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A STUDY ON REMOVAL
OF ORGANIC FLUORINE
FROM WASTEWATERS***

A study was carried out to evaluate new processes of the purification of wastewaters containing fluorinated organic compounds. These processes are alternative to incineration. The basic step is the transformation of organic fluorine to fluorides, the latter being then removed as calcium salt and the reactions studied were acidic and alkaline hydrolyses, chemical oxidation and wet oxidation. The most effective treatment was wet oxidation which reached 90% yield in the transformation of organic fluorine to fluorides.

1. INTRODUCTION

Fluorinated compounds are increasingly employed in agriculture (pesticides), aviation (hydraulic fluids), and electronics (special fluids). The chemicals, for example, some alkyl-substituted products (Trifluralin, Poli-chlorotrifluoro-ethylene, Fomblin Y) are presented in fig. 1. In these compounds fluorine is firmly bonded to carbon because of its small dimensions (Van der Waals radius 1.35 Å; cf. hydrogen 1.2 Å, chlorine 1.8 Å) and strong electronegativity [1]. While dissociation energies of aryl—halogen bonds by nucleophilic substitution generally increase from fluorine to iodine (Ar–F < Ar–Cl < Ar–Br < Ar–I), the dissociation energies of alkyl-substituted products decrease from fluorine to iodine (Alk–F > Alk–Cl > Alk–Br > Alk–I) [2]. The carbon—fluorine (C–F) bond in the trifluoro-methyl group is almost inaccessible to the nucleophilic substitution.

Some dissociation energies of carbon—halogen bonds are reported in tab. 1. The maximum value is found in the tetrafluoromethane (519.0 kJ/mole), and values decrease with decreasing the number of fluorine atoms bonded to the same carbon (514.9, 464.6 kJ/mole); moreover, dissociation energy of carbon—fluorine (C–F) bond is significantly higher than the corresponding

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carbon–chlorine (C–Cl) (314.0 kJ/mole) and carbon–hydrogen (C–H) (422.8 kJ/mole) [3] . For comparison, the dissociation energy of the single carbon–carbon (C–C) bond is 360.0 kJ/mole.
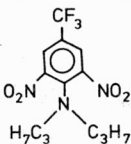
Products	Formula	Use
Trifluralin	CF_3 on benzene ring, O_2N and NO_2 substituents, N with H_7C_3 and C_3H_7	Pesticide
Poly-chlorotrifluoro-ethylene	$-(CClFCF_2)_n$	Hydraulic fluid
Fomblin y (perfluorinated polyethers)	$-\left[(O-\overset{\displaystyle CH_3}{\underset{\displaystyle \mid}{CF}}-CF_2)_n - (O-CF_2)_m \right]-$	Special fluid

Fig. 1. Examples of fluorinated products

Table 1

Estimated energies of bond dissociation

Bond broken R–X	D (R–X) kJ/mole	Bond broken R–X	D (R–X) kJ/mole
CF_3-F	519	CCl_3-Cl	314
C_2F_5-F	515	CH_3-H	423
$(CF_3)_2CF-F$	460	CH_3-F	452*
$(CF_3)_3C-F$	414	CH_2F-F	481*
		CHF_2-F	502*
		CF_3-F	519
C–C	360		

*C–F bond strengthens with increasing fluorine content.

When fluorinated by-products must be docomposed for the purification of wastewaters discharged from the syntheses, it is necessary to break the carbon–fluorine (C–F) bonds and to form inorganic fluorides, which can be easily removed from solutions by means of well known technologies, for example by precipitation with lime, flocculation and clarification of suspensions, and filtration of sludges [4]. Chemical oxidation of fluoro-alkyl-aryl compounds does not break the carbon–fluorine (C–F) bond, even under severe conditions (Fenton reagent: $H_2O_2 +$ $FeSO_4$ at pH 3) [5]–[7] , but it breaks the aromatic ring. Trifluoromethylbenzene under such conditions can be reduced to trifluoracetic acid.

Incineration breaks carbon–fluorine (C–F) bond, but is very expensive because of the special materials (titanium, platinum) needed to prevent corrosion from vapours of hydrofluoric acid, which are formed under the combustion conditions. Therefore most of the existing incinerators are not suitable to treat wastewaters containing more than 100 mg/dm^3 of total fluorine. Before being discharged into the atmosphere, vapours of hydrofluoric acid must be always removed from combustion gases with alcaline solution in a scrubber, fluorides precipitated, suspensions flocculated and clarified, and sludges filtrated [4]. Taking into account this situation, a study was carried out to evaluate new processes of the purification of wastewaters containing fluorinated organic compounds, which could be used in place of incinerators, or as pretreatments, for example, before a biological treatment.

