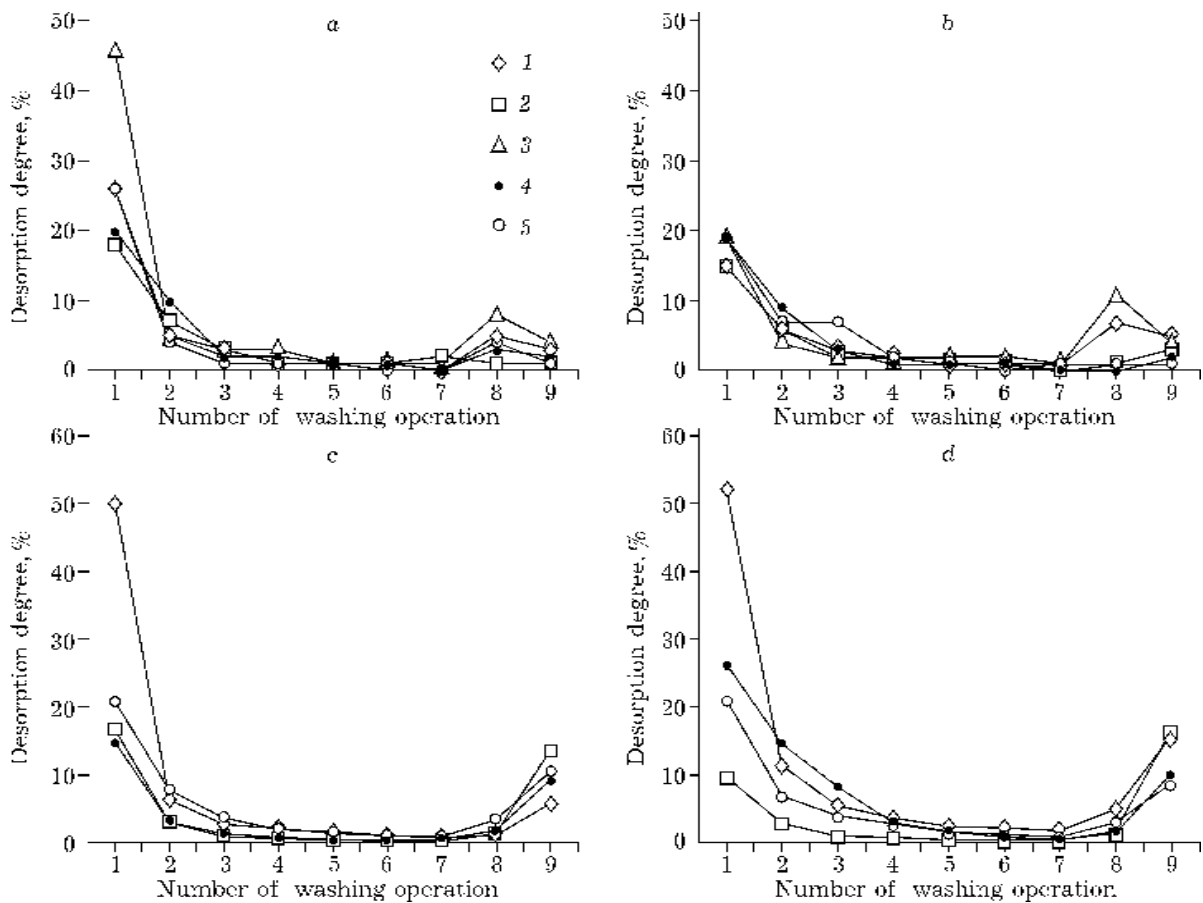


Fig. 1. Desorption of  $^{137}\text{Cs}$  (a, b) and  $^{90}\text{Sr}$  (c, d) sorbed by the samples of hydrolytic lignin after 2 (a, c) and 30 days (b, d) of interaction with the radioactive solution: 1 - acid sample (Bobruysk), 2 - neutralized (Bobruysk), 3 - acid (Rechitsa), 4 - neutralized (Rechitsa), 5 - from dumps (Rechitsa).

radioisotope is washed out with an increase in sorption time (30 days), which points to the prevailing surface sorption processes. The character of sorption of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in HL samples can be seen in desorption curves (Fig. 1).

