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Application of Sorbent Obtained by Pyrolysis of Sewage Sludge for Biological Treatment of Waste Water

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ABSTRACT

The investigation of the behavior of the waste-water sludge of various chemical enterprises during thermal processing shows that effective carbon-mineral sorbents may be obtained by the pyrolysis. The conditions for the preparation of the raw material and the thermal treatment regime are regulated by the type of the reagent used for the conditioning of the sludge. The introduction of sorbents into the biological waste-water treatment system makes it possible to decrease sufficiently waste-water pollution with a simultaneous decrease in the amount of hardly oxidizable substances. The results of experiments in the biosorption regime have shown an improvement in the sedimentation properties of activated sludge and an increase in the degree of its compression.

Index Entries: Waste-water sludge; pyrolysis, carbon sorbents; waste water; biological treatment of waste water.

INTRODUCTION

The sediments formed at all the stages of waste-water treatment and accumulated every day include organic and mineral components. The expenses connected with the removal of sludge are constantly increasing *(1)*. In EEC countries, a question is discussed to prohibit the landfilling of these wastes. Therefore, all over the world, the problem of utilizing waste-water sediments and surplus activated sludge is urgent, in spite of some successful solutions to this problem. For example, over 30 different strategies to utilize sediments are proposed for the pulp and paper industry of the US *(2)*. Combustion is becoming an ever attractive alternative to landfilling *(2,3)*.

Already in the 1980s, various methods for the combustion of activated sludge with subsequent utilization of ash and slurries for the treatment of waste water of different enterprises from hardly oxidizable substances have been developed *(2–4)*.

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The thermal treatment of waste-water sludge is a promising approach for waste utilization both from the point of view of complete utilization of carbon-containing raw materials and production of valuable chemical products, such as sorbents.

The aim of the present work was to determine the application of the sorbents obtained by the pyrolysis of waste-water sediments of the pulp and paper industry for the biosorption treatment.

MATERIALS AND METHODS

This work deals with the characteristics of the sorbents obtained by the pyrolysis of the sewage sludge of the Arkhangelsk Pulp-and-Paper Mill. The pyrolysis was carried out in an industrial plant in a cyclone-type reactor and in a stationary layer reactor on a laboratory scale.

The sediments of the primary and secondary settlers were treated with coagulant (8–10% iron chloride solution and 18–25% slaked lime suspension) or flocculent Zetad-89 (1% in terms of dry substances) to improve the dewatering of sediments.

The sediments treated with coagulant (moisture content: 10.4–10.8%; ash content: 45.0–46.6%; iron content: 17.1–18.1 mg/g; calcium content: 211. 1–222.3 mg/g) were directed to the cyclone reactor. A mill fan was used to prepare an aerosuspension of the raw material. The carbonized product was removed from the reactor by hydraulic flushing.

The operating regime of the cyclone reactor is as follows:

Temperature in the loading chamber, °C	440–500
Temperature in the reactor, °C	800–900
Temperature in the gas bypass, °C	640–740
Reactor capacity in terms of raw material, t/h	4.5–4.8
Carbon yield, % from organic substances	14–16

The sediment treated with flocculent (moisture content: 9.2%; ash content: 22.5%) was pyrolyzed under laboratory conditions in the following carbonization regime:

Temperature in the reactor, °C	900
Pyrolysis duration, h	2
Consumption of steam gas for activation, g/min	0.4
Carbon yield, % from organic substances	13–14

The properties of products obtained are given in Table 1. The porous structure of the carbonized materials was characterized in terms of low-temperature sorption of nitrogen. Adsorption–desorption isotherms were taken on a "Sorptomatic-1900" device. The specific surface was calculated according to the BET method *(5)*, and the distribution of pore volumes were determined according to the theory of Dubinin–Radushkevich *(6)*.

The sorption properties of carbons were characterized in terms of iodine *(7)*, phenol *(8)*, and methylene blue *(9)*. The sorption of heptane vapor was determined by the exiccator method.

