

1 Separation of Pet from Other Plastics by Froth Flotation Combined with Alkaline Pretreatment

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9

10 Abstract

11 Plastics are naturally hydrophobic materials so, in order to employ flotation for the separation of plastic mixtures, the
12 use of appropriate wetting agents is mandatory. In this work, the effect of pretreatment with alkaline solutions of
13 sodium hydroxide on the floatability of four plastics (PET, PS, PMMA and PVC) was studied. The influence of
14 NaOH concentration, treatment time and temperature of the alkaline solution, and influence of particle size was
15 analyzed.

16 Results showed that alkaline treatment had a strong effect on PET floatability, some effect on floatability of PMMA
17 and PVC and no effect on floatability of PS. Plastics floatability decreased with the increase of NaOH concentration,
18 temperature and treatment time of the alkaline solution. Based on flotation behavior of simple plastics, flotation
19 separation after alkaline treatment of bi-component mixtures of PET with PS and PVC was achieved efficiently. The
20 best separation was obtained for PET/PS mixture, a floated with a grade of 98% in PS and a sunk with a grade of
21 100% in PET. PET/PMMA mixture led to the worst separation. For PET/PMMA and PET/PVC mixtures, flotation
22 separation improved with the decrease of the particles size.
23

24 **Keywords:** plastic; froth flotation; alkaline treatment; particle size.
25

26 1. Introduction

27 Since the discovery of plastic in the 50's of last century, its global production has been continuously rising,
28 gradually replacing materials, like glass and metal. In the last decade, the world production of plastics has been
29 grown around 3.5% per year, increasing from 230 million tonnes in 2005 to 359 million tonnes in 2017 [1]. Global
30 plastics consumption is predicted to continue to grow, reaching 400 million tonnes a year by 2025.

31 Despite the constant increase in plastic consumption, as a result of its versatility and excellent properties, over
32 time plastic has acquired a negative reputation and there is some public pressure on the use of plastics, due to its
33 difficult decomposition, since none of the commonly used plastics are biodegradable. Recently, the public pressure
34 has worsened with information about the enormous quantity of plastic waste dumped into the oceans and with the
35 images of marine animals wrapped in plastic or caught with items, like straws in their noses. About 8 million tonnes
36 of plastic enters the sea every year, and if we do not change the way we produce and use plastics, there will be more
37 plastics than fish in our oceans by 2050.

38 It is noted that landfills is the main final destination of plastic waste, and also the main source of plastic pollution.
39 Of the plastic waste produced between 1950 and 2015, only 9% was recycled, 12% was incinerated, and 79% was
40 accumulated in landfills or the natural environment. It is estimated that in 2015, around 55% of global plastic waste

41 was discarded, 25% was incinerated, and 20% was recycled [2]. However, it should be noted that in Europe, in 2017,
42 32.5% of plastic waste was recycled, 42.6% was recovered through energy recovery processes and 24.9% was
43 landfilled [1]. The vast majority of plastic waste ends up in landfills or the natural environment, or are incinerated,
44 causing serious environmental problems. Thus, it is urgent to substantially reduce our use of plastics, reduce plastic
45 waste by recycling and reusing as much as possible. However, in order to recycle plastic waste it is necessary to
46 separate the plastic mixtures into individual plastics, because different plastics cannot be recycled together due to
47 chemical incompatibilities, differences in melting point and thermal stabilities [3,4]. Froth flotation, the most
48 common separation process used by the mineral industry, is a possible alternative for separating plastic mixtures.
49 Froth flotation allows the separation of hydrophobic from hydrophilic material. However, since most plastics are
50 naturally hydrophobic, selective wetting components are required, which can be achieved by adsorption of wetting
51 agents or surface modification.

52 Several wetting agents, such as methyl cellulose, polyvinyl alcohol, polyethylene glycol, gelatin, tannic acid,
53 saponin, terpineol, triton X-100, calcium lignin sulfonate and sodium lignin sulfonate have been successfully used by
54 several authors [5-10]. Surface modification of plastics by treatment with alkaline solutions followed by froth
55 flotation were developed [3,11-22]. Plastic flotation is controlled not only by hydrophobicity, but also by the size of
56 the plastic particles [13,19,23-24].

57 In this study, an alkaline treatment of PET, PVC, PS and PMMA particles with sodium hydroxide (NaOH)
58 solutions followed by froth flotation was performed. The parameters analysed were the NaOH concentration,
59 temperature and treatment time of alkaline solution, and particle size.

60

61 **2. Experimental**

62

63 *2.1 Materials*

64 Four different kinds of post-consumer plastics were used: Polyethylene Terephthalate (PET, transparent),
65 Polyvinyl Chloride (PVC, light green), Polystyrene (PS, black) and Polymethyl methacrylate (PMMA, white). The
66 samples were previously ground and the sieve size fractions used in this study were 2.8-2 mm and 4-2.8 mm.

67 The density of these plastics, measured by an Ultra Pycnometer (AccuPyc 1330), are as follows: PET: 1.364
68 g/cm³; PVC: 1.326 g/cm³; PS: 1.047 g/cm³; and PMMA: 1.204 g/cm³.

69 Sodium hydroxide was used in the alkaline treatment as wetting agent, and Methyl isobutyl carbinol (MIBC)
70 (109916 Sigma Aldrich) was used as frothing reagent.

71

72 *2.2. Alkaline pretreatment*

73 Plastic samples were treated with NaOH solutions, using a Denver stirrer (400 rpm) with a plot plate. The
74 treatment was done in a 1 L glass beaker using 40 g of plastic at a solids concentration of 20 wt%. The beaker was
75 placed on a hot plate in order to adjust and control the temperature. The alkaline treatment was controlled by the
76 operating parameters: NaOH concentration, temperature and treatment time (Table 1). Plastic samples were treated
77 in alkaline solutions at NaOH concentrations of 2%, 6% and 10%, at a temperature range between 20 °C and 80 °C,
78 and a treatment time between 2.5 min and 30 min (Table 1). After alkaline pretreatment, the plastics were taken out
79 from alkaline solutions and rinsed in a stream of tap water to remove the treatment solution, and used to conduct
80 flotation tests.

