

# Separation of PET from other plastics by flotation combined with alkaline pretreatment

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## Abstract

Plastics are naturally hydrophobic, so the selective flotation of plastic mixtures is impossible without changing their surface properties. The objective of this research is flotation separation of PET from PS, PMMA and PVC combined with sodium hydroxide pretreatment. NaOH pretreatment had a strong effect on PET's floatability, medium effect on PMMA and PVC and limited effect on PS. The reduction of PET floatability is ascribed to a sharp decline of contact angle. The optimal pretreatment conditions were: 10% NaOH concentration, 70 °C (PET/PMMA and PET/PVC) to 80 °C (PET/PS) and plastic treatment times in the alkaline solution of 20 min (PET/PMMA and PET/PVC) to 30 min (PET/PS). Flotation separations were achieved efficiently and the best results were obtained for the PET/PS mixture, with a floated PS grade of 98% and a sunk PET grade of 100%. PET and PS was separated effectively, implying that sodium hydroxide treatment possesses superior applicability.

**Keywords:** *alkaline treatment, flotation, particle size, plastic.*

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## 1. Introduction

Since the discovery of plastic in the '50s of the last century, its global production has been continuously rising, gradually replacing materials, like glass and metal. In the last decade, the world production of plastics has been grown around 3.5% per year, increasing from 230 million tonnes in 2005 to 359 million tonnes in 2017<sup>[1]</sup>. PET plays an important role in the packaging industry. The global PET production in 2017 was some 30.3 million ton, and in 2016, 485 billion PET bottles were produced worldwide.

Despite the constant increase in plastic consumption none of the commonly used plastics is biodegradable. The vast majority of plastic waste ends up in landfills or the natural environment, or are incinerated, causing serious environmental problems. In 2015, around 55% of global plastic waste was discarded, 25% was incinerated, and 20% was recycled<sup>[2]</sup>. However, in Europe during 2017, 32.5% of plastic waste was recycled, 42.6% was recovered through energy recovery processes and 24.9% was landfilled<sup>[1]</sup>. Thus, it is urgent to substantially reduce the use of plastics and lessen plastic waste by recycling and reusing. However, in order to recycle plastic waste it is necessary to separate the plastic mixtures into individual plastics, because different plastics cannot be recycled together due to chemical incompatibilities, different melting points and thermal stabilities<sup>[3,4]</sup>. For example, in PET contaminated with PVC, PVC will degrade at the

PET processing temperature and produce char, leading to product discoloration<sup>[5]</sup>.

Froth flotation, the most common separation process used by the mineral industry, is a possible alternative for separating plastic mixtures. Froth flotation allows the separation of hydrophobic and hydrophilic materials. However, since most plastics are naturally hydrophobic, it is necessary to selectively modify the plastic surface before plastic flotation. In the past few years, many modification methods were applied to plastic flotation, including wetting reagents<sup>[6-13]</sup> and surface chemical modification by treatment with chemical reagents, particularly with alkaline solution of NaOH<sup>[3,14-30]</sup>. Surface modification for plastic flotation aims to raise the hydrophilicity by introducing hydrophilic groups on plastic surface. In previous studies, it has been found that the alkaline solution of NaOH was able to destroy the hydrophobicity of PET, making it hydrophilic, whereas the hydrophobicity of others plastics was only slightly affected<sup>[14,16,17]</sup>.

In this study, an alkaline treatment of PET, PVC, PS and PMMA particles with sodium hydroxide (NaOH) solutions followed by froth flotation was performed. Separation of PET from other plastics was achieved by froth flotation combined with NaOH pretreatment in bi-component mixtures of plastics. The mechanism of NaOH treatment was examined by contact angle measurements. The analysed parameters were: NaOH concentration, temperature, and treatment time of alkaline solution, and particle size.