The sorbent obtained on the basis of sediments treated with coagulant was tested on the industrial scale for the biosorption process. The sorbent was milled, and the fraction with a particle size of 0.075–0.100 mm was used for biosorption. The following parameters were chosen to estimate the level of waste-water contamina-

Table 1
Characteristics of Sorbents
on the Basis of Waste-Water Sediments

Properties of sorbents	Sorbents prepared by: Pyrolysis of sludge + coagulant	Sorbents prepared by: Copyrolysis of sludge + flocculent and biomass waste
Sorption eapacity, mg/g		
Iodine	600–800	900–950
Phenol	225–280	300–350
Heptane	250–320	380–400
Methylene blue	350–400	370–420
Total volume of pores, g/cm^3 including:	0.55–0.90	0.65–1.05
Micro	0.10–0.30	0.30–0.40
Mezo	0.20–0.25	0.15–0.35
Macro	0.25–0.35	0.20–0.30
Specific surface, total, m^2/g	850–900	1100–1300
Characteristic radius of micropores, A	5.0	7.5
Ash, %	60–75	25–28

tion: the Chemical Oxygen Demand (COD) and the Biological Oxygen Demand (BOD_5). COD, determined by the bichromate method is the amount of oxygen (mg/L) required for the complete oxidation of the organic substances contained in the sample; BOD_5, determined by the dilution method, is the amount of oxygen (mg) required to oxidize the organic substances contained in 1 L of waste water during 5 d under aerobic conditions *(10)*. The relative error of the measurements was ±5%.

The study of the effect of sorbent on the sedimentation properties and the filtration capacity of activated sludge was carried out under laboratory conditions in accordance with the following method. A control tank was filled with recycled sludge (3.5 L) and waste water (7 L). Then, 35 mL of sorbent suspension were introduced. In this case, the sorbent dose was 1 g/L of the initial waste water (0.69 g/L in terms of the total volume of the aerated mixture; the ratio of the active sludge to the sorbent was 4:1 on dry matter). For the aeration, the air demand was 5 m^3/1 m^3 of waste water. When the experiment was completed, the mixture was allowed to settle in cylinders, and the rate of sedimentation was measured. The purified water was sampled after sedimentation. The filtration properties of the condensed sludge were determined after the decantation of water.

RESULTS

The study carried out in previous work *(11)* has shown that the thermal treatment of sludge in the pyrolysis regime is more attractive as compared to the combustion process. The pyrolysis temperature is lower than that required for sludge combustion and does not usually exceed 900°C. For pyrolysis, no surplus supply of air is required, which reduces the entrainment of solid particles from the pyrolysis zone. Apart from this, a considerable amount of nitrogen oxides is formed during the combustion of the sediments containing activated sludge and owing to the presence of the sulfates in the sediments, sulfide gas is formed. The lower treatment temperature during the pyrolysis process results in a decrease in the formation of the aforementioned toxic gases, improving the environmental acceptability of the process.

The economical attractiveness of pyrolysis, realized at a moisture content of the sediments of not more than 55%, manifests itself also for the possibility to create a closed thermal balance without the involvement of the exterior sources of heat at the expense of the combustion of pyrolysis gases *(12)*.

The application of a mineral coagulant for the treatment of sewage sludge in the pyrolysis process makes it possible to obtain carbon-mineral sorbents without additional steam-gas activation. The properties of these sorbents (Table 1) provide the opportunity for their use in different fields of applications. Varying the composition and dosage of coagulants, choosing the compositions of sediments, and varying the pyrolysis conditions, it is possible to vary, within a wide range, the properties of the carbonized materials to obtain sorbent as well as other products, such as alkaline-neutralizing agents, regenerated reagents for the treatment of sediments for the dewatering, as well as materials with magnetic sensitivity *(13)*.

On pyrolysis, waste-water sediments treated by flocculents yield sorbents with a lower ash content; however, the activation of the carbonized product with water steam becomes a necessary condition to form the porous structure. To obtain sorbents with the properties given in Table 1, we have carried out the copyrolysis of sediments and wood biomass.

It is beneficial to use the sorbents obtained by the pyrolysis of sediments primarily for the treatment of the waste waters of the enterprise where they are formed. In the present work, we used the model waste water of the Arkhangelsk Pulp-and-Paper Mill to investigate the influence of a sorbent on the biosorption process.

