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## EFFECTIVENESS OF FLOTATION TREATMENT WITH FLOCCULANTS APPLIED TO OIL WASTEWATERS

On the basis of the performed investigations it has been stated that cationic flocculants are characterized by a high removal efficiency of oils and suspensions. Therefore they can replace satisfactorily inorganic flocculants. When used in flotation process they give clear wastewater for which the retention time in the activated sludge chamber is two times shorter than that commonly required for biological treatment. Moreover, it has been stated that other components of wastewater, i.e. phosphates, sulphides, naphthene acids and phenols are also partially removed during the treatment process.

Physicochemical flotation process with the addition of chemicals as flocculants is one of the most common methods for removing fine particles and colloidal solids from oil wastewater. Inorganic coagulants and organic flocculants are used as chemicals. High effectiveness of organic flocculants in treating oil refinery wastewaters have been stated recently (MYASNIKOV, BUTZEVA, GANDURINA, 1976; SOKOLOV, CHIKUNOVA, 1977).

The above works offer the opportunity of replacing conventional inorganic coagulants by cationic polyelectrolytes, which improve greatly the efficiency of the system, ensure reliable operation of treatment facilities and, by reducing the volumes of sludges produced during coagulation, reduce the cost of their transportation and storage.

In order to select such parameters of flotation-flocculation process as type of flocculant, conditions for mixing and floc formation, some laboratory and pilot-scale experiments have been performed using cationic flocculants VPK-101, PEI and PPS.

The results of pilot studies on wastewater treatment by pressure flotation have shown that recirculating flotation system with injection of chemicals into the mixing tank (fig. 1) was most effective (tab. 1). Recirculation ratio was 33%. Optimum dosages of cationic flocculants ranged from 4 to 10 mg/dm<sup>3</sup>.

Figure 2 illustrates the effect of floc formation conditions on the residual concentrations of suspended solids in clarified effluent after flotation treatment at optimal dosages

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of flocculants. As seen from the data, optimum conditions for floc formation have been obtained at  $G = 55 \text{ s}^{-1}$  and mechanical mixing time of 27 min, at  $G = 300 \text{ s}^{-1}$  and mixing time of 5 min, which corresponds to  $GR = 90,000$ .

Experimental results of oil refinery wastewater treatment by flotation under optimum conditions are presented in tab. 2.

It may be seen that the removal efficiencies of suspended solids and oil products, achieved with flocculant VPK-101, are 41–96% and 68–86%, respectively. COD is reduced by 30–75%. PEI flocculant results in 51–85% reduction of suspended solids and

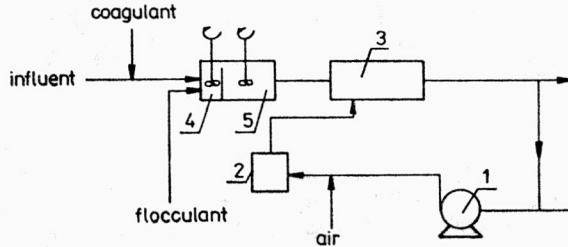


Fig. 1. Flow sheet of flotation with recirculation

1 — feed pump, 2 — saturation tank, 3 — flotation chamber, 4 — mixing tank, 5 — floc formation chamber

Rys. 1. Schemat technologiczny flotacji z recykulacją

1 — pompa zasilająca, 2 — zbiornik nasycaenia, 3 — komora flotacyjna, 4 — zbiornik mieszania, 5 — komora strącania

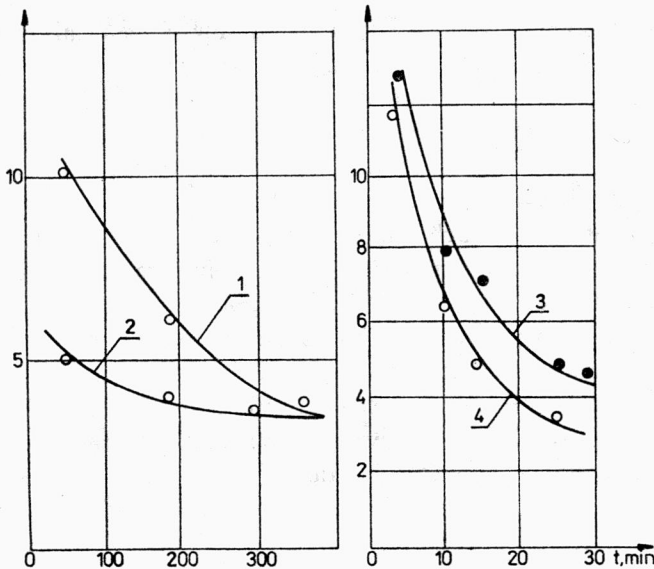


Fig. 2. Effect of floc formation on residual suspended solid concentration in flotation unit effluent