## 2. Experimental

### 2.1 Materials

Four different kinds of post-consumer plastics were used: Polyethylene Terephthalate (PET) (colorless, transparent, lamellar); Polyvinyl Chloride (PVC) (light green to white, translucent, lamellar), Polystyrene (PS) (dark colored, translucent, irregular) and Polymethyl methacrylate (PMMA) (colorless to white, transparent, irregular) (Figure 1). The samples were previously ground and the sieve size fractions used in this study were +2-2.8 mm and +2.8-4 mm. The density of these plastics, measured by an Ultra Pycnometer (AccuPyc 1330), are as follows: PET: 1.364 g/cm<sup>3</sup>; PVC: 1.326 g/cm<sup>3</sup>; PS: 1.047 g/cm<sup>3</sup>; and PMMA: 1.204 g/cm<sup>3</sup>.

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

### 2.2 Alkaline pretreatment

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

### 2.3 Flotation experiments

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

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

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

The effectiveness of the flotation tests was evaluated by the grade and recovery of each type of plastic in the floated and in the sunk products, and by the separation efficiency, defined by Schulz<sup>[31]</sup> as  $\eta = R_{p1} - R_{p2}$  (where  $\eta$  is the separation efficiency,  $R_{p1}$  is the recovery of plastic 1 in the floated and  $R_{p2}$  is the recovery of plastic 2 in the floated). In the flotation tests of the plastic mixtures, the plastics type presented in

**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)

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



**Figure 1.** Original pictures of the four plastics.

the floated and the sunk were separated from each other by manual sorting, weighed, and flotation recovery and grade were calculated based on mass balance. This was possible due to the differences in colours and shapes of the plastics particles. Experiments were done three times under similar operating conditions.

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

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

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 the interaction coefficients; and  $b_{11}$ ,  $b_{22}$  and  $b_{33}$  are the quadratic coefficients. This model represents the effect of NaOH concentration ( $A$ ), temperature ( $B$ ), treatment time ( $C$ ) and their interactions on the plastics floatability. The list of the independent variables ( $A$ ,  $B$  and  $C$ ) with their coded and levels are presented in Table 1. The significance of model equation, individual parameters, and factor interactions were evaluated by analysis of variance (ANOVA) at the confidence intervals of 95% ( $\alpha = 0.05$ ).

#### 2.4 Contact angle measurements

There is a positive correlation between the hydrophobicity and the floatability, i.e., the flotation recovery increases

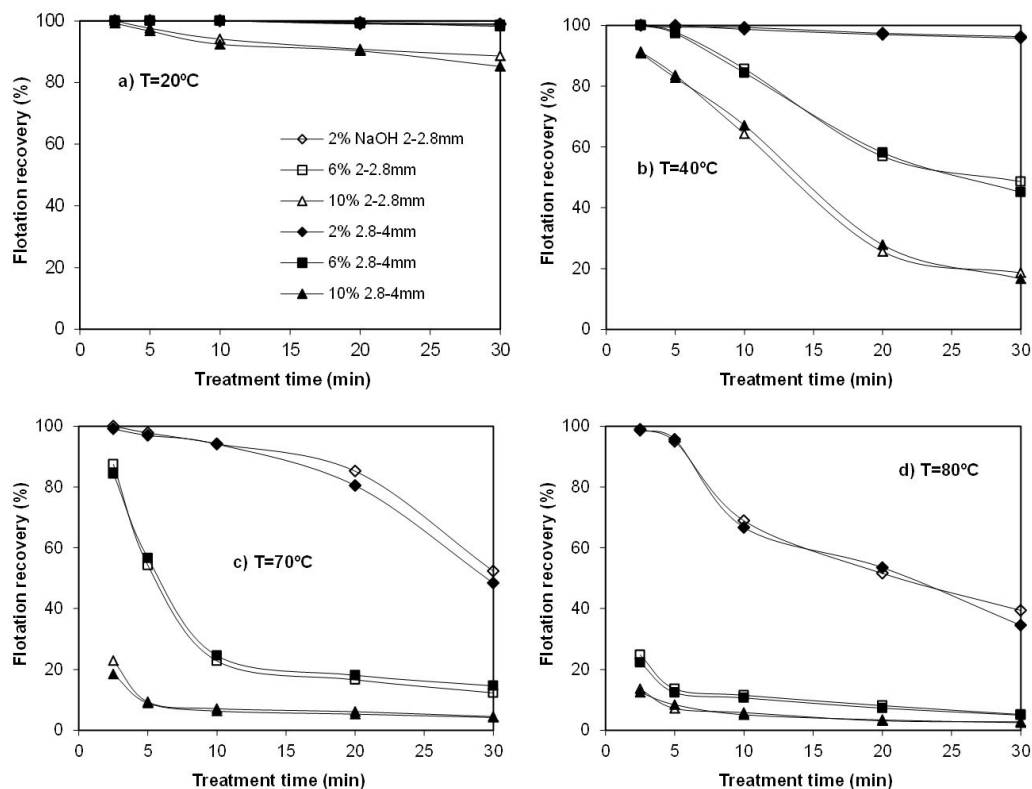
with the increase of the contact angle. Contact angles were measured in the Data Physics Instruments OCA20 equipment, using the sessile drop method. A drop of distilled water was placed onto the surface of plastic particles through a micro-syringe and the contact angle was measured. This process was repeated five times for each plastic and the average value was considered to be the contact angle of the plastic.