The studies carried out in the previous work *(11)* have shown that the introduction of the sorbent into the aerotank makes it possible to decrease the COD of the waste water. However, in this case, BOD_5 varies insignificantly. It is explained by the absence of the period of the adaptation of activated sludge to the sorbent introduced. It is known that the introduction of outside substances into the aerotank during the aeration period results in a reduction in the activity of activated sludge *(12)*. The study of the effect of the aeration time on the sludge and oxygen concentration has shown that, for the adaptation of the activated sludge with the sorbent introduced, it is necessary to carry out a continuous aeration for 20 h *(12)*.

The results of the variations in the COD and BOD_5 of waste water, over the course of the biological treatment, are presented in Fig. 1. The tests were carried out for 18 d, using both the sorbent under study and commercial powder-like coal (type OY-A, Russia). From the experimental data, it follows that the introduction of the sorbents under study to the aeration system has a positive influence on purification of water. The sorbents stabilize the biological treatment process and make it less sensitive to process upsets. For example, when the supply of air was decreased, an abrupt decrease in the activity of sludge in the experiment without sorbent took place (Fig. 1, 13th d). At the same time, in the presence of sorbents, a reduction in activity took place on a considerably lower scale.

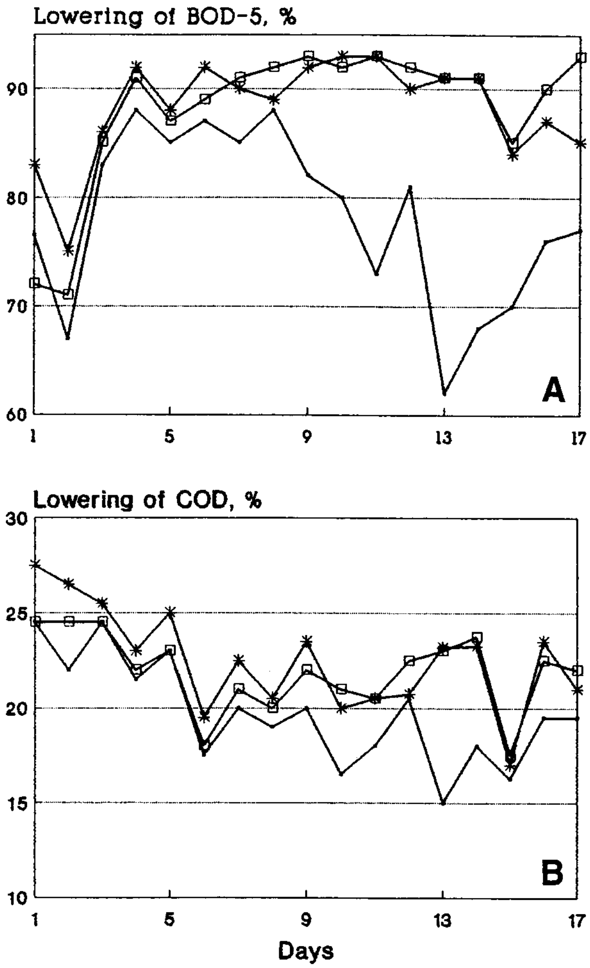

Fig. 1. Alteration of model flowing cleaning. (·) Without sorbent (□) sorbent from sludge + C (*) commercial coal.

The analysis of the experimental data shows that, on the introduction of the sorbent sample, the biosorption process proceeds even more effectively, as compared with the use of commercial coal.

On the 3rd, 10th, and 17th d from the beginning of the process, the kinetics of the COD and BOD_5 of effluents, as well as an increase in activated sludge in the course of the water aeration process for 20 h, were studied (Figs. 2 and 3). From the change in both the indices, the degree of removing contaminations after 3 d in the presence of sorbents is higher. This same trend is observed after 10 and 17 d. When comparing the effect of the commercial powder and the sorbent, it may be concluded that the adaptation process of activated sludge to the sorbent proceeds more slowly. However, when the process is over, the results of purification are better. The accretion of activated sludge during 20 h on the 3rd, 10th, and 17th d is characterized by curves in Fig. 4, showing that, on the 3rd d, the highest rate of increase is observed during the first 8 h for the experiment without sorbent or commercial powder addition. After 8 h from the beginning of aeration, a decrease in accretion takes place, which indicates the self-degradation of the sludge. In the experiment without sorbent or commercial powder the degradation after 8 h manifests itself more prominently. On the 10th and 17th d, during the first 8 h, an increase in sludge activity is greatest for the experiments in which serpent or commercial powder was added. On the 17th d, the highest increase is observed in the presence of the sorbent.