1 — VPK-101,  $T = 5 \text{ min}$ ; 2 — PPS,  $T = 5 \text{ min}$ ; 3 — PPS,  $G = 55 \text{ sec}^{-1}$ ; 4 — VPK-101,  $G = 55 \text{ sec}^{-1}$

Rys. 2. Wpływ strącania na stężenie zawieszonych ciał stałych w odcieku z jednostki flotacyjnej

1 — VPK-101,  $T = 5 \text{ min}$ ; 2 — PPS,  $T = 5 \text{ min}$ ; 3 — PPS,  $G = 55 \text{ sec}^{-1}$ ; 4 — VPK-101,  $G = 55 \text{ sec}^{-1}$

Table 1

Efficiency of VPK-101 addition to various flotation units  
Wydajność VPK-101 w różnych jednostkach flotacyjnych

Pressure flo- tation system	Flocculant	Suspended solids, mg/dm <sup>3</sup>		
		Before treatment	After treatment	Removal efficiency, %
Direct-flow flotation	VPK-101	48	33.5	30
		76.5	27	65
		104	22	79
Flotation with recirculation	VPK-101	48	4.5	91
		104	4.5	96

Table 2

Results of flotation of wastewater with addition of flocculants  
Wyniki flotacji ścieków z dodatkiem flokulantów

Flocculant	Wastewater characteristics, mg/dm <sup>3</sup>						Removal efficiency, %		
	Suspended solids		COD		Oil products		SS	COD	Oil product
	Influ- ent	Efflu- ent	Influ- ent	Efflu- ent	Influ- ent	Efflu- ent			
Waste from the 1st sewer system of petroleum refinery									
VPK-101	30	4.5	180	76	101	32.5	85	858	68
	48	4.5	—	—	—	—	—	—	—
	44	9.5	151	66	200	62	78	56	69
	104	4.5	242	61	—	—	96	75	—
PEI	33	5	151	70	118	28	85	54	76
	42	10	202	140	200	64	76	31	68
PPS	62	4.5	223	30.5	—	—	93	86	—
	70	8	203	71	—	—	88	65	—
Waste from the 2nd sewer system of petroleum refinery									
VPK-101	30.5	17.5	422	141	167	28	41	67	83
	18	6.5	370	264	167	24	64	29	86
PPS	30.55	3.5	370	123	167	16	88.5	67	90.4
PEI	30.5	15	422	158	167	24	51	63	86
	30.5	7.0	370	158	167	17	77	57	90

68–90% of oil products. COD, thereby, is reduced by 31–63%. The addition of PPS flocculant increases the reduction of suspended solid concentration to 88–93%, and of COD value to 67–89%.

From the analysis of the results obtained the following statements may be formulated:

- 1) VPK-101 and PEI flocculants show almost similar effectiveness in wastewater treatment,
- 2) PPS flocculant is the most effective in reducing suspended solids,
- 3) recirculating flotation system with flocculants is more effective than the direct flow one.

In order to verify the data obtained, the experiments have been carried out using a flotation facility of a capacity of 400 dm<sup>3</sup>/h. The plant includes receiving tank continuously supplied with wastes, mixing tank for mixing flocculant solution with waste stream, floc formation chamber with mechanical mixer, flotation basin, aeration tank, filter, saturation tank, chemical feed system, pump with electric motor, and compressor. In the mixing tank the solution is mixed under the action of compressed air, in floc formation chamber the mixing is produced by H-type agitator.

The cylindrical flotation chamber is equipped at the bottom with an arrangement for stirring air-liquid mixture fed from the saturator with flocculated wastewater and at the top with a device for froth removal. Clarified water is removed through the bottom part and passes to biological treatment and filtration.

Water is saturated with air in a saturation tank of nozzle type. Rings of Rarshig of 25 × 25 × 3 mm size and 400 mm thickness have been utilized as nozzles. Air was supplied to the saturation tank by compressor.

In the course of studies the following process parameters have been maintained:

- flow rate — 400 dm<sup>3</sup>/h,
- amount of water being recycled and saturated with air — 50%,
- retention time: in mixing tank — 2 min, in floc formation chamber — 20 min, in saturation tank — 2 min, in flotation chamber — 20 min,
- velocity gradient of mixing liquid in floc formation chamber  $C$  — 55 s<sup>-1</sup>,
- pressure in saturation tank — 400–500 Kp,
- surface loading in flotation chamber — 13 m<sup>3</sup>/m<sup>2</sup>/1 h,
- concentration of chemicals — 0.1%.

