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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Influence of the Reagent Pretreatment of Wastewaters from Chemical Plants on the Efficiency of Their Biological Treatment

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Abstract—Structure formation in the flocculant–wastewater component system was studied by viscometry and IR spectroscopy. Statistical treatment of the experimental data revealed regular trends in the influence of the polymeric reagent on the efficiency of the biological oxidation of phenol, nonionic synthetic surfactants, and oxygen-consuming compounds as a whole.

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A characteristic feature of the operating biological wastewater treatment facilities is variation of the conditions of their functioning due to complication of the wastewater composition and to regular discharge of ecotoxicants and xenobiotics inhibiting biochemical processes. As a result, the quality of the treated wastewater ceases to meet the existing requirements. This primarily concerns wastewater from chemical plants. One of possible solutions of the problem is efficient pretreatment of industrial wastewater before biological treatment. At large amounts of wastewater, it is appropriate to use reagent pretreatment which, owing to its advantages, is widely applied in water treatment to recover coarse and colloidal impurities [1–3].

In contrast to the traditional approach, the goal of this study was to use macromolecular agents for recovering from wastewater mainly dissolved toxic and bioresistant compounds prior to delivering wastewater to the biological treatment unit. Such an approach requires finding an efficient method for evaluating the flocculating properties of the reagent used. In view of the specific features of the objects to be removed (water-soluble impurities) and of the high molecular weight of the flocculants, it is most appropriate to use for this purpose the viscometric method allowing prompt monitoring of the binding of the macromolecular reagent (MMR) with a wastewater component [4].

The goal of our experiments was to reveal regular trends in complexation in MMR–wastewater component systems and to examine the influence of the reagent pretreatment of wastewaters on the efficiency of their biological treatment.

In model tests, we used 0.1 and 5% solutions of modified gelatin [phthaloyl gelatin, PG, $M = 6 \times 10^4$] and of phenol, Oksanol, and Diproksamin. The latter compounds were chosen as control ecotoxicants, taking into account their prevalent content in basic wastewaters from organic synthesis plants.

EXPERIMENTAL

To confirm the complexation in the PG–wastewater component, we used viscometric and spectroscopic methods. The viscosities of solutions of individual compounds and their mixtures were determined at 25°C with an Ubbelohde viscometer with a capillary diameter of 0.73 and 0.86 mm.

To obtain data on the complexation mechanism, we examined the IR spectra of the individual compounds and binary mixtures based on them in the frequency range 400–4000 cm^{-1}. The spectra were recorded on a Specord 75-IR spectrophotometer from mulls in mineral oil and thin films. In the latter case, a polymer paste was uniformly applied onto a KRS-5 plate, with the subsequent drying at 45–50°C. Mathematical processing of the results was performed with Statgraphics Plus 3.0 program package.

Primary processing of the viscometric data involved comparison of the experimental curve with the hypothetical (additive) curve that would be obtained if there were no

Table 1. Conditions of maximal complexation in PG–wastewater component systems

System	Optimal component ratio	Extremum of η/Ση
PG–phenol	25:75–75:25	0.54
PG–Oksanol	20:80	0.59
PG–Diproksamin	35:65	0.63

interaction in the binary system. We revealed deviation of the experimental curves from the additive curves, suggesting formation of associates. Using the approach suggested by Tarasenko et al. [5], we revealed regions at which the complexation between the polymeric reagent and wastewater component is the most efficient (Table 1). As seen from Table 1, the most stable complexes in a broad range of component concentrations are formed in the PG–phenol system, as indicated by an almost twofold decrease in the viscosity η of the binary system relative to the additive value.

With synthetic surfactants, phthaloyl gelatin forms less stable associates in a narrow range of the ratios of the interacting components.

Whereas viscometric data allow qualitative detection of the structure formation in the systems and quantitative estimation, to certain extent, of the stability of the associates from the relative viscosity, vibration spectroscopy offers information on the binding mechanism and on participation of definite functional groups of PG and wastewater pollutants in the binding [6]. Taking into account the structure and properties of the pollutants under consideration, we can assume association by hydrogen bonding involving –C=O, –C–O–C–, –NH, and –OH groups.

The spectroscopic data for the individual substances and their binary systems are given in Table 2.