### 3. Results and Discussion

The four plastics (PET, PS, PMMA and PVC) are naturally hydrophobic, and the flotation recovery of untreated plastics is near 100%. Therefore, in order to separate plastic mixture by flotation, it is necessary to selectively modify the plastics floatability.

#### 3.1 Effect of alkaline pretreatment on PET floatability

Figure 2 shows the effects of NaOH concentration, temperature, and treatment time of the alkaline solution on the flotation recovery of PET of the two size fractions. NaOH treatment affects significantly the PET floatability. The flotation recovery of PET decreased with increasing NaOH concentration, temperature, and treatment time. Also, others studies<sup>[3,14,16-19,24,25]</sup> verified that recovery of PET in the floated decreased with increasing NaOH concentration, temperature, and treatment time. They found that alkaline treatment rendered the PET surface more hydrophilic, which may be a result of the hydrolysis of ester bonds in PET chains.



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

The overall effect of particle size was minimal, since the results were similar for both size fractions (Figure 2). The reduction of PET flotation is more pronounced in strong alkaline solutions, under a long treatment time, and at an elevated temperature, since it substantially improves the kinetics of the hydrolysis reaction of the PET surface. So, the lowest recovery of 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 NaOH concentration (10%), the highest treatment time (30 min) and the highest temperature (80 °C).

The temperature of 20 °C had not effective impact in the PET hydrophilization, since its recovery is close to 100%. This situation can be explained because NaOH could not hydrolyze on the PET surfaces at this temperature. Other studies<sup>[14,16,23]</sup> verified similar behavior, saying that PET particles start to be affected by NaOH only when the temperature reaches about 30 °C. Also, for low NaOH concentration and short pretreatment time, PET floatability is still significant (Figure 2). Similar behaviour was found by Burat et al.<sup>[16]</sup> and Wang et al.<sup>[23]</sup>.

At 40 °C and a 2% NaOH concentration, a change in treatment time had a low effect in PET recovery (Figure 2b). But for higher NaOH concentrations (6% or 10%), the flotation recovery of PET decreased significantly with increasing treatment time.

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

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

The analysis of variance (ANOVA) for the PET recovery model of the two size fractions is shown in Table 2. Based on all statistical analysis, the model presented was considered adequate to predict PET floatability after alkaline treatment. The coefficients of determination ( $R^2$ ) obtained for the PET recovery of size fractions +2-2.8 mm and +2.8-4 mm were 0.8885 and 0.8881 respectively. The significance level

of each independent variable, as well as their quadratic terms and interaction between the variables, was evaluated based on corresponding F-values and p-values. For the two size fractions the model F-value was about 44 at 99.99% confidence level and the model Prob > F value is less than 0.05, shows that the model is significant.