In a pilot plant the experiments lasted for six months. The waste flow entering the plant had the following characteristics:

- suspended solids — 20–200 mg/dm<sup>3</sup>,
- COD — 200–1250 mg/dm<sup>3</sup>,
- oil products — 17–260 mg/dm<sup>3</sup>,
- pH — 5–9.0.

Results obtained are presented in tab. 3. As seen from the table, flotation treatment with the addition of VPK-101 flocculants (5 mg/dm<sup>3</sup>) reduces on the average oil products by 85%, COD by 53% and suspended solids by 83%.

Table 3

Results of pilot-plant wastewater flotation with addition of flocculant VPK-101  
Wyniki flotacji ścieków z dodatkiem flokulanta VPK-101 w zakładzie doświadczalnym

Dosage of VPK-101	Characteristics of wastewater, mg/dm <sup>3</sup>						Removal efficiency, %		
	COD		SS		Oil products		COD	SS	Oil products
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment			
Wastes from the 1st sewer system of petroleum refinery									
2.5	529	369	53.5	10	31	5.6	30	81	82
5.0	497	337	43	12.5	32.5	1.3	32	72	96
10.0	356	242	40	3.5	24	4.5	32	91	81
7.0	420	178	61	2.0	50	2.5	58	97	95
2.5	260	93	33	11	76	15.0	72	66	80
5.0	222	93	22	6.0	51	8.0	58	74	85
10.0	229	93	72	1.5	114	10.0	69	98	91.5
10.0	241	187	61	8.6	44	11.0	23	86	75
5.0	224	149	88	8.5	43	6.5	33	90	85
2.5	206	168	93	7.4	58	11.5	18	92	80
10.0	311	194	23	5.0	73	29.0	62	78	60
10.0	454	184	32	8.0	110	44.0	59	75	60
5.0	661	301	53	5.0	209	20	54	90	90
5.0	661	326	34	6.0	132	33	17	82	75
Wastes from the 2nd system of petroleum refinery									
5	494	162	83	9	87.0	17	67	89	80
5	1457	405	189	7	—	—	72.5	96	98
5	1247	348	157	9	261	15.5	72.5	94	94
2.5	482	482	65	16	51	46	—	75.5	12
5.0	1321	250	67	10	92	24	81	85	74

In this case, the effluent after flotation was characterized by the following parameters (in mg/dm<sup>3</sup>): SS — 6–16, COD — 93–337, oil products — 6–29.

The investigations involved wastewaters with oil products of the concentration ranging from 17 to 260 mg/dm<sup>3</sup>. Experimental results show that with the increasing concentration of oil products in the influent, their removal efficiency slightly decreases. Thus, the 85% oil product removal is obtained when the content of oil products in the influent is 52 mg/dm<sup>3</sup>, the 82% efficiency being obtained at the average initial concentration of 170 mg/dm<sup>3</sup>. For comparative reasons studies have been made on pilot plant in which floc formation stage was excluded. The investigations have shown that in absence of floc formation chamber the treatment efficiency is reduced significantly.

Froth being removed from liquid surface during flotation treatment has a low (82.5–91.9%) moisture content and high (~10–15%) concentration of solids and oil products. Thus, the transport and handling of such concentrated foams present some difficulties.

Table 4

Results of complete chemical analysis of wastewaters before and after treatment  
 Wyniki całkowitej analizy chemicznej ścieków przed i po oczyszczaniu