81

82 **Table 1** – Experimental range and levels of the independent variables for the alkaline treatment.

| Parameters | Symbol | Range values and coded level () | | | | |
|------------------------|--------|---------------------------------|----------|----------|----------|------|
| NaOH concentration (%) | A | 2 | 6 | 10 | | |
| | | (-1) | (0) | (+1) | | |
| Temperature (°C) | B | 20 | 40 | 70 | 80 | |
| | | (-1) | (-0.333) | (+0.666) | (+1) | |
| Treatment time (min) | C | 2.5 | 5 | 10 | 20 | 30 |
| | | (-1) | (-0.818) | (-0.455) | (+0.273) | (+1) |

83 -1: factor at low level; 0: factor at medium level; +1: factor at high level.

84

85 *2.3 Flotation experiments*

86 The froth flotation experiments were performed in a Denver cell, with a capacity of 3 dm³, at a low rotational
87 speed of 600 rpm. Each flotation test used 40 g of plastics previously treated with an alkaline solution and rinsed,
88 that was conditioned with the frother (MIBC) for about 2 minutes before the flotation tests. MIBC was added at a
89 constant concentration of 30x10⁻³ g/L in all experiments. After conditioning, the air valve was opened and the floated
90 product was collected over 6 minutes. Both the floated and the sunk (non-floated) were dried and weighed. Tap
91 water was used in the flotation tests.

92 The pH in the flotation cell was not adjusted, but it was measured periodically along the experiment. The pH
93 remained approximately constant, in the range of 7.0-7.3.

94 Firstly, flotation tests were carried out with one-component plastic samples previously treated with an alkaline
95 solution. According to the floatability of plastics, it was possible to separate the four plastics into two groups: the
96 first group constituted only by PET, which has low floatability, and the second group that includes the other three
97 plastics (PS, PMMA and PVC), which have similar floatability. Then, flotation separation of binary plastic mixtures
98 was performed using three bi-component mixtures: PET/PS, PE/PMMA and PET/PVC. Plastic mixtures were
99 previously treated with an alkaline solution, and each plastic contributed with 50% (20 g) for the total mixture
100 weight.

101 The effectiveness of the flotation tests was evaluated by the grade and recovery of each type of plastic in the
102 floated and in the sunk products, and by the separation efficiency, defined by Schulz [25]. In the flotation tests of the
103 plastic mixtures, the plastics type presented in the floated and the sunk were separated from each other by manual
104 sorting, weighed, and flotation recovery and grade were calculated based on mass balance. This was possible due to
105 differences in colours and shapes of the plastics particles. Experiments were done three times under similar operating
106 conditions.

107 A second order polynomial equation was chosen to investigate the effect of different operating parameters of the
108 alkaline treatment on the floatability of the plastics (Equation (1)):

109

$$110 \quad Y = b_0 + b_1A + b_2B + b_3C + b_{12}AB + b_{13}AC + b_{23}BC + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 \quad (1)$$

111

112 where, Y is the predicted response, b_0 is model constant; b_1 , b_2 and b_3 are linear coefficients; b_{12} , b_{13} and b_{23} are
113 the interaction coefficients; and b_{11} , b_{22} and b_{33} are the quadratic coefficients. This model represents the effect of
114 NaOH concentration (A), temperature (B), treatment time (C) and their interactions on the plastics floatability. The
115 list of the independent variables (A, B and C) with their coded and levels are presented in Table 1. The significance
116 of model equation, individual parameters, and factor interactions were evaluated by analysis of variance (ANOVA)
117 at the confidence intervals of 95% ($\alpha = 0.05$).

118

119 3. Results and discussion

120

121 3.1. Effect of alkaline pretreatment on PET floatability

122 Two size fractions (2-2.8 mm and 2.8-4 mm) of the four plastics were treated with different concentrations of
123 NaOH solutions, at different temperature and treatment time. Figure 1 shows the effect of NaOH concentration,
124 temperature and treatment time of the alkaline solution on the flotation recovery of PET of the two fractions. The
125 floatability of PET was strongly influenced by the NaOH concentration, temperature and treatment time. The
126 flotation recovery of PET decreased with increasing NaOH concentration, temperature and treatment time, of
127 alkaline solution. Also, Kangal et al. [3], Drelich et al. [11], Burat et al. [13], Nagy et al. [15], Wang et al. [10,19],
128 Guo et al. [20], verified that recovery of PET in the floated decreased with increasing NaOH concentration,
129 temperature and treatment time of alkaline solution. They found that alkaline treatment rendered the PET surface
130 more hydrophilic, which may be a result of the hydrolysis of ester bonds in PET chains.