These results provide one more evidence for flocculant–ecotoxicant interactions, which are manifested in shifts of vibration frequencies of functional groups of the interacting compounds and in changes in the intensities of absorption bands of the bonds involved in the complexation.

For example, in the PG–phenol system the Amide I and Amide II bands are observed as a broad unresolved band at 1600–1550 cm–1. In the spectra of the binary systems consisting of PG and a synthetic surfactant (Oksanol, Diproksamin), these bands were resolved, with a certain high-frequency shift of the carbonyl band. The C–O–C stretching vibration bands of the synthetic surfactants studied remained essentially unchanged.

Table 2. Characteristic vibration frequencies of functional groups of interacting components and their compositions

Bond (group)	ν, cm^{-1}	Bond (group)	ν, cm^{-1}
Phthaloyl gelatin		PG–Phenol (35:65)	
–O–H	3340	–O-H (–N–H)	3313
(–N–H)	1630	Amide I	1600–1550
Amide I	1550	Amide II	
Amide II			
Phenol		PG–Oksanol (20:80)	
–O–H	3345	–O–H (–N–H)	3364
Oksanol		Amide I	1690
–O–H	3402	AmideII	1577
–C–O–C–	1120	–C–O–C–	1120
Diproksamin		PG–Diproksamin (25:75)	
–O–H(–N–H)	3495	–O-H (–N–H)	3304
–C–O–C-	1150	Amide I	1666
		Amide II	1530
		-C-O-C-	1156

For all the systems, the most significant changes in the spectrum were observed in the range 4000–3000 cm^{-1} corresponding to stretching vibrations of the hydroxy and amino groups. This is due to intermolecular interaction in the polymer–low-molecular-weight compound system, with rearrangement of the system of H bonds involving hydroxy and amino groups of the individual compounds.

Good agreement of the spectroscopic and viscometric data allows us to suggest a new approach to screening of reagents and prompt evaluation of their flocculating power toward specific dissolved or colloidal wasterwater pollutants. One more argument in favor of using the viscometric method is its simplicity. It does not require sophisticated equipment and is prompt and informative.

Experiments aimed to reveal regular trends in the effect of reagent pretreatment on the biological treatment of multicomponent wastewaters were performed on an installation schematically shown in Fig. 1. The parameters of the mechanical and biological treatment processes in model tests (settling time, aeration time, concentration of dissolved oxygen, amount of active sludge, etc.) corresponded to those used in industry.

Experiments aimed to evaluate the efficiency of industrial wastewater pretreatment with the polyampholyte under dynamic conditions were performed as follows. Wastewater treated with a macromolecular reagent in the primary settling unit was fed to a 10-l model aeration tank containing an industrial culture of active sludge. Simultaneously we performed the control experiment

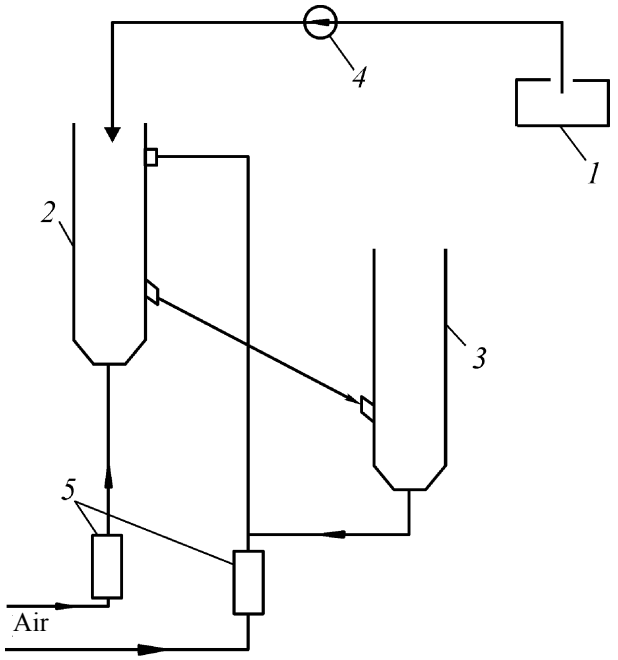

Fig. 1. Scheme of the flow-type installation: (*1*) primary settler, (*2*) aeration tank, (*3*) secondary settler, (*4*) dosing pump, and (*5*) rotameters.

without preliminary reagent treatment of the wastewater. The interval of the PG concentrations studied was 1–10 mg l^{-1}.