The quadratic effect of the three variables and the interaction between NaOH concentration and time treatment and between temperature and treatment time had no statistical significance. The actual model equation for fractions +2-2.8 mm and +2.8-4 mm are given in Equations 2 and 3, respectively:

$$\text{PET recovery (\%)} = 62.46 - 22.12A - 33.38B - 14.83C - 15.88AB + 0.31AC - 3.54BC + 7.52A^2 - 3.84B^2 + 1.83C^2 \quad (2)$$

$$\text{PET recovery (\%)} = 61.83 - 22.10A - 33.70B - 15.10C - 15.27AB + 0.50AC - 5.31BC + 7.43A^2 - 3.78B^2 + 4.38C^2 \quad (3)$$

where  $A$  is the NaOH concentration (%),  $B$  the temperature (°C), and  $C$  the treatment time (min). The coefficients of the three parameters were negative values indicating a negative correlation between PET floatability and parameter levels. For both size fractions, PET recovery presented an equal order of relative impact of the operating parameters. The equation coefficients clearly showed that PET recovery was mainly affected by temperature, followed by NaOH concentration, treatment time, and interaction between the NaOH concentration and temperature.

### 3.2 Effect of alkaline pretreatment on PS floatability

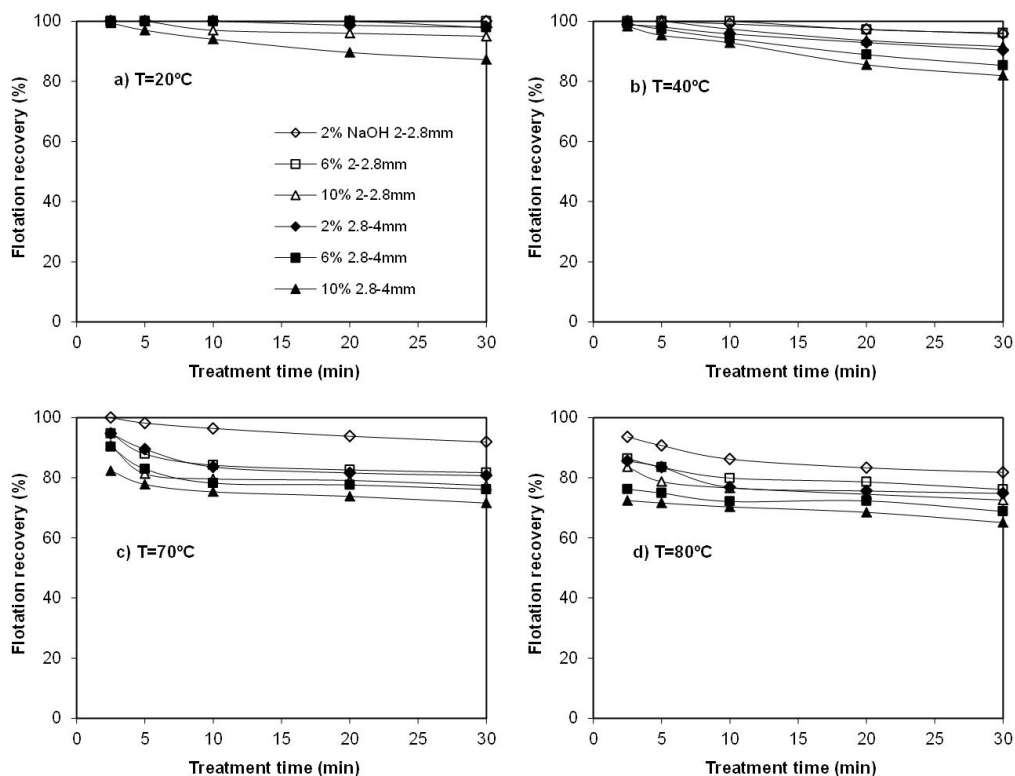
The floatability of PS was not influenced by alkaline pretreatment, since the results of the PS recovery in the float were always of 100%, suggesting that the alkaline pretreatment had not promoted the hydrophilization of PS. Also Wang et al.<sup>[23]</sup> verified that alkaline treatment has a low effect on PS floatability.

### 3.3 Effect of alkaline pretreatment on PMMA floatability

Flotation recovery of PMMA decreased slightly with increasing NaOH concentration, temperature, and treatment time (Figure 3). The temperature had a considerable effect on the alkaline pretreatment of PMMA. At 20 °C, for the three NaOH concentrations and for all treatment times, there was no hydrophilization of PMMA, since PMMA recovery was about 100%. The effects of NaOH concentration, temperature, and treatment time of the alkaline solution on the flotation recovery of PMMA for the two fractions (+2-2.8 mm and +2.8-4 mm) were similar. However, PMMA recovery of fraction +2.8-4 mm was lower than that observed for fraction +2-2.8 mm. Also, other authors<sup>[6,15,32-34]</sup> found that large plastic particles were more difficult to float than smaller ones.