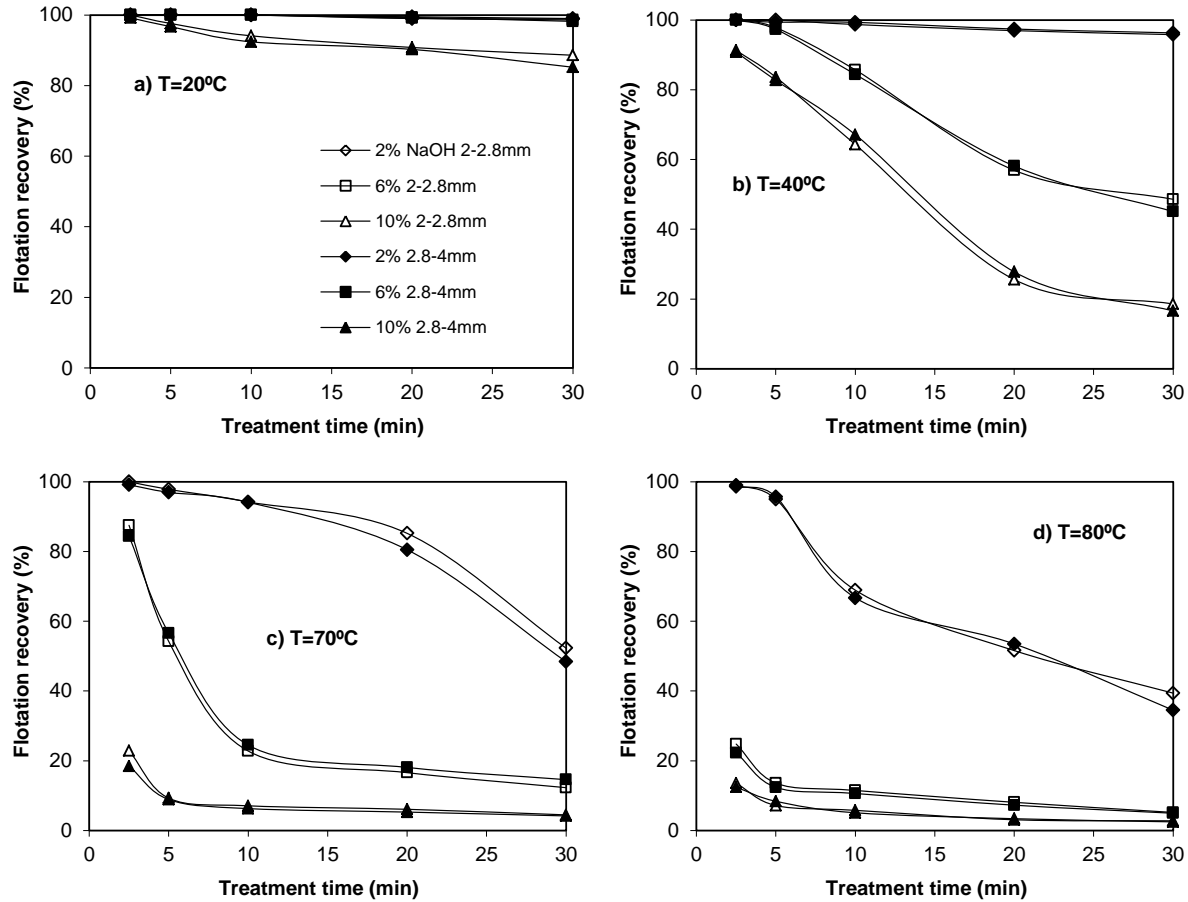
131 The two size fractions showed similar results. This means that the effect of particle size was minimal. The effect
132 of NaOH concentration depended on the values of temperature and treatment time, and the effect of treatment time
133 depended on the values of NaOH concentration and temperature and vice versa (Figure 1). At higher temperature, the
134 NaOH concentration or treatment time needed to make PET hydrophilic was low. Also, at higher NaOH
135 concentration, the temperature or treatment time needed to make PET hydrophilic was low. The lowest recovery of
136 PET in the floated (2.5% for fraction 2.8-4 mm and 2.8% for fraction 2-2.8 mm) was obtained with the highest
137 NaOH concentration (10%), the highest treatment time (30 min) and the highest temperature (80 °C).

138 When temperature was at the lowest value (20° C), a change in NaOH concentration or treatment time had a low
139 effect in PET recovery. PET is naturally hydrophobic since alkaline treatment with low NaOH concentration
140 solutions and at a temperature of 20 °C, the flotation recovery of PET was about 100%. At a temperature of 20 °C
141 and low NaOH concentration (2% and 6%), there was no hydrophilization of PET (Figure 1a).

142 At a temperature of 40 °C temperature, when NaOH concentration was 2%, a change in treatment time had low
143 effect in PET recovery (Figure 1b). But when NaOH concentration was at 6% or 10%, flotation recovery of PET
144 decreased significantly with increasing treatment time.

145 At temperatures of 70 °C and 80 °C (Figure 1c and 1d), flotation recovery of PET decreased with increasing
146 treatment time. At a temperature of 80 °C and for fraction 2.8-4 mm, the flotation recovery dropped from 98.6% to
147 34.5%, when the treatment time increased from 2.5 min to 30 min for a NaOH concentration of 2%. However, for a
148 higher concentration of NaOH (10%), the hydrophilization of PET was achieved for low treatment time.

149



150

151

152 **Figure 1** - Influence of NaOH concentration, temperature and treatment time of the alkaline solution on floatability
 153 of PET for fractions 2-2.8 mm and 2.8-4 mm.

154

155 To find the effect of the NaOH concentration, temperature and treatment time in PET recovery, statistical
 156 analysis of the experimental data was done and models were developed for optimization of the parameters. A
 157 quadratic relationship was shown to describe the dependence of the plastic floatability on the three operating
 158 variables of the alkaline treatment. The equations presented are in terms of coded levels: the low levels of the
 159 parameters were coded as -1 and the high levels as +1 (Table 1). Therefore, the relative impact of the NaOH
 160 concentration, temperature and treatment time in PET recovery can be identified by comparing the coefficients of the
 161 equation.

162 The analysis of variance (ANOVA) for the PET recovery model of the two size fractions is shown in Table 2.
 163 Based on all statistical analysis, the model presented was considered adequate to the prediction of PET floatability
 164 after alkaline treatment. The coefficients of determination (R^2) obtained for the PET recovery of size fraction 2-2.8
 165 mm and 2.8-4 mm were 0.8885 and 0.8881 respectively, showing that the fit was good. The significance level of
 166 each independent variable, as well as their quadratic terms and interaction between the variables was evaluated based
 167 on corresponding F-values and p-values. For the two size fractions the model F-value was about 44 at 99.99%
 168 confidence level and the model Prob > F value is less than 0.05, shows that the model is significant.