The characteristics of the variations in the compression degree, shown in Fig. 5, indicate that the introduction of sorbents to the aeration system improves the sedimentation properties of the surplus-activated sludge, which should promote the decrease in the removal of the suspended particles. The compressed surplus-activated sludge obtained in comparative experiments was subjected to filtration, simulating the conditions of the operation of a drum vacuum filter (Table 2).

As a result of the change in the filtration properties of the sediments containing the sorbent, the capacity of the vacuum filter is increased two to three times. In this case, the cake obtained had a lower moisture content, which reduced the energy and reagents for the drying process considerably.

The improvement in the sedimentation properties of the activated sludge at the introduction of a sorbent is very important for the technology with two-stage biological purification. A high removal of activated sludge from intermediate settlers to the second step of the biological treatment is a drawback of the existing technology.

The results of the experiments in the biosorption regime have shown that the introduction of sorbents into the aerotanks of the first step of the biological treatment results in the increase in the degree of the compression of sludge, respectively of tests without sorbent, and the decrease in the removal of the suspended particles from intermediate settlers. The decrease in the BOD_5 and COD indices of effluents at the first step, when sorbents are used, decreases the load on the activated sludge at the second stage, which results in the decrease in the sludge index determining the coagulant properties of the sludge.

DISCUSSION

The investigation of the behavior of the waste-water sludge of the Pulp-and Paper Mill at thermal processing shows that effective sorbents may be obtained by the pyrolysis method. The conditions for the preparation of the raw material and the regime of pyrolysis are regulated by the type of the reagent used for the pretreatment of the sludge: when an iron salt-based coagulant is used, the formation of the porous structure takes place owing to oxidation reduction reactions with the participation of an iron cation *(13)*, and no additional activation stage is required; when flocculent is used, an additional steam-gas activation stage is required, and copyrolysis of the sludge and wood biomass is necessary to obtain qualitative sorbents.

The introduction of sorbents into the biological waste-water treatment system makes it possible to decrease waste-water pollution in terms of the BOD_5 index by 50%, with a simultaneous decrease in the amount of barely oxidizable substances.

The results of experiments in the biosorption regime have shown an improvement ill the sedimentation properties of activated sludge and an increase in the degree of its compression. The introduction of the sorbent at the first step of the biological treatment decreases the load on the second step because of the decrease in the removal of suspended particles from intermediate settlers.

