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STUDIES ON WASTEWATER TREATMENT WITH APPLICATION OF FLOCCULANTS

An efficient application of anionic and cationic flocculant chemicals to the treatment and final decontamination of wastewaters from petroleum refining plants, petroleum terminals, pulp and paper mills has been studied.

Separation of flocculated pollutants has been carried out by settling, flotation and filtering. The efficiency of SS removal was 72-95%. The COD value was reduced by 36-60%.

At present flocculant and coagulant chemicals find wide applications in natural water and wastewater treatment. Production of new highly efficient flocculants contributes to a successful physicochemical treatment of industrial and municipal wastewater. As a rule, organic flocculants given in smaller doses than the inorganic ones make it possible to reduce sediments and to intensify all the technological processes of the industrial influent treatment.

The paper presents the results of studies on wastewater treatment by applying flocculants and their combinations with mineral coagulants. The experiments were carried out on the effluents from chemical, petroleum chemical, and paper and pulp industries.

Solid phase (flock) and liquids were separated by settling in cylinders for 1 h or 2 h, filtered through a paper filter and subject to compression flotation in flotation chamber of 100 mm in diameter and 1500 mm of height.

As the most pollutants in industrial effluents have a negative charge, the study of water-soluble cationic flocculants, the macroion of which is positively charged, is of particular interest. Such flocculants are able to coagulate directly the negatively charged particles.

The greatest emphasis in our work is placed on oil-containing sewage treatment because of its complex composition and a high content of organic substances. These chemicals are hardly oxidized.

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To study the high treatment rate of oil-containing sewage, high-molecular synthetic flocculants were used, both independently and together with mineral coagulant (aluminium sulphate), the relatively high rate of its hydrolysis occurs at pH 6.5–7.5.

Highly basic water-soluble polyelectrolytes of HPS series (pyridine salts on vinylpyridine base) were taken as a flocculant. Characteristics of the mentioned polyelectrolytes are presented in tab. 1. In the combined wastewater treatment with aluminium sulphate and HPS flocculants (HPS-46, HPS-47, HPS-48, HPS-49), followed by two hour settling, HPS-47 was found to be the most effective one (tab. 2). After such a treatment, the removal of COD, suspended solids and oil products amounted to 80%, 93.2% and 73%, respectively, the corresponding initial values being 558 mg O₂/dm³, 64 mg/dm³ and 40.8 mg/dm³.

Table 1

Properties of polyelectrolytes
Właściwości polielektrolitów

Flocculant marks	Vinylpyridines	Alkylating agent	Viscosity character (dl/g)	M 10 ⁻⁶	Exchange volume (mg-equiv/g)
HPS-46		CH ₃	0.75	—	3.94
HPS-47		C ₂ H ₅	0.76	—	3.23
HPS-48	4-vinylpyridine	C ₃ H ₇	0.70	—	3.47
HPS-49		C ₄ H ₉	0.20	—	3.48
HPS-411		C ₂ H ₅ Br	0.78	—	4.05
HPS-11			C ₂ H ₅ Br	0.4	0.112
	2-methyl-5-vinylpyridine	C ₂ H ₅ Br	2.26	0.726	4.2
		C ₂ H ₅ Br	4.0	1.26	4.16
		C ₂ H ₅ Br	9.4	3.24	3.80
HPS-7		C ₂ H ₅	0.4	—	3.5

Note: Molecular mass of polyelectrolytes HPS-11 was calculated from the following formula $[\eta] = 7.16 \times 10^{-6} M \times 94$.

It should be emphasized that under the same conditions but without flocculant, the COD value decreased only by 13.1%. It seems that high treatment efficiency is due to the interaction of the flocculant and pollutants which were not only emulsified but also dissolved in water.

From the mentioned materials it is apparent that by applying HPS-47 the removal rate of suspended solids and oil products also increases. Doubling the coagulants dose does not change the removal of suspended solids but it increases the COD in treated water from 20 to 70%.