169

170 **Table 2** - Analysis of Variance (ANOVA) of the response surface quadratic model for PET recovery of the two size
 171 fractions.

| | | model | A | B | C | AB | AC | BC | A ² | B ² | C ² |
|---|---------|---------|---------|---------|---------|---------|--------|--------|----------------|----------------|----------------|
| 2-2.8 mm | p-value | <0.0001 | <0.0001 | <0.0001 | <0.0001 | <0.0001 | 0.9635 | 0.1169 | 0.0588 | 0.4583 | 0.1557 |
| | Prob>F | | | | | | | | | | |
| Sum of Square=79831; Mean of square= 8870; degree of freedom=9; F _{model} =44.3; R ² =0.8885; Adjusted R ² =0.8680 | | | | | | | | | | | |
| 2.8-4 mm | p-value | <0.0001 | <0.0001 | <0.0001 | 0.0002 | <0.0001 | 0.8789 | 0.1242 | 0.0667 | 0.4283 | 0.2593 |
| | Prob>F | | | | | | | | | | |
| Sum of Square=79999; Mean of square=8889; degree of freedom=9; F _{model} =44.1; R ² =0.8881; Adjusted R ² =0.8680 | | | | | | | | | | | |

172
 173 The quadratic effect of the three variables and the interaction between NaOH concentration and time treatment
 174 and between temperature and treatment time had no statistical significance, and hence can be neglected. The
 175 variables that influenced PET floatability were the linear terms of NaOH concentration, temperature and time
 176 treatment, and the linear term of interaction between NaOH concentration and temperature. For fraction +2-2.8 mm
 177 and +2.8-4 mm, the model developed using these factors and their interaction is given in Eqs. (2) and (3),
 178 respectively.

179
 180
$$\text{PET recovery (\%)} = 62.46 - 22.12A - 33.38B - 14.83C - 15.88AB \quad (2)$$

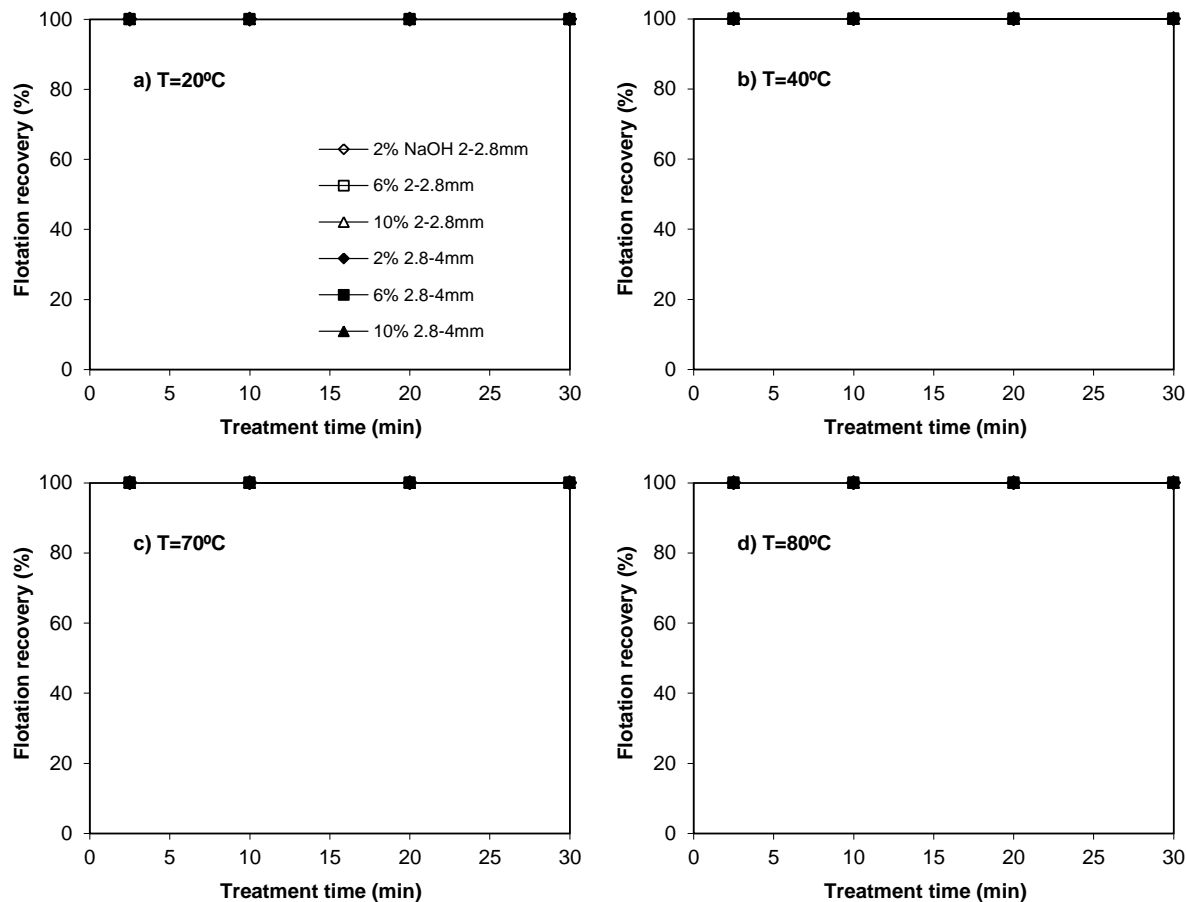
181
$$\text{PET recovery (\%)} = 61.83 - 22.10A - 33.70B - 15.10C - 15.27AB \quad (3)$$

182
 183 where A is the NaOH concentration (%), B the temperature (°C), and C the treatment time (min). The coefficients of
 184 the three parameters were negative values indicating a negative correlation between PET floatability and parameter
 185 levels. For both size fractions, PET recovery presented an equal order of relative impact of the operating parameters.
 186 The equation coefficients clearly showed that PET recovery was mainly affected by temperature, followed by NaOH
 187 concentration, treatment time and interaction between the NaOH concentration and temperature. The quadratic effect
 188 of the three variables was not significant, and therefore it was not considered.