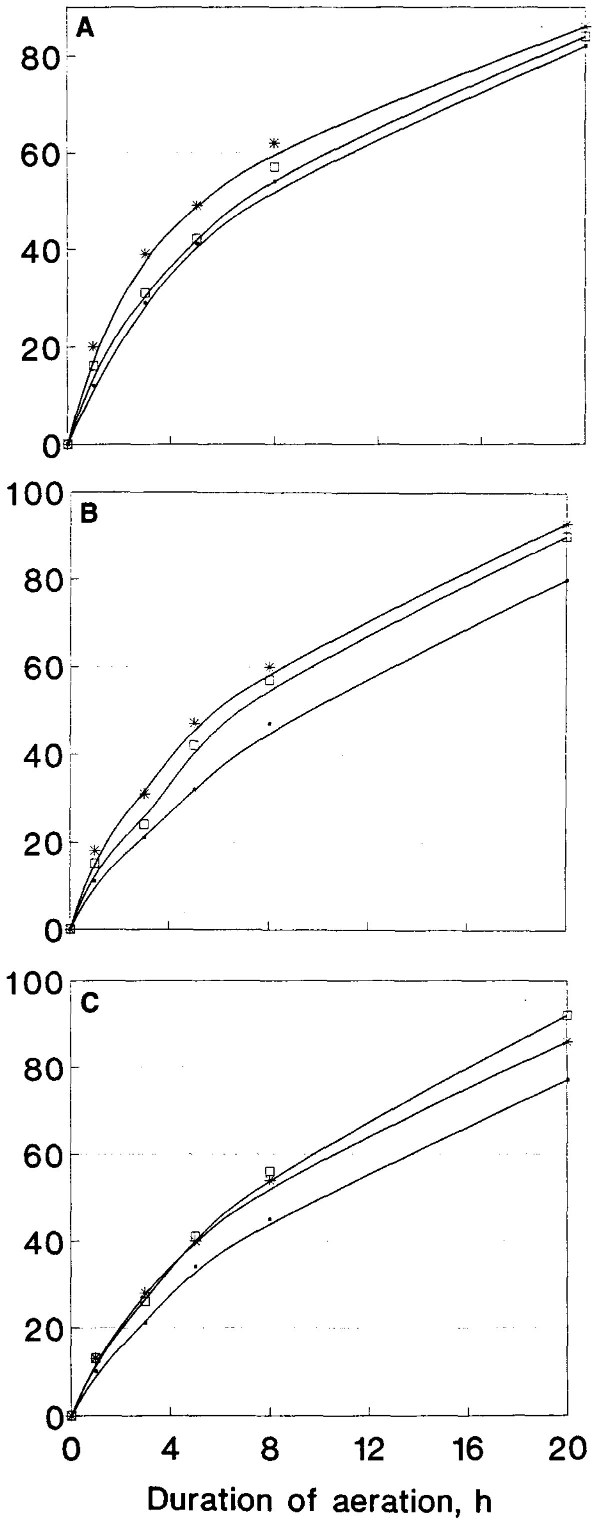

Fig. 2. Kinetic of flowing BCO-5 decrease (%). **(A)** 3 d **(B)** 10 d **(C)** 17 d (·) without sorbent, (□) sorbent from sludge + C, (*) commercial coal.