2. EXPERIMENTAL

2.1. EFFLUENT

The research carried out deals with effluents from the production if Trifluralin and the results obtained may serve as a model for other compounds containing organic fluorine. Trifluralin (1-trifluoromethyl,3,5-dinitro,4-N-di-n-propylamine benzene) has a molecular weight of 335, a melting point of 49°C; it is soluble in apolar solvents, but it is only slightly soluble in water (50–100 μg/dm^3). Trifluralin is obtained from 1-trifluoromethyl,3,5-dinitro,4-chlorobenzene and di-n-propylamine.

The reactions, in which organic fluorine is converted to fluorides, are as follows: acidic and alcaline hydrolyses, chemical oxidation by sodium hypochlorite, hydrogen peroxide, and wet oxidation. (Wet oxidation is an oxidation in water under pressure at high temperature by means of air or pure oxygen).

Table 2

Chemical composition of fluorinated effluents

Chemical compound	Concentration (mg/dm^3)
4-chloro,3,5-dinitro benzoic acid	10
Trifluralin	740
di-N-propylamine	1980
4-chloro-3,5-dinitro,trifluoromethyl benzene	1960
4-hydoxy,3,5-dinitro,trifluoromethyl benzene	1180
4-chloro,3-nitro,trifluoromethyl benzene	3
NaCl	9000
NaOH	290
HF	14
HCl	350
H$_2$SO$_4$	210
HNO$_3$	1100
NaNO$_2$	1470

The chemical composition of fluorinated effluent is presented in tab. 2. The concentration of trifluralin, the reaction product, is 740 mg/dm^3, and those of the reagents used in the synthesis, i.e., di-n-propylamine and 4-chloro, 3,5-dinitro,trifluoromethyl benzene amount to 1980 and 1960 mg/dm^3, respectively. The analysis of the same wastewater is reported in tab. 3. The concentration of fluorine is $260-480$ mg/dm^3, out of which more than 95% consists of organic and linked to carbon fluorine, chemical oxygen demand amounts to 6.3 -6.9 g/dm^3, and total Kjiedhal nitrogen, $232-325$ mg/dm^3. Content of fluorides was determined using reversible electrode in aqueous solution buffered at pH $4.5-5$. To determine the content of organic fluorine it was necessary to convert it to fluoride by alcaline melt; a known volume of effluent was adsorbed on Na_2CO_3 and the obtained slurry was dried on hotplate, melted and dissolved in a known volume of water. Fluorides were determined by means of the reversible electrode technique.

Table 3

Analysis of fluorinated effluent

Parameter	Range
pH	$3-3.28$
Suspended solids (mg/dm^3)	$1.6-7.5$
Ethereal extract (mg/dm^3)	$822-881$
COD (mg/dm^3)	$6338-6927$
TKN (mg/dm^3)	$232-325$
F^- (mg/dm^3)	$13.8-17.8$
F_{total} (mg/dm^3)	$260-480$
Cl^- (mg/dm^3)	$5664-5734$
Residue at $105^{o}C$ (mg/dm^3)	$14334-15266$
Residue at $600^{o}C$ (mg/dm^3)	$10855-11062$

2.2. EQUIPMENT, RESULTS AND DISCUSSION

Hydrolyses. The hydrolysis was carried out either in alkaline solution of sodium hydroxide at pH 12 or in acidic solution of sulfuric acid at pH 1. In both cases solutions were boiled in reflux condenser for $2-9$ h, then cooled, filtered and analysed. Results are shown in tab. 4. In alkaline solution of sodium hydroxide (pH = 12), the hydrolysis was quite good. Conversion of organic fluorine to fluoride decreased from $92-95$% to 70%, 57%, and 27% after 2, 4, and 9 h, respectively. In sodium hydroxide solution (pH = 10) or in lime solution (pH = 12) there was stated a lower conversion. In acidic solution (H_2SO_4) the hydrolysis was very slow and organic fluorine remained unchanged in $79-81$% after $4-9$ h of reaction.

In the most favourable conditions (hydrolysis in sodium hydroxide solution at pH = 12 for 9 h) the content of organic fluorine in solution was lowered from 480 to 100 mg/dm^3.

