6th International Conference
ðComputational Mechanics and Virtual Engineering ð
COMEC 2015
15-16 October 2015, Braşov, Romania

CONSIDERATIONWASTEWATERFROM OIL MILLS IN ROMANIAN

Drd. Fiz.Elena Scutelnicu (Păun)[1], Prof. Univ. Emerit. Dr. Eng. Constantin D. Stanescu[2], Eng. Daniel Vane[3]
[1]Polytechnic University of Bucharest; Bucharest, Romania, e-mail:ellenapaun@yahoo.com
[2]Polytechnic University of Bucharest; Bucharest, Romania, e-mail:prof_cstanescu@yahoo.com
[3]Polytechnic University of Bucharest; Bucharest, Romania, e-mail:daniel.vane@yahoo.com

Abstract:_This paper presents the evaluation of the degree of pollution of wastewater from oil mills and margarine in Romania. Preliminary experimental researches were conducted on polymer flocculent material obtained by irradiation with accelerated electrons, type PA (AMD -AA -40), copolymers of acrylamide and acrylic acid, used alone or in combination with classical electrolytes in difficult waters, in relation to the effectiveness of the treatment of classical chemical agents, such as ferrous sulphate, aluminum and lime._
Kay-words: _margarine, oil, waste water_

1. INTRODUCTION

Oil factories in Romania have a working regime estimated at 300 days / year with 24 hours per day. The researches were carried on processing 100,000 tons sunflower flower seeds annually. The Ecological Engineering Laboratory within the Alimentary Research Institute highlights the data on which the researches are based.
Table 1 shows the characteristic data of an oil and margarine factory.

Table 1: Characteristic data of oil and margarine factory

Title	Symbol	The amount	UM
The annual volume ofmeasured water	$Q_{apaevacuata}$	1 260 000	m3 / year
Materials in suspension	$M_{suspensie}$	184 458	t/ year
Organic material contained inwater discharged annually (biochemical oxygen consumption for 5 days)	M_{CBO_5}	239.837	t/ year
Oil content in water discharged annually	$M_{S.ext.}$	50 946	t/ year

Of the total volume of wastewater discharged annually, 30% are heavily polluted wastewater and 70% weak polluted wastewater.Table 2 shows the evaluation of the polluting levels recorded in 20 oil and margarine factories in Romania.

Table 2: Evaluation of polluting levels of oil and margarine factories in Romania.

Title	Symbol	The amount	UM
Water discharged	$Q_{apaevacuata}$	22 700 000	m^3/an
Table of suspended solids	$M_{suspensie}$	3 500 000	t/an
Organic material contained in water discharged annually	M_{CBO_5}	3 800 000	t/an
Oil content in water discharged annually	$M_{S.ext.}$	764 200	t/an

The data presented demonstrate high polluting levels produced only by 20 industrial units producing edible oil and margarine in Romania. The situations do not fall within the parameters required by the legislation in force.For these types of water represent a category of wastewater which is very hard to purify by the already known classical chemical methods.

2. TYPES OFTREATMENTOFSEWAGEWATERSUPPLYFOROILREFINING

There have beenpreliminaryexperimental researcheson the treatment ofpolymeric materialsflocculentproduced byaccelerated electron irradiationtypePA(AMD-AA-40), copolymers of acrylamideandacrylic acid, usedalone orin combinationwithclassicalelectrolytesindifficultwatersin relation to theeffectiveness of thetreatment ofclassical chemicalagents, such as ferrous sulphate, aluminumandlime.

Stepsapplyingwaterpurificationtreatmentsforrefiningedible oilsare:

•Sampling of"hard water", oilrefiningwastewaterfromfood;

•Makingcharacterizationof water samplesbymain indicatorsof pollution;

•Makingtreatmenttypes ofwater samplesby applyingtwodifferent methods:

- ❖ classictreatmentwith varioususual electrolytes, aluminum sulphate, ferrous sulphate, lime leading totheidentification and final characterizationof thetreated waterthat gavethe best results;
- ❖ the combined treatmentbased on theuse ofclassicalelectrolyteswithpolyelectrolyteswhich gavethe best results;

•Comparison of the resultsobtained by the twomethods;

• Development ofmoderntreatmentmethodswhich shouldimprovethe indicatorsof pollutionwithinthe limits permitted byNTPA.