The quality of the purified wastewater (after mechanical and biological treatment) was monitored in all the experiments by the following parameters: chemical oxygen demand (COD) and content of phenols, nonionic synthetic surfactants (NSS), and suspended substances. Analytical determination of these parameters was performed by commonly accepted unified procedures [7].

The composition of industrial wastewaters in the experimental studies was varied within the following limits (mg l^{-1}): COD 900–1100, phenol 10–15, NSS 15–25, and suspended substances 150–200, which corresponded to real industrial conditions in the case of volley discharge of pollutants.

The efficiency of the reagent pretreatment was evaluated by the relative efficiency parameter E (%) characterizing the extent to which the pretreatment improved the control parameters after mechanical and biological treatment [8].

The results we obtained (Figs. 2, 3) unambiguously show that reagent pretreatment of industrial wastewaters to reduce their toxicity by removing, along with suspended substances, also dissolved toxic and bioresistant pollutants enhances the intensity of subsequent biochemical processes in the biological treatment unit.

The dependences obtained are nonlinear, and there is a certain optimal interval of phthaloyl gelatin concentration for removing a definite ecotoxicant or xenobiotic in the case of the volley discharge: 3–5 mg l^{-1}. In the mechanical treatment units, COD decreased on the average by 16%, and the concentrations of phenols, synthetic surfactrants (SS), and suspended substances, by 23, 17, and 33%, respectively (Fig. 2a). The positive result of changes in the wastewater composition is improved quality of the biologically treated wastewater with respect to all the examined parameters (Fig. 2b).

As compared to the control (no flocculant), reagent pretreatment substantially enhances the efficiency of the biological pretreatment of multicomponent wastewaters from organic synthesis plants: *E*, on the average, reached 40% for COD, 60% for phenols, and 33% for

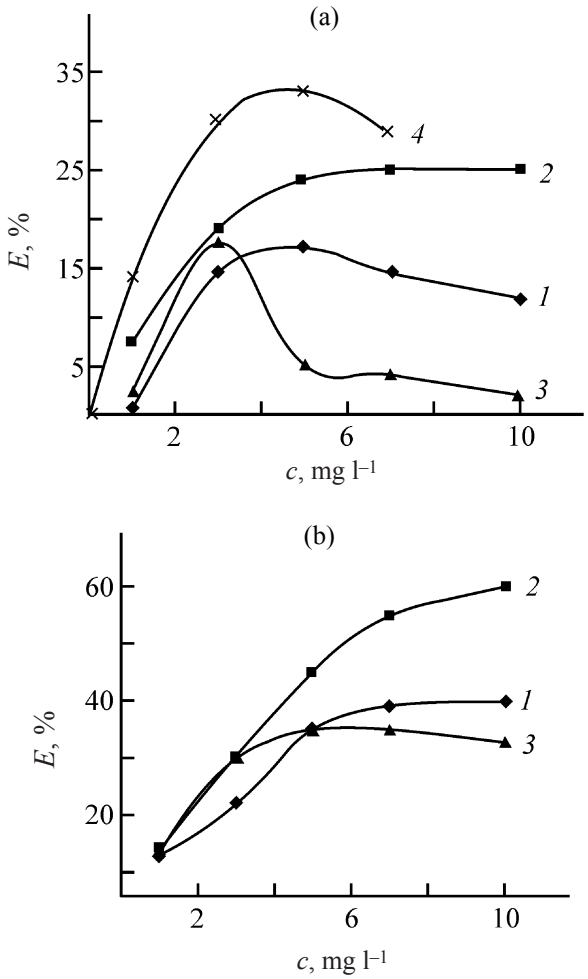

Fig. 2. Influence of the PG concentration c on the efficiency E of pollutant removal in (a) mechanical and (b) biological treatment units: (*1*) chemical oxygen demand, (*2*) phenol, (*3*) nonionic synthetic surfactants, and (*4*) suspended substances.