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

		model	A	B	C	AB	AC	BC	A <sup>2</sup>	B <sup>2</sup>	C <sup>2</sup>
+2-2.8 mm	p-value Prob>F	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.9635	0.1169	0.0588	0.4583	0.1557
		Sum of Square=79831; Mean of square= 8870; degree of freedom=9; F <sub>model</sub> =44.3; R <sup>2</sup> =0.8885; Adjusted R <sup>2</sup> =0.8680									
+2.8-4 mm	p-value Prob>F	<0.0001	<0.0001	<0.0001	0.0002	<0.0001	0.8789	0.1242	0.0667	0.4283	0.2593
		Sum of Square=79999; Mean of square=8889; degree of freedom=9; F <sub>model</sub> =44.1; R <sup>2</sup> =0.8881; Adjusted R <sup>2</sup> =0.8678									



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

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

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

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

The analysis of variance (ANOVA) for PMMA recovery model of the two size fractions is shown in Table 3. For fractions +2-2.8 and +2.8-4 mm, the R<sup>2</sup> values were 0.9485 and 0.9584, respectively, and the F-value at 99.99% confidence level and the Prob > F value were less than 0.05, showing the model goodness of fit.

For fractions +2-2.8 mm and +2.8-4 mm, the Equations 4 and 5, respectively, dictate that linear terms of the NaOH concentration, temperature, and treatment time, linear term of interaction between NaOH concentration and temperature, and quadratic term of the temperature had a negative effect on PMMA floatability of the two size fractions. Interaction between temperature and treatment time had a negative effect on PMMA floatability for the size fraction +2.8-4 mm. The linear term of interaction between NaOH concentration and treatment time, and the quadratic

effect of NaOH concentration and treatment time had no statistical significance.

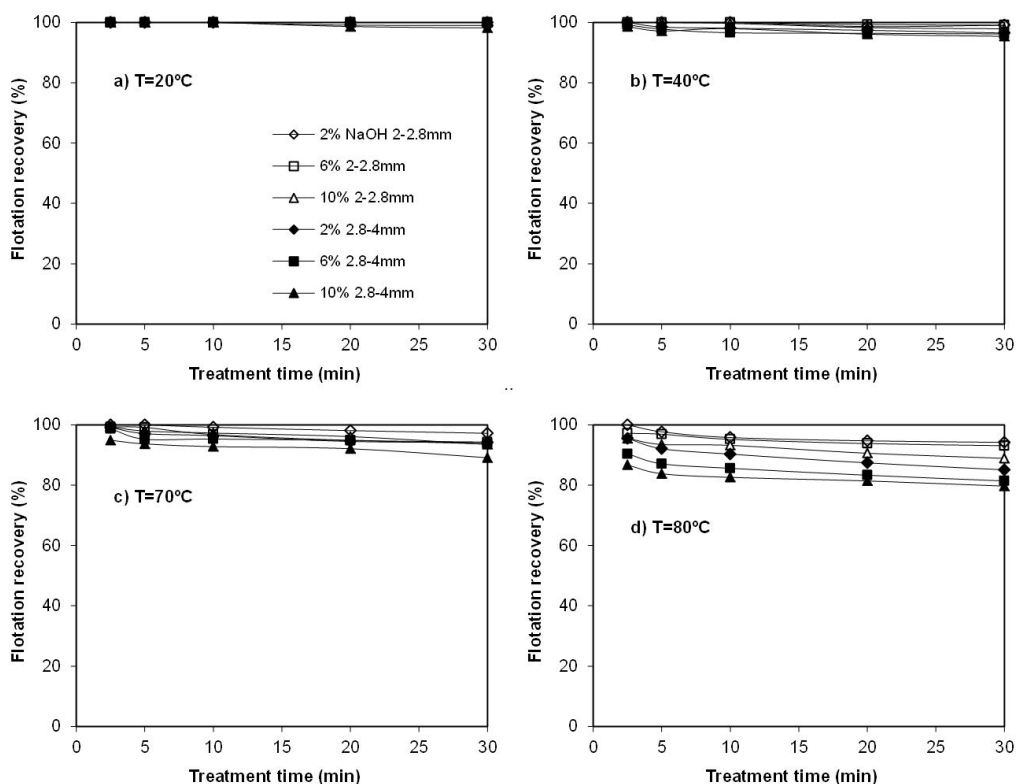
$$\text{PMMA recovery (\%)} = 95.12 - 3.35A - 9.01B - 3.17C - 2.79AB - 0.32AC - 1.98BC + 0.37A^2 - 5.23B^2 + 0.58C^2 \quad (4)$$