189
 190 *3.2. Effect of alkaline pretreatment on PS floatability*

191 Figure 2 shows the effect of NaOH concentration, temperature and treatment time of the alkaline solution on the
 192 flotation recovery of PS, for fractions 2-2.8 mm and 2.8-4 mm. The floatability of PS was not influenced by alkaline
 193 pretreatment, since for all tests the recovery in the float was 100%. For all tests of alkaline pretreatment, there was no
 194 hydrophilization of PS.

195



196

197

198 **Figure 2** - Influence of NaOH concentration, temperature and treatment time of the alkaline solution on floatability
 199 of PS, for fractions 2-2.8m and 2.8-4 mm.

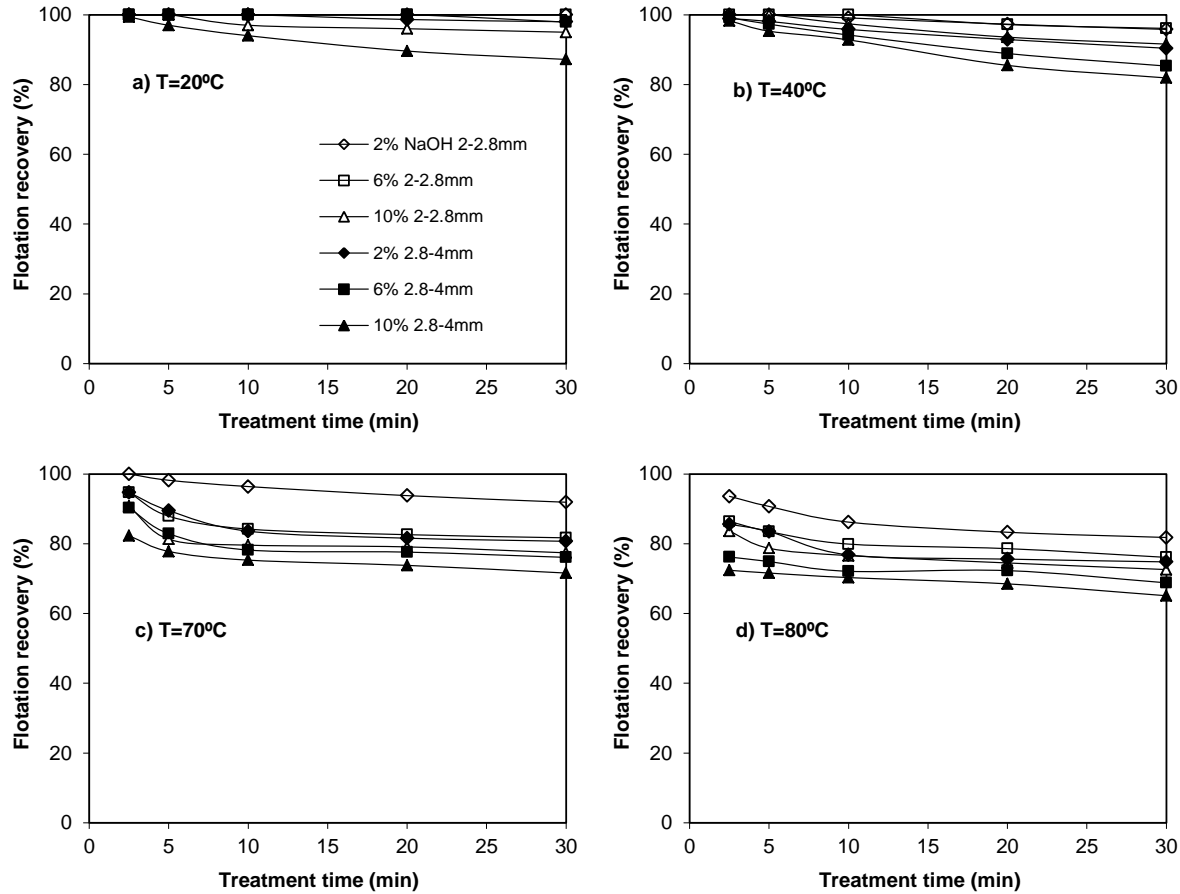
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201 3.3. Effect of alkaline pretreatment on PMMA floatability

202 Flotation recovery of PMMA decreased slightly with increasing NaOH concentration, temperature and treatment
 203 time (Figure 3). However, the effect of these three parameters on PMMA recovery was smaller than that observed
 204 for PET. Temperature had a considerable effect on alkaline pretreatment of PMMA. At 20 °C, for the three NaOH
 205 concentrations and for all treatment times, there was no hydrophilization of PMMA, since PMMA recovery was
 206 about 100%. The effect of NaOH concentration, temperature and treatment time of the alkaline solution on the
 207 flotation recovery of PMMA for the two fractions (2-2.8 mm and 2.8-4 mm) was similar. However, PMMA recovery
 208 of fraction 2.8-4 mm was lower than that observed for fraction 2-2.8 mm. Also, Shen et al. [5,23], Fraunholz [12],
 209 Wang et al. [19,21], Pita and Castilho [24], Marques and Tenório [26], found that large plastic particles were more
 210 difficult to float than smaller ones.

211 The lowest recovery of PMMA in the floated was obtained with the highest NaOH concentration (10%), the
 212 highest temperature (80 °C) and the highest treatment time (30 min), with 67.6% recovery for fraction 2-2.8mm and
 213 56.5% recovery for fraction 2.8-4 mm.

214



215

216

217 **Figure 3** - Influence of NaOH concentration, temperature and treatment time of the alkaline solution on floatability
 218 of PMMA, for fractions 2-2.8m and 2.8-4 mm.