One can see in Fig. 1, *a, b* that for all the HL samples at the first stages of  $^{137}\text{Cs}$  desorption we observe a sharp decrease in the activity; the highest peak of activity is characteristic of the acid HL from the Rechitsa Hydrolysis Plant. This allows us to conclude that the major part of cesium ions sorbed by HL samples is weakly bound easily enters isotope exchange. After 3–4 washing procedures the curves of  $^{137}\text{Cs}$  desorption from HL samples approach the abscissa axis, independently of the time of the interaction with the radioactive solution. Therefore, gradual fixation of  $^{137}\text{Cs}$  in HL with the transformation into a non-exchangeable fixed state occurs; this is also evidenced by the data on its additional desorption under static conditions; the sum with the dynamic data gives less than 50 %. The occurrence of a peak of activity under the dynamic conditions (during the interaction for 30 days) for the samples from dumps suggests some non-homogeneity of sorption sites, which may be connected with changes in the physicochemical properties of HL under the atmospheric action. It is known [13, 20] that long-term storage above ground or in dumps causes changes in HL due to chemical and biochemical oxidative processes; their depth depends on temperature and pH of the medium. The acidity of HL decreases in these processes (see Table 1), which allows one to use the HL from dumps without additional treatment.

The curves of  $^{90}\text{Sr}$  desorption from HL samples (see Fig. 1, *c, d*) except for acid HL from the Bobruysk Hydrolysis Plant exhibit a more uniform character independently of the time

of interaction with the radioactive solution in comparison with  $^{137}\text{Cs}$  desorption curves, which points to stronger binding of the absorbed  $^{90}\text{Sr}$  ions with HL.

Table 3 shows the distribution coefficients  $K_d$  for  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  isotopes determined from the ratios of the concentrations of distributing radionuclide in the solid phase to its concentration in the liquid phase. The  $K_d$  value determines the sorption ability of ions under the given conditions and provides evidence of the direction of sorption process depending on the kind of HL.

One can see from the data shown in Table 3 that HL samples sorb  $^{137}\text{Cs}$  better than  $^{90}\text{Sr}$ ;  $K_d$  values for  $^{137}\text{Cs}$  sorption are mainly 1.5–2 times larger for longer desorption (30 days). This is evidence that the HL samples are prone to  $^{137}\text{Cs}$  sorption; along with the rapid ion exchange at the initial stage, a slower process of irreversible character goes on with time. It should be noted that the largest distribution coefficients with respect to  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  are characteristic of HL from the dumps, which points to its good sorption capacity.

## CONCLUSIONS

Investigation of the sorption capacity of different kinds of hydrolysis lignin (acid, neutralized, and from dumps) with respect to cesium and strontium radionuclides revealed that HL, except the samples of acid lignin, sorbs  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  almost equally. Sorption value after 30 days of interaction with radioactive solutions varies within the range from 68 to 78 %; among this amount, 30–48 % of the sorbed ions get desorbed under dynamic and static conditions, and 39–58 % is present

TABLE 3

Coefficients of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  radionuclides distribution depending on the kind of HL

Sample (sampling site)	$K_d$ ( $^{137}\text{Cs}$ ), ml/g		$K_d$ ( $^{90}\text{Sr}$ ), ml/g	
	2 days	30 days	2 days	30 days
Acid (Bobruysk)	8.9	13.7	2.1	1.6
Neutralized (Bobruysk)	15.2	38.8	4.2	10.3
Acid (Rechitsa)	1.8	4.8	–	–
Neutralized (Rechitsa)	15.9	25.2	7.0	8.1
From dumps (Rechitsa)	42.5	44.2	11.8	14.9

in non-exchangeable fixed state. The maximal distribution coefficient of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  is observed for HL taken from dumps.

So, HL from dumps is the most promising material for use as a component of land reclamation sorbents and organomineral mixtures due to its physicochemical properties, including increased sorption and fixing capacity. The use of HL from dumps will allow one to develop highly efficient, economical, technologically available operations and methods of rehabilitation of soil polluted with radionuclides, and to provide efficient and reasonable solution of the problems connected with storage and utilization of large-scale wastes of hydrolysis plants.

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