Table3 shows thetypesof treatmentsusedto treat the water which is used forrefiningedible oilsmanufacturedinRomania.

Tabel3: Types of treatments used to purify the water which is used for refining edible oil

Treatment type	Amount of classic chemical agents and polymersper 1 dm^3 treated water			
	$Al_2(SO_4)_3$ mlsol.20%	$FeSO_4$ ml.Sol.5%	$CaCO_3$ mlsol.5%	Polimer ml.0.1%
Clasic type 1	0.3	-	1.98	-
Clasic type 2	-	1.19	1.98	-
Clasic type 3	-	1.66	2.6	-
Clasic type 4	4	-	-	-
Type 1+polymer	0.3	-	1.98	8
Type 2+polymer	-	1.19	1.98	8
Type 3+polymer	-	1.66	2.6	8
Type 4+polymer	4	-	-	8

Table 4presents the results ofcomparativetestscarried out. The comparative analyse of theresults,highlights the following aspects:

1) of the polymerstestedmainlyfourtypes of evidence were chosen: modest, acceptable, goodand verygoodin order to correlatepollutionreduction efficiencyindicatorsinrelation to the mainphysicochemical characteristicsof these polymers, CC, $V_{\text{int}\,r.}$ and k_H ;
2) the wastewaterschosenfor testingwere the most"resistant" to all known treatments: such watersare part ofCategory III:difficult wastewater for which the classictreatment doesn't show indicatorsof pollutionwithin thelimits ofNTPA-002/1997;for this category ofwastewater,onlythe combined treatmentofelectrolytes with several types of polyelectrolytesmaybe effectivefor improving theindicatorsof pollutionorframingthem,in full,within the limits ofNTPA[11,12].Inthis case, the required amount ofclassic electrolytesis reduced only bytheir use incombinationwithpolyelectrolytesthus being obtained thecleansingandthe classificationof the indicators within the limits permitted byNTPA
3) the classic treatmentsapplied arethose currently usedfor purifyingthewastewatercoming fromedible oilsrefining industry;
4) there is no current standard treatmentto frame all the indicatorsof pollutionwithinthelimits permitted byNTPA;
5) thebesttreatmentswithpolymersfor reducing the indicator"suspensions" are:
   -Type 3+PA-5-F1-2 (Sample 263- good sample test)withη=83.8%, 4.4times better thanthe best classic treatment-Classic Type2(lowers theindicator"suspensions" 5 timesmorethanstandard treatment)
   -Type4 +PA-1-F1-2 (Sample 260-good sample test)withη=78.4%, 4.1times better thanthe yield ofthe best classictreatment-classictype 2 (reduces the "suspensions"3.75timesmore);
   -Type1 +PA-1-F4 (Sample 285-verygood sample test) withη=70.2% 10 timesbetter thantheyieldof the ClassicType1(reducessuspensions with 2.73ormore);
6) the worsttreatmentwithpolymersfor reducingthe indicator"suspensions" is:

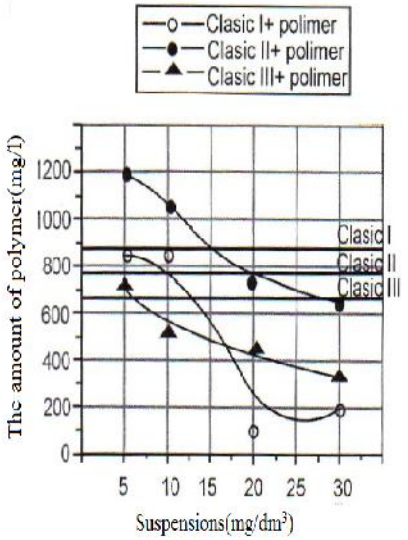
$\Leftarrow$ $\Leftarrow$ Type1 +PA-1-F4-2 (Sample 264-acceptable sample test) toyield2.7%