Table 2

Influence of the type of flocculant on treatment efficiency of petroleum-containing waste-waters, using coagulation and settling (2 h)
 Wpływ różnych flokulantów na wydajność oczyszczania ścieków z ropy naftowej; zastosowano koagulację i osadzanie przez 2 h

Flocculant type	Dose (mg/dm ³)		Treatment efficiency (%)		
	Al ₂ (SO ₄) ₃	flocculant	COD	Suspended solids	Oil product
HPS-46	48	2.0	23.1	90.8	—
HPS-47	48	2.0	80	93.2	73
	96	2.0	33.2	96.5	88
HPS-48	48	2.0	70	95.4	—
	96	2.0	33.2	91.5	70.5
HPS-49	48	2.0	19.7	86.0	—
	48	0	13.1	90.5	69
	96	0	26.6	95.5	77.5

Thus, the application of aluminium sulphate (50 mg/dm³) and flocculant (2 mg/dm³) gives more promising effects compared with that of one coagulant (100–150 mg/dm³) usually employed at oil refineries.

The possibility of water treatment using flocculants alone was also studied. The preliminary experiments have demonstrated low efficiency of 4-vinyl-pyridine-based flocculants during 2 h settling. Consequently, the removal of flocculated flocks by filtering was to be studied.

The treatment of wastewater, at COD = 52 mg/dm³ and petroleum products = 58 mg/dm³ with 10 mg/dm³ polyelectrolyte, gave the results presented in tab. 3.

Table 3

Treatment efficiency when flocculation with filtration are used
 Wydajność oczyszczania podczas flokulacji i filtracji

Flocculant type	Treatment efficiency (%) Petroleum products	COD
HPS-46	91.0	14.1
HPS-47	88.4	87.5
HPS-48	93.4	37.9
HPS-19	91.0	—
HPS-411	91.0	87.5
HPS-7	88.5	65.6
HPS-11 M s = 1120000	95.4	38.2
HPS-11 M s = 2726000	92.5	87.5

From the analysis of the obtained data it is apparent that 2-methyl-5-vinyl-pyridine and 4-vinyl-pyridine-based polyelectrolytes alkylated with ethyl bromide and ethyl iodide (HPS-47, HPS-411, HPS-11) are more efficient in flocculation and filtration process than other polymer flocculants. Application of these flocculants makes it possible to reduce COD value by 87.5% and oil concentration by 93.4%. Increase of molecular weight of HPS-11 flocculant from 112,000 to 726,000 results in COD removal by 50%. This is due to the fact that the increase in macromolecule size brings about the aggregation of a large number of colloid particles to the macromolecule, forming large flocks.

In order to determine the influence of the molecular weight of flocculant on the treatment process, some experiments have been performed on the treatment of coagulated wastewater by settling and compression flotation.

The data demonstrate that the removal efficiency increases with the increasing molecular mass of polyelectrolyte. At the same time, 10 min flotation provides a better removal of suspended solids than that obtained by 1 h settling. Flotation treatment of oil-containing sewages pretreated with HPS-11 polyelectrolyte ($M = 3.24 \times 10^{-6}$) and containing 57 and 75 mg/dm³ of suspended solids resulted in residual concentration of 4.0 and 9.0 mg/dm³, respectively, yielding the efficiencies of 80.5% and 93%. Wastewater COD in the treatment process decreased by 70.6% and 75.6% and oil products by 75% ($C_0 = 36$ mg/dm³).

Among other types of polyelectrolytes, we have studied VA-2 (polystyrene-based quaternary ammonium salt), PEI (polyethyleneimine) and cationic polyacrylamide. The investigations of the rate of preflocculated wastewater treatment by settling and filtration methods show that PEI (molecular weight = 80,000) is the most efficient polyelectrolyte. Optimum dose of PEI determined by experimental coagulation method averaged

Table 4

Results of treatment of oil-containing sewage with flocculants
Wyniki oczyszczania ścieków zawierających olej z flokulantami

Indices	After oil separator	Sewage composition after physical and chemical treatment C — 5 mg/dm ³ PEI
pH	7.1-7.7	7.1-7.8
COD, mg/dm ³	580-1300	270-660
BOD, mg O ₂ /dm ³	98.0-130	15.0-24.5
Suspended solids, mg/dm ³	87.6-133	2.1-4.6
K-P, mg/dm ³	9.55-155.8	0.75-5.4
Volatile phenols with vapour, mg/dm ³	0.65-9.6	0.6-8.9
Non-ionogenic detergents, mg/dm ³	6.5-16.0	5.5-14.5
Chlorides, mg/dm ³	2950-5700	—
PEI, mg/dm ³	—	0.003-0.07

5 mg/dm³. Results obtained during the treatment of oil-containing sewage with flocculants are given in tab. 4.