219

220 A second order polynomial equation was chosen to describe the dependence of the PMMA floatability on the
 221 three operating variables of the alkaline treatment. The analysis of variance (ANOVA) for PMMA recovery model of
 222 the two size fraction is shown in Table 3. For size fractions of 2-2.8 and 2.8-4 mm, the R^2 values of 0.9485 and
 223 0.9584 respectively, implies that the model fit was good. For the two size fractions, the F-value at 99.99%
 224 confidence level and the Prob > F value was less than 0.05, showing that the model was significant.

225

226 **Table 3** - Analysis of Variance (ANOVA) of the response surface quadratic model for PMMA recovery of the two
 227 size fractions.

| | model | A | B | C | AB | AC | BC | A ² | B ² | C ² |
|----------|--|---------|---------|---------|---------|--------|--------|----------------|----------------|----------------|
| 2-2.8 mm | p-value | <0.0001 | <0.0001 | <0.0001 | <0.0001 | 0.2060 | 0.0001 | 0.3750 | <0.0001 | 0.086 |
| | Prob>F | | | | | | | | | |
| | Sum of Square=4316; Mean of square= 480; degree of freedom=9; F _{model} =102.4; R ² =0.9485; Adjusted R ² =0.9393 | | | | | | | | | |
| 2.8-4 mm | p-value | <0.0001 | <0.0001 | 0.0002 | 0.0088 | 0.1793 | 0.3509 | 0.5321 | <0.0001 | 0.088 |
| | Prob>F | | | | | | | | | |
| | Sum of Square=6645; Mean of square= 738; degree of freedom=9; F _{model} =128.0; R ² =0.9584; Adjusted R ² =0.9509 | | | | | | | | | |

228

229 For fractions +2-2.8 mm and +2.8-4 mm, the equations (4) and (5), respectively, dictate that linear terms of the
 230 NaOH concentration, temperature and treatment time, linear term of interaction between NaOH concentration and
 231 temperature, and quadratic term of the temperature had a negative effect on PMMA floatability of the two size
 232 fractions. Interaction between temperature and treatment time had a negative effect on PMMA floatability for the
 233 size fraction +2.8-4 mm. The linear term of interaction between NaOH concentration and treatment time, and the
 234 quadratic effect of NaOH concentration and treatment time had no statistical significance, and hence were not
 235 considered.

236

$$237 \text{ PMMA recovery (\%)} = 95.12 - 3.35A - 9.01B - 3.17C - 2.79AB - 1.98BC - 5.23B^2 \quad (4)$$

$$238 \text{ PMMA recovery (\%)} = 89.08 - 3.65A - 11.63B - 4.64C - 1.30AB - 4.25B^2 \quad (5)$$

239

240 For both size fractions, PMMA recovery presented an equal order of relative impact of the three independent
 241 variables. PMMA recovery was mainly affected by temperature, followed by NaOH concentration (A), treatment
 242 time (C) and interaction between the NaOH concentration and temperature (AB).

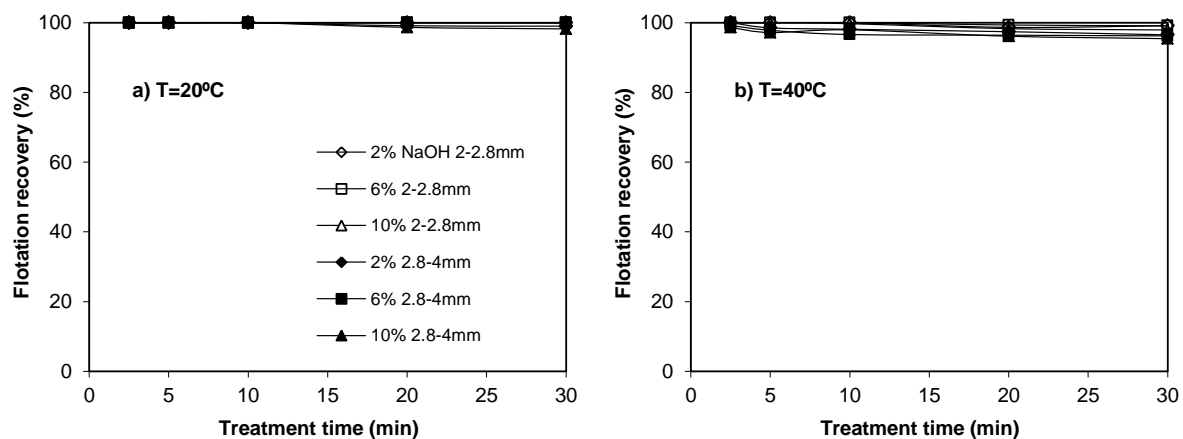
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244 3.4. Effect of alkaline pretreatment on PVC floatability