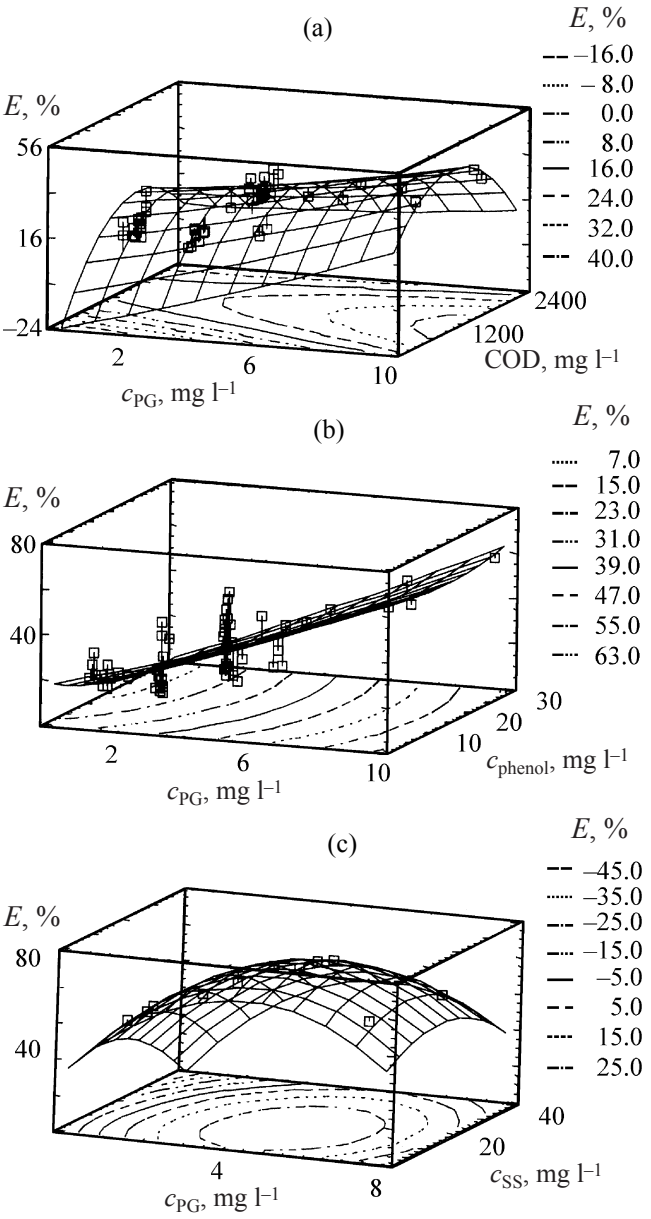

Fig. 3. Influence of the PG concentration c_{PG} and of (a) COD, (b) phenol concentration cphenol, and (c) synthetic surfactant concentration c_{SS} on the efficiency E of removal of the corresponding components.

NSS. Worsening of the flocculation conditions in the mechanical treatment unit at reagent dosage beyond the optimal range affects the quality of the purified wastewater as a whole, especially with respect to NSS. With an increase in the polyampholyte dosage, the efficiency of NSS removal in the mechanical settling unit drastically decreases, which leads to a decrease in the efficiency of the biological treatment with respect to this pollutant. With respect to phenol and COD, the efficiency of the biological treatment regularly grows with increasing PG concentration.

Systematization and generalization of the experimental data proved the validity of our approach to evaluating the performance of the polymeric reagent from changes in characteristics of only the initial chemically contaminated and biologically purified wastewaters.

In view of the multicomponent and variable composition of wastewaters, it seemed interesting to reveal general trends in the influence of the reagent pretreatment on the biological treatment of wastewaters from organic synthesis plants under different conditions of functioning of the biological treatment unit. To this end, we chose as mathematical model a regression equation in the form of a second-order polynomial function of a number of variables [8]:

$$y = b + \sum_{j=1}^{k} b_j x_j + \sum_{j=1}^{k-1} \sum_{l=j+1}^{k} b_{jl} x_j x_l + \sum_{j=1}^{k} b_{jj} x_j^2,$$

where y is the wastewater treatment efficiency with respect to the control parameters (%); b_j, coefficients of the regression equations; and x_j, concentrations of the corresponding pollutants or flocculant (mg l^{-1}).