7) all thetreatments with polymersto reduce the indicator CCO-Mn are better thanthe best classic treatment(classic type 4);
8) the worsttreatmentwithpolymersto reducethe indicator « CCO-Mn »is:
   $\Leftarrow$ Type4 +PA-6-F1-2 (Sample 264-good sample test)with61.7%
9) the best treatmentswith polymerto "petroleum ether extractablesubstances" (fat substances) are the following:
   $\Leftarrow$ Type 3 + PA-6-F1-2 (Sample 264-good sample test) with η = 93.4%, 1.3 times better than the yield of the classic type (reduces the indicator "fatty substances" by 4.25 times more than the standard treatment);
   $\Leftarrow$ Type 4 + PA-6-F1-2 (Sample 264-good sample test) with η = 91.8% to 1.32 times better than the yield of the classic type (reduces the indicator "fatty substances» 3.7 times more than the standard treatment);
   $\Leftarrow$ Type 1 + PA-6-F1-2 (Sample 285- very good sample test) with η = 90.1%, 2.65 times better than the yield of the classic type 1 (reduces the indicator "fatty substances" with 6.66 more than the classical treatment);
   $\Leftarrow$ Type 2 + PA-1-F2-2 (Sample 284- good sample test) with η = 88.5% to 1.86 times better than the yield of the classic type 2 (reduces the indicator "fatty substances» 4.5 times morethan the standard treatment);
   $\Leftarrow$ Type 4 + PA-7-F1-2 (Sample 257-good sample test) with η = 88.5% to 1.27 times better than the yield of the classic type 2 (reduces the indicator "fatty substances" by 2.64 times more than the standard treatment);
10) the weakesttreatmentwithpolymerfor reducing theindicator"extractable substances" with petroleum etheris»
   $\Leftarrow$ Type 3+PA-1-F1-2 (Sample 257-goodsample test)withη=21.8%;
11) the best treatmentswith polymerto reduce theindicator"BOD" are:
   $\Leftarrow$ Type 3+PA-1-F1-2 (Sample 259-very good sample test) withη=83.6%, reduces6times more CBO_5 than the treatmentClassicType 3;
   $\Leftarrow$ Type 3+PA-7-F1-2 (Sample 257-good sample test)withη=82.9%, reduces« CBO_5 »5.83times more than thetreatmentClassicType 3;
12) the worsttreatmentwithpolymersto reducethe indicator« CBO_5 »is:
   $\Leftarrow$ (Type 1+PA-1 Sample 283-very good sample testF1-2verygood) withη=3.57%;
13) all the conventionaltreatmentstestedare weakat reducing the indicator« CBO_5 »;
14) for each indicatorof pollutionthere is oneoptimaltreatment which differs from theoptimaltreatmentsforotherindicatorsof pollution;
15) ofall treatmentstestedso far, "the best" treatment"Type 3 +PA-5-F1-2 (Polymer sample 263)» which reducessimultaneouslywithhighefficiency, all the indicators of pollution:"suspensions" are reduced by 6.2times compared tothe standard treatmentthat reducesthem by 1.2 times; "CCO-Mn" is reducedby5.45times compared to

thestandard treatmentthat reduces it by 1,9 times, the "petroleum ether extractablesubstances" are reduced to 6times compared to thestandard treatmentthat reducesthem by3.57times; «CBO_5»is reduced by4.7times compared tothe standard treatmentthat does *not reducethis indicator*.

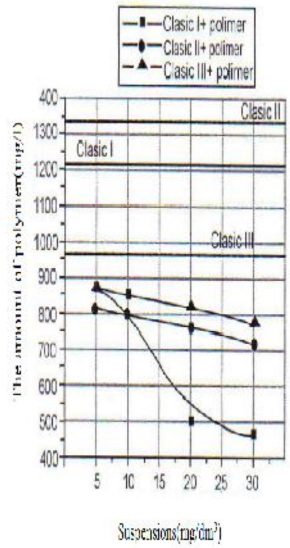
Table 4:Summaryof the bestandworstclassictreatmentsandcombination treatments,"classical+polymers"