Characteristics	Before	After	Before	After	Before	After	Before	After	Flow from	After
	flota- tion	flota- tion	flota- tion	flota- tion	flota- tion	flota- tion	flota- tion	flota- tion	the 2nd system to flota- tion	flota- tion
Colour	dark- grey	light yellow	dark grey	light grey	light grey	yellowish grey				
pH	8.0	8.0	8.5	8.5	8.5	8.5	8.0	—	7.5	8.0
COD, mg/dm <sup>3</sup>	1170	678	552	246	608	202.8	438.5	138	996	109
N as NH <sub>4</sub> , mg/dm <sup>3</sup>	22.4	16.8	40.6	35	196	49	23	29	19.6	18.2
N as NO <sub>2</sub> , mg/dm <sup>3</sup>	none	trace	none	none	none	none	none	none	—	0.005
N as NO <sub>3</sub> , mg/dm <sup>3</sup>	5.6	8.4	14.7	11.9	8.4	21	5.6	2.1	6.3	7.0
Phosphates, mg/dm <sup>3</sup>	0.6	0.34	0.08	0.08	0.56	0.44	0.4	0.2	0.32	0.5
SS, mg/dm <sup>3</sup>	128	9.0	63.5	18	120	16.0	114	7.5	145	5.0
Sulphides, mg/dm <sup>3</sup>	10.5	1.8	42.1	1.8	4.5	1.2	9.7	6.7	4.5	3.3
Thiosulphates, mg/dm <sup>3</sup>	7.2	none	none	none	3.6	none	none	none	7.1	—
Extractable ether, mg/dm <sup>3</sup>	1333	18.5	80	19	76	8.5	99	17.7	136	6.5
Naphthenic acids, mg/dm <sup>3</sup>	83.3	8.7	14.4	9.6	14.8	10.9	27	11	23.9	10.0
Petroleum products, mg/dm <sup>3</sup>	102	7.6	20.2	12	10.6	6.8	18.8	7.0	38.8	5.5
BOD <sub>5</sub>	264	173	62.4	32.8	90.4	24	24.0	14.4	151	8.6
BOD <sub>total</sub>	539	453	352	174.8	186.4	47	147.0	88.0	270	49.0
Temperature, °C	10-9	10-9	—	—	—	—	19	—	—	—
Phenols, mg/dm <sup>3</sup>	9.075	0.95	1.3	—	2.04	1.26	0.1	none	0.88	—
Chlorides, mg Cl/dm <sup>3</sup>	—	—	585	549.6	681	765	479	—	345	429

Experimental results have proved high efficiency of cationic flocculants and the possibility of their substitution for inorganic coagulants. Clarified effluent from flotation facility can be treated in aeration tanks at considerably short detention time as compared with that used in practice. The later studies on biological treatment showed that detention time may be two times reduced.

Results of a complete chemical analysis of influent and effluent from flotation treatment with VPK-101 flocculant are presented in tab. 4. From the data obtained it is evident that in flotation-flocculation treatment with subsequent aeration of wastewaters besides oil products and suspended solids a number of other components may be removed. In this way the concentration of phosphates, sulphides, naphthene acids, and fenols can be reduced.

#### REFERENCES

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#### EFEKTYWNOŚĆ FLOTACYJNEGO OCZYSZCZANIA ŚCIEKÓW OLEJOWYCH Z ZASTOSOWANIEM FLOKULANTÓW

Na podstawie przeprowadzonych badań stwierdzono, że flokulanty kationowe charakteryzuje bardzo duża efektywność w usuwaniu ze ścieków olejów i zawiesin, dlatego też mogą z powodzeniem zastąpić flokulanty nieorganiczne. Użycie ich w procesie flotacji daje klarowne ścieki, których czas przetrzymywania w komorze osadu czynnego w celu dalszego biologicznego oczyszczania jest dwukrotnie krótszy niż powszechnie stosowany. Stwierdzono ponadto, że wraz z olejem i zawiesinami usuwane są częściowo inne składniki ścieków, tj.: fosforany, siarczki, kwasy naftenowe i fenole.

#### REINIGUNG ÖLHALTIGER ABWÄSSER MITTELS FLOTATION UND UNTER ANWENDUNG VON FLOCKUNGSMITTELN

Kationenaktive Flockungsmittel weisen eine sehr gute Wirkung bei der Abscheidung von Ölen und Schwebestoffen auf und können mit Erfolg anorganische Flockungsmittel ersetzen. Durch die Anwendung im Flotationsverfahren ergeben sich klare Abwässer, die im nachfolgenden Belebtschlammverfahren nur die Hälfte der Kontaktzeit benötigen. Festgestellt wurde ausserdem, daß neben den Ölen und Schwebestoffen auch andere Abwasserinhaltsstoffe zum Teil ausgeschieden werden. Zu denen gehören Phosphate, Sulfide, Naphtensäuren und Phenole.

## ЭФФЕКТИВНОСТЬ ФЛОТАЦИОННОЙ ОЧИСТКИ МАСЛЯНЫХ СТОЧНЫХ ВОД С ПРИМЕНЕНИЕМ ФЛОКУЛЯНТОВ

На основе проведенных исследований отмечено, что катионные флокулянты обладают весьма высокой эффективностью удаления из сточных вод масел и суспензий и могут успешно заменить неорганические флокулянты. Использование их в процессе флотации даёт прозрачные сточные воды, для которых время выдержки в камере активного ила при дальнейшей биологической очистке в два раза меньше, чем обычно применяемое. Кроме того, было отмечено, что вместе с маслом и суспензиями частично удаляются другие компоненты сточных вод: фосфаты, сульфиды, нефтеная кислота и фенолы.