$$\text{PMMA recovery (\%)} = 89.08 - 3.65A - 11.63B - 4.64C - 1.30AB - 0.70AC - 1.49BC + 0.41A^2 - 4.25B^2 + 2.14C^2 \quad (5)$$

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

### 3.4 Effect of alkaline pretreatment on PVC floatability

Floatability of PVC was influenced by NaOH concentration, temperature, and treatment time (Figure 4). However, this effect was much smaller than that observed for PET, and slightly smaller than that observed for PMMA. PVC recovery for fraction +2-2.8 mm was greater than that for



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

fraction 2.8-4 mm. Flotation recovery of PVC decreased slightly with increasing NaOH concentration, temperature, and treatment time. Thus, the lowest recovery of PVC in the floated was obtained with the highest NaOH concentration (10%), the highest temperature (80 °C) and the highest treatment time (30 min), with 87.8% recovery for fraction +2-2.8mm and 76.4% recovery for fraction +2.8-4 mm. These values are slightly lower than those observed by other authors<sup>[14,16,18,19,24]</sup>, whose recoveries were close to 95%.

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

The analysis of variance (ANOVA) for PVC recovery model of the two size fractions is shown in Table 4. For size fractions of +2-2.8 mm and +2.8-4 mm, the  $R^2$  values of 0.928 and 0.872 respectively, imply that the model fits well.

The linear term of interaction between NaOH concentration and treatment time and the quadratic term of NaOH concentration and treatment time had no statistical significance. For fractions +2-2.8 mm and +2.8-4 mm, the Equations 6 and 7, respectively, dictate that NaOH concentration, temperature, and treatment time of alkaline pretreatment had a negative effect on PVC floatability of the two size fractions. Also, the interaction between NaOH concentration and temperature, interaction between temperature and treatment time, and quadratic term of temperature had a negative effect on the PVC floatability.

$$\text{PVC recovery (\%)} = 99.01 - 0.75A - 2.64B - 1.29C - 0.97AB - 0.30AC - 1.33BC - 0.79A^2 - 1.81B^2 + 0.59C^2 \quad (6)$$

$$\text{PVC recovery (\%)} = 97.37 - 1.38A - 5.84B - 1.85C - 1.57AB - 0.30AC - 1.42BC - 0.08A^2 - 4.30B^2 + 0.75C^2 \quad (7)$$

PVC recovery was mainly affected by temperature ( $B$ ). The three independent variables presented less impact on PVC recovery than on PET recovery.

### 3.5 Effect of alkaline pretreatment on contact angle

Contact angle measurements were conducted to assess the effects of alkaline pretreatment on plastics surface. In the absence of alkaline pretreatment, all plastics untreated showed large contact angle, with PS presenting the highest value, followed by PVC, PMMA and PET. Contact angles measured in the four plastics decreases with increasing NaOH concentration, temperature, and treatment time (Table 5). However, the contact angle of PET drops remarkably after alkaline treatment, while the contact angle of PS and PVC decrease only slightly. This is consistent with the results of flotation tests of single plastics. So, the dropping of flotation recovery of PET with alkaline treatment is ascribed to a significant decline of contact angle, which implies an increase on surface wettability. On the other hand, the contact angle of PS is larger than those of the other plastics in any treatment conditions, meaning that PS is the most hydrophobic plastic.