Type oftreatment	Effectivenessin reducingpollutionindicators				Qualificative
ClassicType1	6.7	53	34	0.3	The worstof allconventionaltreatmentstested (treatments usedat presentinedible oilsrefiningunits
ClassicType2	19	49.2	48.2	5.75	The bestclassic treatmentto reduceindicator CBO_5 and suspension
ClassicType3	-	47.8	72	0	The best treatmentto reduceindicatorclassic"fatty substances"
ClassicType 4	-	55	69.5	0	The bestclassictreatmentto reduceIndicator CCO-Mn
Type 3+PA-5-F1-2(Sample 263 – good sample test)	83.8	81.7	83.5	78.6	The best treatment with polymerto reduce theindicator "suspensions"
Type4 +PA-6-F1-2 (Sample 264- good sample test)	2.7	61.7	91.8	39.3	The best treatmentpolymerreduceindicator "suspensions"
Type4 +PA-1-F1-2 (Sample 260- good sample test)	78.4	83.6	86.8	35.8	The bestclassic treatmentto reduce the indicator CCO-Mn
Type4 +PA-6-F1-2(Sample 264- good sample test)	2.7	61.7	91.8	39.3	The bestclassic treatmentto reduce the indicator CCO-Mn
Type 3+PA-6-F1-2 (Sample 264- good sample test)	35.1	66.7	93.4	31.4	The best classic treatmentto reduce theindicator"fatty substances»
Type 3+PA-7-F1-2 (Sample 257- good sample test)	-	81.7	21.8	82.9	The best classic treatmentto reduce theindicator"fatty substances" "fatty substances»
Type 3+PA-1-F1-2 (Sample 259- very good sample test)	-	80	-	83.6	The bestclassic treatmentto reduce the indicator CBO_5
(Type 1+PA-1-F1-2 (Sample283- very good sample test)	24.3	67.5	38.3	3.75	The bestclassic treatmentto reduce the indicator CBO_5



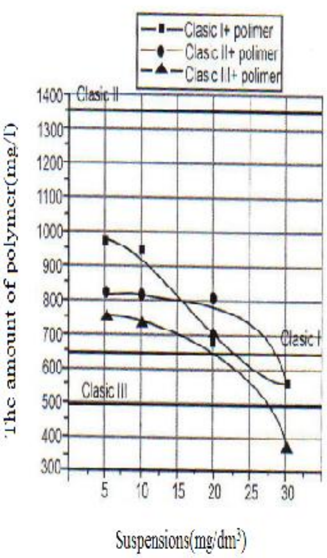
Polymer characteristics :CC=95,93%
V_{int}=15,9dl/g
K_H=0,0057
classical I:
200mg/l $Al_2(SO_4)_3$+500mg/l $CaCO_3$
Classical II:
200mg/l $FeSO_4$+500mg/l $CaCO_3$
Classical III:
200mg/l $Al_2(SO_4)_3$+800mg/l $CaCO_3$
Stage 3 water- cooking oil factory

Figure 1: Variation indicator " suspension " for the amount of polymer



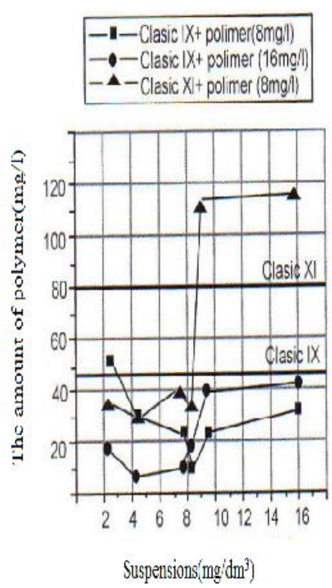
Polymer characteristics :
CC=95,93%
V_{int}=15,9dl/g
K_H=0,0057
classical I:
200mg/l $Al_2(SO_4)_3$+500mg/l $CaCO_3$
Classical II:
200mg/l $FeSO_4$+500mg/l $CaCO_3$
classical III:
200mg/l $Al_2(SO_4)_3$+800mg/l $CaCO_3$
Stage 3 water- cooking oil factory

Figure 2: Variation indicator "CCO-Mn" for the amount of polymer



fatty substances
Polymer characteristics :
CC=95,93%
V_{int}=15.9dl/g
K_H=0.0057
Classical I:
200mg/l $Al_2(SO_4)_3$+500mg/l $CaCO_3$
Classical II:
200mg/l $FeSO_4$+500mg/l $CaCO_3$
Classical III:
200mg/l $Al_2(SO_4)_3$+800mg/l $CaCO_3$
Stage 3 water- cooking oil factory