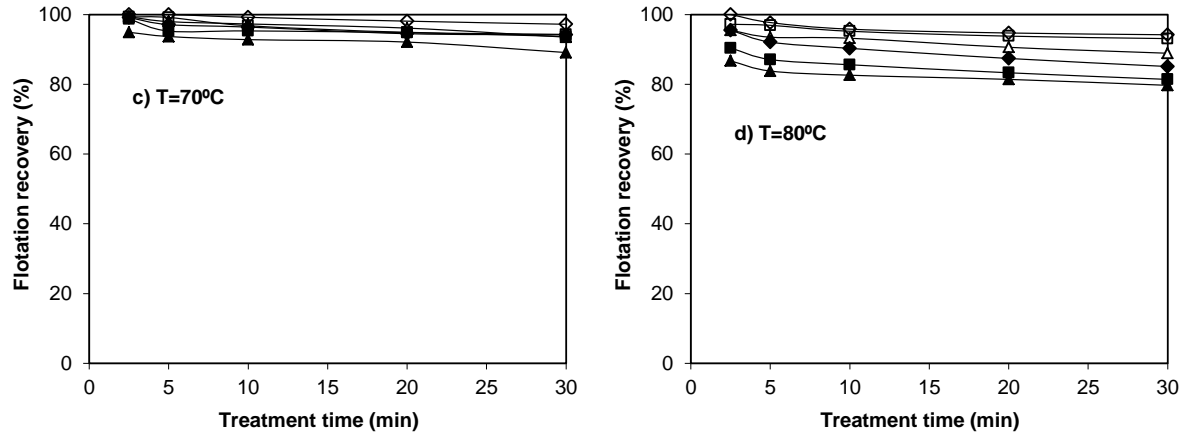
245 Floatability of PVC was influenced by NaOH concentration, temperature and treatment time (Figure 4).
 246 However, this effect was very smaller than that observed for PET, and slightly smaller than that observed for
 247 PMMA. PVC recovery for fraction 2-2.8 mm was greater than for fraction 2.8-4 mm. Flotation recovery of PVC
 248 decreased slightly with increasing NaOH concentration, temperature and treatment time. Thus, the lowest recovery
 249 of PVC in the floated was obtained with the highest NaOH concentration (10%), the highest temperature (80 °C) and
 250 the highest treatment time (30 min), with 87.8% recovery for fraction 2-2.8mm and 76.4% recovery for fraction 2.8-
 251 4 mm.

252 At a temperature of 20 °C, for three NaOH concentrations and all treatment times, there was no hydrophilization
 253 of PVC, since PVC recovery was about 100%. Also, at 40 °C, the hydrophilization of the PVC was small, since the
 254 PVC recovery was close to 100%.

255



256



257 ..
 258 **Figure 4** - Influence of NaOH concentration, temperature and treatment time of the alkaline solution on floatability
 259 of PVC, for fractions 2-2.8m and 2.8-4 mm.
 260

261 The analysis of variance (ANOVA) for PVC recovery model of the two size fractions is shown in Table 4. For
 262 size fractions of 2-2.8 mm and 2.8-4 mm, the R^2 values of 0.9282 and 0.8720 respectively, implies that the model fit
 263 was good. Model F-value of size fractions 2-2.8 mm and 2.8-4 mm was 71.8 and 38.0, respectively, with a 99.99%
 264 confidence level and the Prob > F value lower than 0.05, showing that the model was significant.
 265

266 **Table 4** - Analysis of Variance (ANOVA) of the response surface quadratic model for PVC recovery of the two size
 267 fractions.

| | | model | A | B | C | AB | AC | BC | A ² | B ² | C ² |
|----------|--|---------|---------|---------|---------|---------|--------|---------|----------------|----------------|----------------|
| 2-2.8 mm | p-value | <0.0001 | <0.0001 | <0.0001 | <0.0001 | <0.0001 | 0.1006 | <0.0001 | 0.8151 | <0.0001 | 0.0651 |
| | Prob>F | | | | | | | | | | |
| | Sum of Square=406; Mean of square= 45.1; degree of freedom=9; F _{model} =71.8; R ² =0.9282; Ajusted R ² =0.9153 | | | | | | | | | | |
| 2.8-4 mm | p-value | <0.0001 | 0.0005 | <0.0001 | <0.0001 | 0.0088 | 0.7543 | 0.0051 | 0.8912 | <0.0001 | 0.3082 |
| | Prob>F | | | | | | | | | | |
| | Sum of Square=1695; Mean of square= 188; degree of freedom=9; F _{model} =38.0; R ² =0.8720; Ajusted R ² =0.8495 | | | | | | | | | | |

268
 269 The linear term of interaction between NaOH concentration and treatment time and the quadratic term of NaOH
 270 concentration and treatment time had no statistical significance, and hence were neglected. For fractions +2-2.8 mm
 271 and +2.8-4 mm, the equations (6) and (7), respectively, dictate that NaOH concentration, temperature, and treatment
 272 time of alkaline pretreatment had a negative effect on PVC floatability of the two size fractions. Also, the interaction
 273 between NaOH concentration and temperature, interaction between temperature and treatment time, and quadratic
 274 term of temperature had a negative effect on the PVC floatability.
 275

276 PVC recovery (%) = 99.01 - 0.75A - 2.64B - 1.29C - 0.97AB - 1.33BC - 1.81B² (6)

277 PVC recovery (%) = 97.37 - 1.38A - 5.84B - 1.85C - 1.57AB - 1.42BC - 4.30B² (7)

278

279 The three independent variables presented an equal order relative impact on PVC recovery for both size fractions.
280 PVC recovery was mainly affected by temperature (B). The three independent variables presented less impact on
281 PVC recovery than on PET recovery.

282

283 *3.5 Separation of bi-component mixtures of PET with PS, PMMA and PVC*

284 Previous results illustrated that alkaline treatment had a strong effect on PET floatability, some effect on
285 floatability of PMMA and PVC, but no effect on PS floatability. Thus, floatability of PET can be significantly
286 reduced in hot alkaline solutions, showing smaller floatability than the other three plastics, particularly than PS. So,
287 one can assume that the alkaline treatment is not efficient to separate PS, PMMA and PVC plastics from each other,
288 but may allow the separation of PET from PS, PMMA and PVC. In face of these results, further alkaline treatment
289 and flotation tests were developed using bi-component plastic mixtures of PET with PS, PMMA and PVC, in equal
290 proportions, for two size fractions (2-2.8 mm and 2.8-4 mm), in order to render the PET hydrophilic and maintain the
291 other component in a hydrophobic state. The alkaline treatment conditions chosen for each of the three bi-component
292 mixtures (PET/PS, PET/PMMA and PET/PVC) were those that led to maximum differences between PET
293 floatability and floatability of the other plastics, to obtain a selective separation.