Wastewater treatment by flotation, using PEI, allows us to decrease the SS content by 72–95%, ether extractable by 89–91% and COD value by 36–56%.

In ballast and industrial sewage treatment of petroleum reservoirs, the use of some flocculants of cationic, anionic, and nonionic character was also studied.

The following cationic polyelectrolytes were tested: polyethyleneimin, poly-1.2-dimethyl-5-vinylpyridine-methyl sulphate (PPS), poly-1-ethyl-2-methyl-5-vinylpyridine-bromide (HPS-11) and polyelectrolytes of VA series, i.e.: VA-212, VA-112 and VA-102. Among nonionic and anionic flocculants, metas (copolymer of metacrylamide and metacrylic acid), polyacrylamide and its derivatives PAA-H and RAA-R were used.

When studying the combined effect of aluminium sulphate with anionic and nonionic flocculants on the treatment rates of ballast and industrial sewage, it has been found that the highest treatment efficiency was due to polyacrylamide ($C = 1.0$ mg/dm³) and metas ($C = 2$ mg/dm³) for ballast and industrial waters, respectively, the concentration of aluminium sulphate being 50 mg/dm³. Thus, at the optimum doses of chemicals, the concentration of suspended solids after 1 h settling of ballast and industrial sewage of oil transshipping reservoirs was reduced by 68 and 92%, and the sewage COD by 75% and 30%, respectively.

In order to achieve the same rate of sewage treatment with aluminium sulphate, after 1 h settling, its dose was 150–190 mg/dm³.

Ballast and industrial sewage treatment with cationic flocculant and subsequent sewage settling made it possible to evaluate the kind of flocculant and its dose in the treatment efficiency.

The obtained data indicate that flocculants VA-112, PPS and HPS-11 (mol. mass. = 726,000) are the most efficient materials, 5 mg/dm³ dose of which allowed us to reduce the suspended solids concentration by 75–83.5% and COD value by 40–50%.

Flocculation and settling of industrial sewage of oil transshipping reservoirs gave the best results when PPS strong basic polyelectrolyte in concentration of 3 mg/dm³ is used; for example the application of PPS flocculant allows us to reduce suspended solid concentration to 22 mg/dm³ (with the initial dose of 108 mg/dm³), COD to 40 mg O₂/dm³ (with the initial dose of 170 mg/dm³).

It has been found that high treatment efficiency may be achieved either by application of a mixture of anionic and nonionic-type flocculants or by the use of cationic flocculants. Thus, the flotation of ballast sewages, treated with aluminium sulphate ($C = 8$ mg/dm³) and metas ($C = 2$ mg/dm³), gives the possibility of reducing oil concentration to 1.7 mg/dm³ (from 45 mg/dm³). The use of one coagulant ($C = 8$ mg/dm³) only allowed the reduction of oil concentration to 5.8 mg/dm³.

Among flocculants of cationic type, PPS was the most efficient. Thus, the treatment with the mentioned flocculant, given in concentration of 3 mg/dm³, decreased the suspended solids in sewage from 30.5 to 11.0 mg/dm³, and petroleum products from 7.6 to 2 mg/dm³.

SEWAGE POST-TREATMENT WITH APPLICATION OF CHEMICALS

Chemical treatment of sewage treated biologically with mineral coagulants with the subsequent separation of coagulated pollutants by pressure flotation method is one of the efficient post-treatment methods. The investigations included treated biologically, sewages of oil refinery (OR), integrated pulp and paper (IPPM) and chemical mills (ICM). Characteristics of the treated water are given in tab. 5.