Figure 3: Variation indicator "fatty substances" for the amount of polymer



Suspensions
intrinsic viscosity
Polymer characteristics :
Classical IX:
800mg/l $FeSO_4$+1000mg/l $CaCO_3$
Classical XI:
400mg/l $FeSO_4$+1000mg/l $CaCO_3$
Stage 3 water- cooking oil factory

Figure 4: Variation indicator "Suspensions" in relation to the intrinsic viscosity of polymers

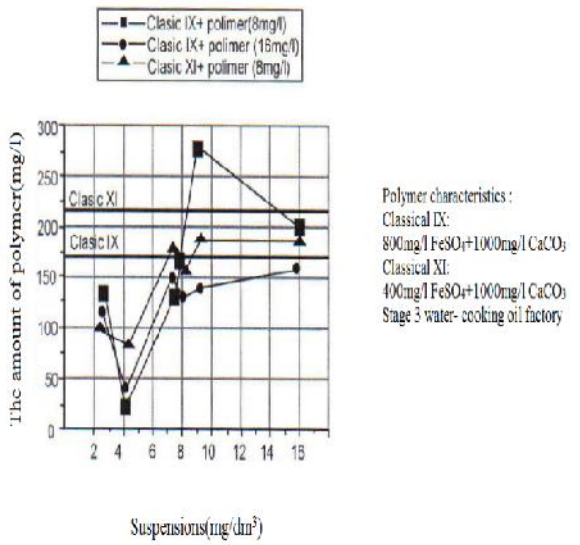


Figure 5: Variation indicator "fatty substances" in relation to the intrinsic viscosity of polymers

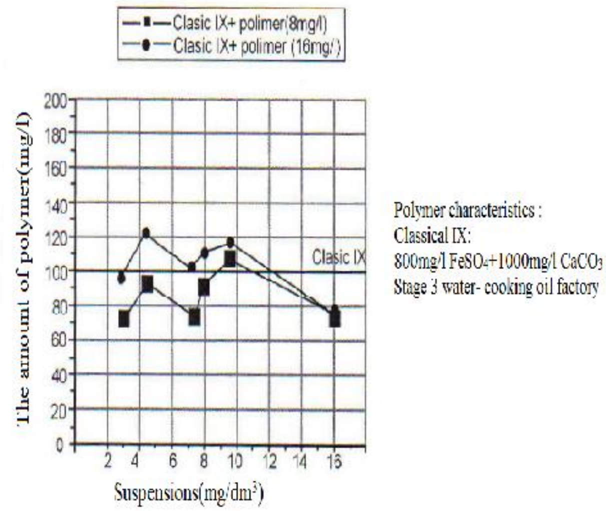


Figure 6: Variation indicator "CBO$_5$" in relation to the intrinsic viscosity of polymers

2. CONCLUSIONS

The researchesconductedfor100,000tonsofsunflowerseeds processed annually by theoil millsin Romaniahave an estimated workingprogram of300days /year,24 hoursa day.The dataunderlying theresearchwereprovided by theLaboratory ofEcologicalEngineeringinthe AlimentaryResearch Institute.

Of the total volume of wastewater discharged annually, 30% are heavily polluted wastewater and 70% weak polluted wastewater.

The data presented demonstrate high polluting levels produced only by 20 industrial units producing edible oil and margarine in Romania. The situations do not fall within the parameters required by the legislation in force. These types of water also represent a category of wastewater which is very hard to purify by the already known classical chemical methods.

Rezultatele prezentate in acest articol au fost obtinute cu sprijinul Ministerului Fondurilor Europene prin Programul Operational Sectorial Dezvoltarea Resurselor Umane 2007-2013, Contract nr. POSDRU 187/1.5/S/155420.

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU 187/1.5/S/155420.

3.REFERENCES

[1] Bikales M., Water soluble polymers,CRC Pres, 1997.
[2]Dferry J., Vascoelastic properties of polymers,J.Willey and Sons Inc.,New York, 1970.
[3] Dekker Marcel, Materials and manufacturing Processes, Vol.14,nr.3,1997.
[4] Gould R.F., Irradiation of Polymers,ACS,New York, 1967.
[5] Guven O., Guven A.-Polymer,22,(1981),1987.
[6] Potter R.C., Gamma Radiation Induced Polymerisation of Styrene,PhD thesis,Londra, 1967.