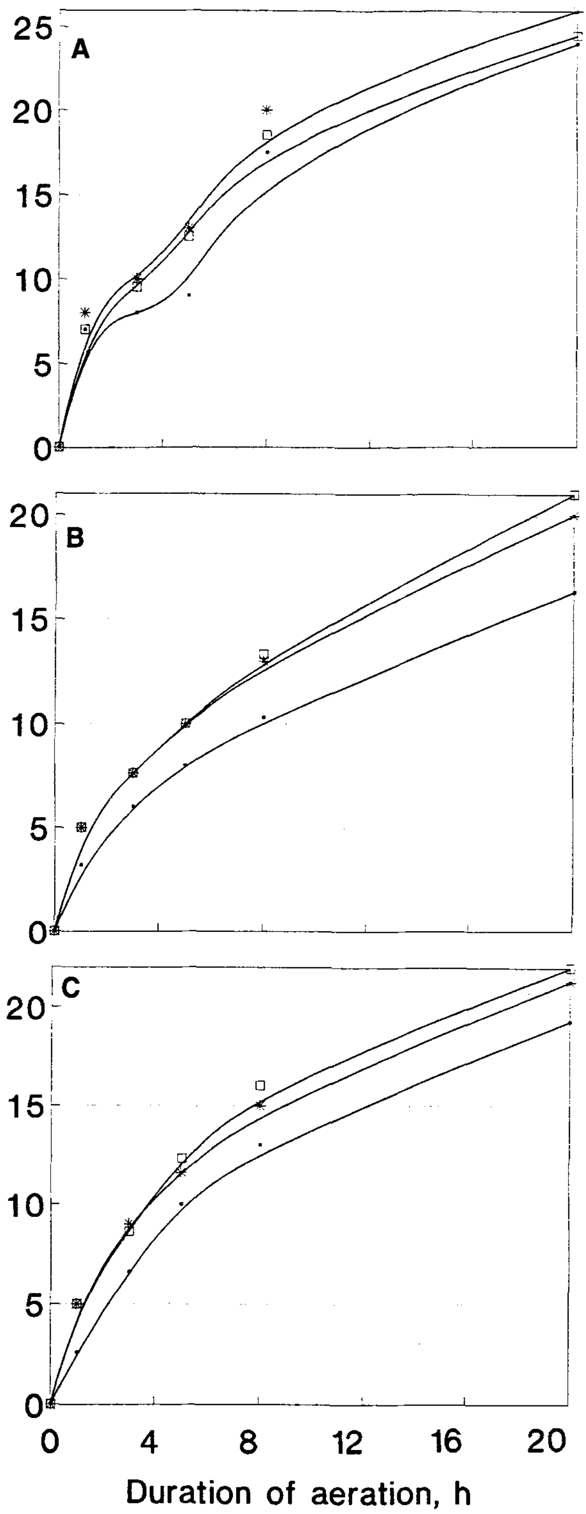

Fig. 3. Kinetic of flowing CCO decrease (%). **(A)** 3 d **(B)** 10 d **(C)** 17 d (·) without sorbent, (□) sorbent from sludge + C, (*) commercial coal.

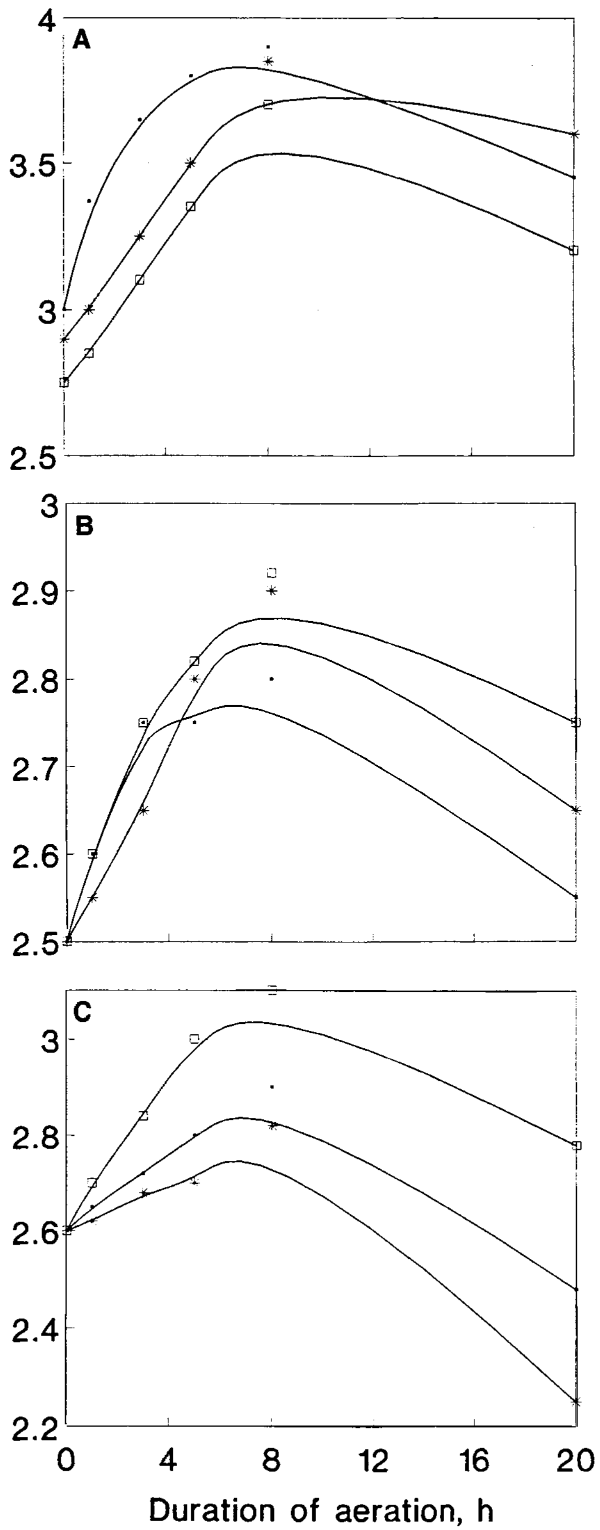

Fig. 4. Kinetic of increase of active sludge mass (g/L). **(A)** 3 d **(B)** 10 d, **(C)** 17 d (·) without sorbent, (□) sorbent from sludge + C, (*) commercial coal.