High determination coefficients R are indicative of the good agreement of the experimental and calculated data and confirm the adequacy of the regression equations obtained (Table 3).

Graphic presentation of the dependences obtained allows evaluation of the influence exerted by the polymeric agent dosage, COD, and concentration of phenols and synthetic surfactants in the initial wastewater on the quality of the wastewater biochemically treated after pretreatment with phthaloyl gelatin.

Figure 3a shows that the dependence obtained for COD (general characteristic of wastewater pollution) is complex and has an extremum. The highest purification effects, at any examined dosage of phthaloyl gelatin, are observed at COD = 800–1200 mg l^{-1}. At higher COD, the purification becomes less efficient.

With increasing concentration of the polyampholyte, at a fixed COD value, the treatment efficiency regularly increases. The influence of the PG dosage is stronger for wastewaters with low and medium COD (200–600 mg l^{-1}). For the COD values typical of volley discharges (1600–2100 mg l^{-1}), an increase in the PG dosage from 1 to 10 mg l^{-1} leads to an increase in the treatment efficiency from 18 to 35% on the average.

Analysis of the dependence obtained (Fig. 3b) shows that the removal of phenols from industrial wastewater

in the presence of modified gelatin is noticeably affected by the flocculant dosage. The purification effect increases to 63% in the examined range of the polyampholyte and toxicant concentrations. The influence of the phenol concentration in the wastewater is less significant. At a low dosage of phthaloyl gelatin (3 mg l^{-1}), an increase in the toxicant concentration somewhat decreases the effect of the reagent. At high PG concentrations (8–10 mg l^{-1}), the trend is opposite. With SS, a parabolic dependence is observed (Fig. 3c), with a well-defined maximum at intermediate PG concentrations (5–7 mg l^{-1}). With an increase in the SS content in the wastewater to 30 mg l^{-1}, the purification effect remains essentially unchanged, reaching the limit of 13–16%.

The results obtained can be attributed to a change in the wastewater composition and to a decrease in the concentration of toxic and bioresistant components owing to their association with the polymeric reagent, followed by their removal before delivery to the biological treatment unit. A decrease in the flocculant solubility is apparently due to the fact that the macromolecule becomes more hydrophobic as a result of intermolecular binding of polar functional groups of PG with the wastewater components.

The nonmonotonic dependences obtained for COD and SS are due to the specific conditions of the polyampholyte complexation with the corresponding pollutants. In the PG macromolecule, there are numerous active centers capable of donor–acceptor interaction, including H bonding. Furthermore, relatively high molecular weight of the modified gelatin is favorable for the flocculating power. A decrease in the performance of the individual flocculant at a considerable increase in COD is apparently associated with saturation of the active centers of the macromolecules. With synthetic surfactants, the degree of their removal depends on the stoichiometry of the polycomplexes formed. As for phenol (a low-molecular-weight compound), according to the experimental data, in the range of the examined toxicant concentrations, the efficiency of its recovery is directly associated with the saturation of the active centers of the PG macromolecule.

CONCLUSIONS

(1) Conditions and mechanism of the complexation of phthaloyl gelatin with soluble toxicants in industrial wastewater are examined. The viscometric method shows promise for screening of reagents and for prompt evaluation of their flocculating power toward specific dissolved and colloidal wastewater pollutants.

(2) The flocculating power of phthaloyl gelatin was examined. It is possible and appropriate to use this reagent for decreasing the toxicity of multicomponent wastewater. Regular trends in the effect of the polymeric reagent on the quality of purified wastewater in mechanical and biological treatment units were revealed.

(3) Mathematical models of the biological treatment of industrial wastewater were constructed. These models allow prediction of the purified wastewater quality at increased loads and volley discharges of exotoxicants and bioresistant pollutants.

Table 3. Coefficients of the regression equation

Coefficient	COD	Phenol	SS
b_0	–23.574	17.8335	–6.71768
b_1	3.70012	3.88814	5.40717
b_2	0.0573522	1.10634	0.432321
b_{11}	0.0682659	0.074425	–0.468378
b_{22}	–0.0000191764	0.0202388	–0.0100837
b_{12}	–0.0014855	0.0473093	0.00616383
R, %	71.6074	75.8131	84.3844

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