Table 4

Hydrolysis of fluorinated effluent at boiling point

Feed				Experimental conditions			Treated effluents			
F_{tot}	F^-	F_{org}	$\dfrac{F_{org}}{F_{tot}} \cdot 100$	Reagent	pH	t	F_{tot}	F^-	F_{org}	$\dfrac{F_{org}}{F_{tot}} \cdot 100$
mg/dm^3						h	mg/dm^3			
319	24	295	92.5	NaOH	12	2	300	90	210	70
				Ca(OH)$_2$	12	4	322	42	280	87
				H$_2$SO$_4$	1	4	306	57	249	81.4
480	18	462	96.2	NaOH	12	2	340	88	252	74.1
				NaOH	12	4	325	140	185	56.9
				NaOH	10	4	340	130	210	61.8
				NaOH	12	9	335	245	90	26.9
				Ca(OH)$_2$	12	9	325	225	100	30.8
				H$_2$SO$_4$	1	9	290	62	228	78.6

Chemical oxidation. Experiments were carried out using the following oxidizing agents: sodium hypochlorite at pH = 12–14 and hydrogen peroxide plus iron sulphate at pH = 3 (Fenton reagent). The molar ratio of oxygen supplied to chemical oxygen demand was in the range 1–2. Solutions were boiled for 2–4 h in reflux condenser, then cooled, filtered and analysed. After oxidation, the volumes of the treated solutions were 1.5–2 times greater than initial volume because of the dilution effect of reagents. Results are presented in tab. 5. Chemical oxidation with Fenton reagent carried out using O_2/COD weight ratios of 1 and 2 was very poor. Oxidation with sodium hypochlorite decreased organic fluorine content from 95 to 50%. Taking into account the fact that the transformation under alkaline conditions without oxidants gave the same yield, it could be concluded that under these conditions oxidation alone was ineffective.

Wet oxidation. The wet oxidation was carried out in 2.5 dm^3 rocking bomb, coated with titanium and heated electrically (fig. 2). 1.5 dm^3 of the fluorinated effluent and oxygen
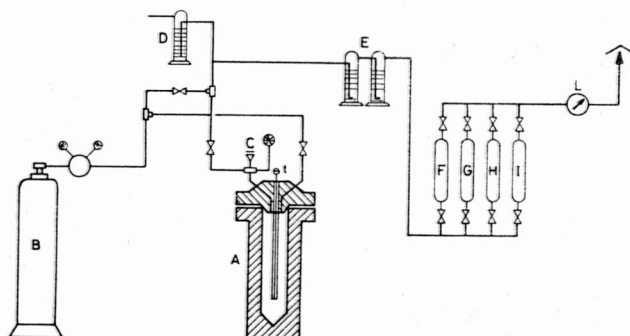

Fig. 2. Diagram of wet oxidation equipment
A – titanium rocking bomb, B – oxygen cylinder, C – rupture disk, D – hydraulic safety,
E – alkaline absorbers, F, G, H, I – gas samplers, L – gas meter

Table 5

Chemical oxidation of fluorinated effluents at the boiling point

Feed				Experimental conditions				Reaction products				Dilution due to treatment
F_{tot}	F^-	F_{org}	$\frac{F_{org}}{F_{tot}}\cdot 100$	Reagent	O_2/COD	pH	t h	F_{tot}	F^-	F_{org}	$\frac{F_{org}}{F_{tot}}\cdot 100$	
	mg/dm^3								mg/dm^3			
469	28	441	94	NaClO	1.00	13.9	4	266	144	122	45.9	1:1
480	18	462	96.2	NaClO	2.00	14	4	268	136	132	49.2	1:1
480	18	462	96.2	H_2O_2	1.00	3	4	470	70	400	85.1	—
480	18	462	96.2	H_2O_2	2.00	3	4	380	30	350	92.1	—
400	24	376	94	ClO_2	1.00	12	4	212	36	176	83	1:0.5
480	18	462	96.2	ClO_2	2.00	12	2	210	14	196	93.3	1:0.9

Table 6

Wet oxidation of fluorinated effluents at 250°C

Feed				Experimental conditions					Reaction products			
F_{tot}	F^-	F_{org}	$\frac{F_{org}}{F_{tot}}\cdot 100$	Reagent	O_2/COD	pH	P MPa	t h	F_{tot}	F^-	F_{org}	$\frac{F_{org}}{F_{tot}}\cdot 100$
	mg/dm^3									mg/dm^3		
260	19	241	92.7	O_2	1.2	2.6	6.9	2	260	230	30	11.5
319	24	295	92.5	O_2	0.60	1.9	6.0	2	278	260	18	6.5
319	24	295	92.5	O_2	0.30	2.0	5.5	2	275	200	75	27.3