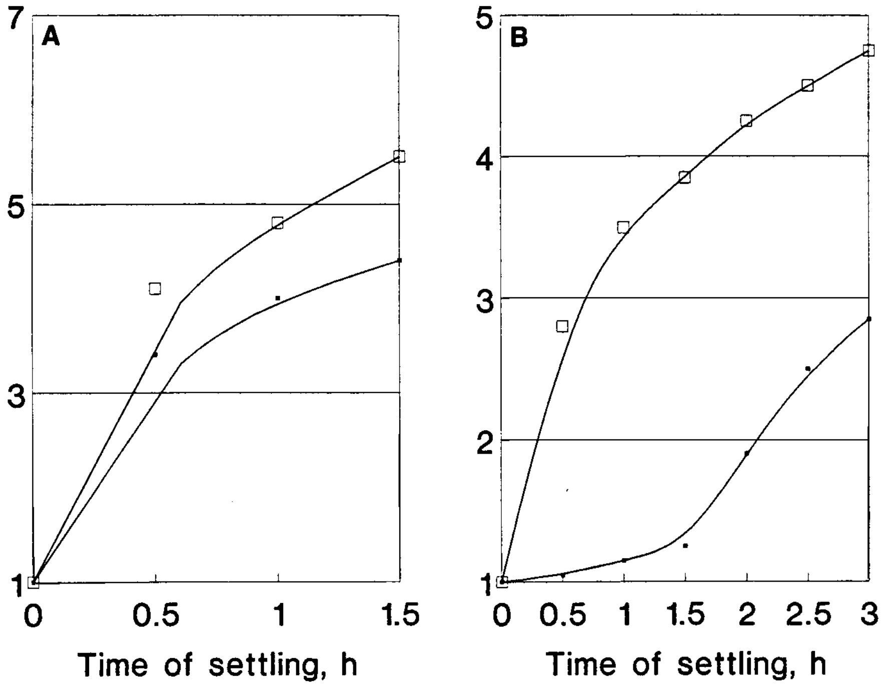

Fig. 5. Alteration of degree of condensation depending on time. **(A)** First step of biological cleaning **(B)** second step of biological cleaning (·) without sorbent (□) with sorbent.

Table 2
Filterability of Waste-Water Sludge

Stage of biological treatment	Amount of the sorbent, g/L of the aerated mixture	Concentration of condensed sludge, g/L	Filterability, kg/m^2 h	Moisture of the cake, %
1	0	11.1	4.1	78.6
	0.69	20.5	13.9	76.1
2	0	16.8	8.2	81.1
	0.69	23.6	14.4	77.4

The pyrolysis of waste-water sludge may be effective in producing sorbents that can be used to treat waste-water streams more efficiently. This will be pursued in more detail in future work.

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REFERENCES

1. Modell, M., Larson, J., and Sobezynski, S. S. (1992), *Tappi J.* **75(6)**, 195–202.
2. Gellman, I. and Wigand , P. (1994), Proceedings of the Second International Technical Conference PAPFOR '94, October 10–12, St. Petersburg, pp. 149–165.

3. Sell, N. Y. and Intosh, T. H. (1988), *Tappi J.* **71(3)**, 135–139.
4. Dybey, R. K. and Joshi, R. C. (1980), *Ind. Pulp and Pap.* **34(6)**, 13–17.
5. Gregg, S. J. and Sing, K. S. (1984), *Adsorption, Surface Area and Porosity*, Moscow, pp. 53–64.
6. Dubinin, M. M. (1967), *J. Colloid Interface Sci.* **23**, 487–491.
7. Kolishkin, D. A. and Miehailova, K. K. (1972), *Active Carbons*, Moscow.
8. Drozhalina, N. D. and Burlakova, N. O. (1974), *J. Appl. Chem.* **(2)**, 298–300.
9. USSR standard 4453-4474.
10. Lur'e, Yu. Yu. (1984), *Analytical Chemistry of Commercial Water Waste*, Moscow.
11. Bogdanovich, N. I., Kuznetsova, L., and Dobele, G. V. (1994), *Biomass for Energy and Industry*. 1216–1219.
12. Bogdanovich, N. I. (1989), *Pap. Ind.* **(10)**, 22,23.
13. Dobele, G. V., Bogdanovich, N. I., Dizhbite, T. N., Telysheva, G. M., and Osadshaya, T. N. (1993), *Cellulosic Materials for Selective Separations and Other Technologies*, Chichester, West Sussex, UK, pp. 194–205.