Table 5

Characteristics of treated water
Parametry oczyszczonej wody

Item	OR	ICM	IP. PM
pH	7.1	7.0	7.0
Suspended solids, mg/dm ³	8.0-20.0	25.0	20-100
Ethersoluble, mg/dm ³	14-20	—	—
Sulphides, mg/dm ³	34	—	—
Chlorides, mg/dm ³	610	—	—
Phosphate, mg/dm ³	2	—	1.8
Ammonia nitrogen, mg/dm ³	3.5	5.2	—
Nitrite nitrogen, mg/dm ³	2.5	0.22	—
Nitrate nitrogen, mg/dm ³	12.0	46.7	—
Phenol, mg/dm ³	0.35	—	—
Salt content, mg/dm ³	840	—	—
COD, mg O ₂ /dm ³	90-200	40	600
BOD full, mg O ₂ /dm ³	75	—	—
BOD ₅ , mg O ₂ /dm ³	7.0	3.0	20-50
Dissolved oxygen, mg O ₂ /dm ³	2.9	—	3.0

As a result of investigations of coagulation of sewages and oil refinery wastes with aluminium sulphate and subsequent treatment by pressure flotation method, it has been stated that coagulant applied in doses of 12-60 mg/dm³ increases the sewage treatment rate. Thus, at 60 mg of aluminium sulphate/dm³ the concentration of suspended solids was reduced to 1.7 mg/dm³ (initial concentration 9.0 mg/dm³, ether-soluble fraction to 6.7 mg/dm³ (initial concentration 16.7 mg/dm³), COD value to 84 mg/dm³ (initial value 188 mg/dm³).

The sewages of the pulp and paper industry were examined after treatment by pressure flotation method with and without coagulant. Aluminium sulphate of the concentration ranging from 12 to 120 mg/dm³ (of Al) was used as a coagulant.

The optimum 60 mg/dm³ concentration of aluminium sulphate yielded the removal of suspended solids by 80-90%, and that of phosphorus by more than 50%. BOD₅ and COD values were reduced by 40% and 70%, respectively. The saturation of oxygen taking place at the same time increased the oxygen concentration 2-3 times after a 10 min flotation.

In conclusion, it may be said that in all the cases the application of flocculant to treatment of sewages of different composition is accompanied by the increase of treatment rate.

BADANIA NAD ZASTOSOWANIEM FLOKULANTÓW W OCZYSZCZANIU ŚCIEKÓW

Badano efektywność zastosowania kationowych i anionowych flokulantów chemicznych w oczyszczaniu i końcowej dekontaminacji ścieków z przemysłu petrochemicznego i papierniczego. Do separacji flokulowanych zanieczyszczeń stosowano sedymentację, flotację i filtrację.

Wydajność usuwania zawiesin wynosiła 72-95%. Osiągnięto również 36-60 procentową redukcję ChZT w ściekach.

ANWENDUNG VON FLOCKUNGSMITTELN ZUR ABWASSERREINIGUNG

Untersucht wurde die Wirkung von kationen- und anionenaktiven Flockungsmitteln bei der Reinigung und endgültiger Dekontaminierung von Abwässern der petrochemischen und der Papierindustrie. Die Abscheidung der ausgeflockten Verunreinigungen erfolgte durch Absetzen, Flotation und Filtration.

Die Ausscheidung von Schwebstoffen betrug 72-95%, der CSB wurde in einer Höhe von 36-60% abgebaut.

ИССЛЕДОВАНИЯ ПО ПРИМЕНЕНИЮ ФЛОКУЛЯНТОВ ПРИ ОЧИСТКЕ СТОЧНЫХ ВОД

Исследована эффективность применения катионных и анионных химических флокулянтов при очистке и конечном обеззараживании сточных вод нефтяной и бумажной промышленности. Для отделения флокулируемых загрязнений применялась седиментация, флотация и фильтрация.

Эффективность удаления суспензий составляла 72-95%. Было также достигнуто 36-60 процентное уменьшение ХПК в сточных водах.