(calculated as a per cent of COD) were introduced into the bomb at room temperature. The bomb in the rocking position was then heated at 250°C for 2 h. The final pressure was 5.5–6.9 MPa, depending on the initial oxygen pressure. After cooling, reaction gases were let slowly through a 10% sodium hydroxide solution to adsorb carbon dioxide and acids. The residual gases were sampled and analysed by means of gas chromatography.
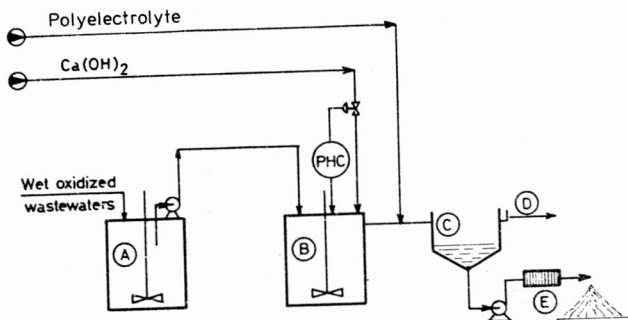

Fig. 3. Process of fluoride removal from wastewaters
A – equalization, B – neutralization and pH control (8.5–9), C – flocculation and clarification,
D – defluorinated effluent, E – filtration of sludges, PHC – pH control system

The oxidation was very effective in the transformation of organic fluorine into inorganic salts: a yield of about 90% was obtained when initial molar ratio of O_2/COD was 0.6, temperature 250°C, and reaction time 2 h (tab. 6). The fluorides formed during oxidation were removed from the solution by precipitation with lime, flocculation and clarification of suspension, and filtration of sludges (fig. 3). In this case fluorine concentration was low enough (50 mg/dm^3) to meet the conditions for burning the wastewaters in existing incinerators, corrosion problems being omitted.

3. CONCLUSIONS

The basic step in the removal of organic fluorine from wastewaters is its transformation to fluoride. Incineration can break carbon–fluorine (C–F) bond, but is too expensive because of the special materials (titanium, platinum) needed to prevent corrosion from hydrofluoric acid, which is formed under these conditions. To overcome this problem, some conversions of organic fluorine to fluoride were tested. The most effective was wet oxidation, which reached 90% yield. Alkaline hydrolysis reached 70% yield, while acidic hydrolysis was almost ineffective (tab. 7). Also chemical oxidation at atmospheric pressure was ineffective, since 50% yield did not depend on NaClO action, but on the alkaline hydrolysis.

On the basis of these results it can be concluded that the wet oxidation seems to be very useful to pretreat organic fluorinated wastes in order to reduce total fluorine concentration lower than 100 mg/dm^3. In such a concentration, wastes can be burned in existing incinerators, and corrosion problem being omitted.

Table 7

Conversion of organic fluorine to fluoride

Test	Reagent	pH	t $^{\circ}C$	Time h	Yield %
Chemical oxidation	H_2O_2	3	100	4	10
Chemical oxidation	ClO_2	12	100	4	15
Hydrolysis	H_2SO_4	1	100	9	20
Chemical oxidation	NaClO	14	100	4	50
Hydrolysis	NaOH	12	100	9	70
Wet oxidation*	O_2	2	250	2	90

*Pressure = 6.0 MPa.

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BADANIA NAD USUWANIEM ORGANICZNEGO FLUORU ZE ŚCIEKÓW

Oceniono nowe metody oczyszczania ścieków zawierających fluorowe związki organiczne. Są to metody alternatywne do procesu spalania. Zasadniczym etapem każdej z badanych metod jest konwersja fluoru zawartego w związkach organicznych do jonów fluorkowych, które następnie usuwa się z roztworu w postaci nierozpuszczalnych soli wapnia. Zastosowano reakcje hydrolizy w środowisku kwaśnym i zasadowym, chemiczne utlenianie i utlenianie „mokre", tzn. w roztworze wodnym pod zwiększonym ciśnieniem. Ostatnia z wymienionych metod okazała się najbardziej efektywna. Uzyskano 90% konwersji fluoru do jonów fluorkowych.

ИССЛЕДОВАНИЯ УДАЛЕНИЯ ОРГАНИЧЕСКОГО ФТОРА ИЗ СТОЧНЫХ ВОД

Оценены новые методы очистки сточных вод, содержащих вторированные органические соединения. Это альтернативные методы к процессу сгорания. Основным этапом каждого из исследуемых методов является конверсия фтора, содержащегося в органических соединениях во вторидные ионы, которые, затем, удаляется из раствора в виде нерастворимых солей кальция.Применены реакции гидролиза в кислой и щелочной средах, химическое окисление и окисление "мокрое", т.е. в водном растворе при повышенном давлении. Последний из вышеперечисленных методов оказался наиболее эффективным. Получена 90% конверсия фтора во фторидные ионы.