294 For PET/PS mixture, alkaline treatment conditions that led to the maximum difference between floatability of PS
295 and floatability of PET were: NaOH concentration of 10%, temperature at 80 °C and treatment time of 30 min. In
296 these conditions, PET floatability was minimized, while PS floated recovery was 100%. These were the conditions
297 used in the alkaline treatment of PET/PS mixture. The results of froth flotation tests are presented in Table 5.

298 For PET/PMMA and PET/PVC mixtures, alkaline treatment conditions that led to the most efficient separation
299 were: NaOH concentration of 10%, temperature at 70 °C and treatment time of 20 min. Thus, these were the
300 conditions used in the alkaline treatment of plastic mixtures subsequently subject to flotation separation, whose
301 results are shown in Table 5.

302 The best result was obtained in the PET/PS mixture separation, having the highest separation efficiency (near
303 98%) and a sunk with a grade of 100% in PET and a floated with a grade of 98% in PS. On the other side,
304 PET/PMMA mixture had the lowest separation efficiency. These results were consistent with the floatability of
305 plastics observed in the mono-component tests (Figure 1, 2, 3 and 4).

306 The influence of the particle size on separation quality of the PET/PS mixture was not evident, since the two size
307 fractions presented similar results (Table 5). The effect of particle size on PET floatability was minimal, and PS
308 floatability was not influenced by particle size, since all PS particles floated.

309 Coarse fraction of PET/PMMA mixture had the worst results. The difference between floatability of PMMA and
310 floatability of PET was smaller for the coarse size fraction. The separation was more efficient for the fine fraction
311 because there was a great amount of PMMA recovered in the floated, leading to a sunk with a grade of 82.8% in PET
312 and a floated with a grade of 92.8% in PMMA.

313 For the PET/PVC mixture, the quality of separation worsened slightly with the increase of the particles size
314 (Table 5). PVC recovery in the floated decreased with the increase of the particles size, and PET recovery in the
315 floated was not affected by particles size. For the fine fraction, PET recovery in the sunk was 94.3%, with a grade of
316 97.0%; and PVC recovery in the floated was 97.1% with a grade of 94.5%.

317 Floatability of PS, PMMA and PVC increased with decreasing particle size, because their particles presented
318 regular shapes, while the effect of the particle size on PET floatability was minimal because their particles presented

319 lamellar shape and low weight. For the mixtures of PET/PMMA and PET/PVC, the worst results for coarse fraction
 320 can be explained by the more regular shape of PMMA and PVC and by the higher weight of these particles that
 321 hinders flotation. Thus, the particles size control is important for flotation separation of plastic mixtures.

322

323 **Table 5** - Results of the flotation tests on the mixtures of PET with PS, PMMA and PVC for two size fractions.
 324

| Plastic Mixtures | Fraction (mm) | Products | Recovery (%) | | Grade (%) | | Separation Efficiency (SE) (%) |
|------------------|---------------|----------|--------------|------|-----------|------|--------------------------------|
| | | | PET | OP* | PET | OP* | |
| PET/PS | 2-2.8 | Floated | 1.9 | 100 | 1.9 | 98.1 | 98.1 |
| | | Sunk | 98.1 | 0 | 100 | 0 | |
| | 2.8-4 | Floated | 2.2 | 100 | 2.2 | 97.8 | 97.8 |
| | | Sunk | 97.8 | 0 | 100 | 0 | |
| PET/PMMA | 2-2.8 | Floated | 6.2 | 80.5 | 7.2 | 92.8 | 74.3 |
| | | Sunk | 93.8 | 19.5 | 82.8 | 17.2 | |
| | 2.8-4 | Floated | 5.5 | 73.8 | 6.9 | 93.1 | 68.3 |
| | | Sunk | 94.5 | 26.2 | 78.3 | 21.7 | |
| PET/PVC | 2-2.8 | Floated | 5.7 | 97.1 | 5.5 | 94.5 | 91.4 |
| | | Sunk | 94.3 | 2.9 | 97.0 | 3.0 | |
| | 2.8-4 | Floated | 5.2 | 92.6 | 5.3 | 94.7 | 87.4 |
| | | Sunk | 94.8 | 7.4 | 92.8 | 7.2 | |

325 OP* denotes the other plastics, namely PS, PMMA or PVC.

326

327 Conclusions

328 The four plastics (PET, PS, PMMA and PVC) are naturally floatable and thus, it was necessary a selective
 329 wetting component to achieve a selective flotation separation of plastic mixtures. The effect of treatment of plastics
 330 with alkaline solutions of NaOH on the floatability of the four plastics was studied. It was verified that alkaline
 331 solutions had a strong influence on PET floatability, medium influence on PVC and PMMA floatability and no effect
 332 on PS floatability. The flotation recovery of PET, PMMA and PVC decreased with increasing NaOH concentration,
 333 temperature and treatment time of alkaline solution. From the statistical data analysis, the most significant factor
 334 with respect to alkaline pretreatment on plastics floatability was temperature, followed by NaOH concentration, and
 335 treatment time. Also, the interaction between NaOH concentration and temperature had a significant negative effect
 336 on the plastics floatability.

337 After alkaline treatment of the plastics under optimal conditions, flotation separation of PET from PS, PMMA or
 338 PVC was successfully achieved. The best result was obtained in the PET/PS mixture separation. PET recovery in the
 339 sunk was about 98%, with a grade of 100%; and PS recovery in the floated was 100% with a grade of about 98%,
 340 with the following pretreatment conditions: 10% NaOH concentration, temperature at 80 °C, and treatment time of
 341 30 min. For this mixture, the two size fractions (2-2.8 mm and 2.8-4 mm) presented similar results.

342 PET/PMMA mixture had the worst separation. For PET/PVC, a good separation was obtained. For these two
 343 mixtures, the quality of separation worsened slightly with the increase of the particles size as a consequence of the
 344 decrease of the recovery of PMMA and PVC in the floated for the coarser particles.

345

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350

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352

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