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

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

**Table 5.** Experimental conditions and contact angle results.

Conditions			Contac angle (°)			
NaO concentration (%)	Temperature (°)	Treatment time (min)	PET	PS	PMMA	PVC
2	20	2.5	71.6	93.3	75.5	82.7
2	20	30	68.5	91.5	73.0	81.1
2	40	2.5	69.9	93.0	74.7	81.6
2	40	30	68.1	91.0	68.4	80.6
2	70	2.5	70.1	91.0	72.1	80.8
2	70	30	58.2	89.0	66.5	78.4
2	80	2.5	68.4	88.0	67.6	77.7
2	80	30	53.4	85.7	59.7	73.9
10	20	2.5	70.8	91.8	74.8	80.6
10	20	30	66.2	89.5	70.2	79.5
10	40	2.5	64.7	90.1	72.9	78.9
10	40	30	51.5	88.6	63.8	77.6
10	70	2.5	52.6	88.5	65.1	76.5
10	70	30	42.3	86.7	59.2	73.1
10	80	2.5	45.9	85.2	59.4	71.4
10	80	30	40.1	83.3	55.7	68.2

Previous results illustrated that alkaline treatment had a strong effect on PET floatability, some effect on floatability of PMMA and PVC, but no effect on PS floatability. Thus, the floatability of PET can be significantly reduced in hot alkaline solutions, showing smaller floatability than the other three plastics, particularly than PS. So, one can assume that the alkaline treatment is not efficient to separate PS, PMMA and PVC plastics from each other, but may allow the separation of PET from PS, PMMA and PVC.

### 3.6 Separation of bi-component mixtures of PET with PS, PMMA and PVC

In face of the flotation behavior of single plastic, further alkaline treatment and flotation tests were developed using bi-component plastic mixtures of PET with PS, PMMA and PVC, in equal proportions, for two size fractions (+2-2.8 mm and +2.8-4 mm), in order to render the PET hydrophilic maintaining the other plastic components in a hydrophobic state. The alkaline treatment conditions chosen for each of the three bi-component mixtures (PET/PS, PET/PMMA and PET/PVC) were those that led to maximum flotation differences between PET and the other plastics, to obtain a selective separation.

The optimal pretreatment conditions to separate PET/PS mixture were: NaOH concentration of 10%, at 80 °C, and treatment time of 30 min. In these conditions, PET floatability was minimized, while PS floated recovery was 100%. The results of froth flotation tests are presented

in Table 6. For PET/PMMA and PET/PVC mixtures, the optimal pretreatment conditions to separate PET from the other plastic were: NaOH concentration of 10%, temperature at 70 °C and treatment time of 20 min.

The best result was obtained in the PET/PS mixture separation, having the highest separation efficiency (near 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, PET/PMMA mixture had the lowest separation efficiency. These results were consistent with the floatability of plastics observed in the mono-component tests.

The influence of the particle size on separation quality of the PET/PS mixture was not evident, since the two size fractions presented similar results (Table 6). The effect of particle size on PET floatability was minimal.

Coarse fraction of PET/PMMA mixture had the worst results. The separation was more efficient for the fine fraction because there was a great amount of PMMA recovered in the floated.

For the PET/PVC mixture, the quality of separation worsened slightly with the increase of the particles size (Table 6). PVC recovery in the floated decreased with the increase of the particles size, and PET recovery in the floated was not affected by particles size.

Floatability of PS, PMMA and PVC increased with decreasing particle size, because their particles have more regular shapes, while the effect of the particle size on PET

**Table 6.** Results of the flotation tests on the mixtures of PET with PS, PMMA and PVC for two size fractions.

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	

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

floatability was minimal because their particles have lamellar shape and low weight. Also, other studies<sup>[15,32-34]</sup> verified that small particles and particles with lamellar shape are easier to float than coarse particles and particles with regular shape.

For PET/PMMA and PET/PVC, the worst results for coarse fraction can be explained by the more regular shapes and higher densities of PMMA and PVC that hinders flotation. Thus, the particles size control is important for flotation separation of plastic mixtures.

#### 4. Conclusions

As four plastics (PET, PS, PMMA and PVC) are naturally floatable, it is necessary a selective wetting component to achieve a selective flotation separation of plastic mixtures. The effect of treatment with alkaline solutions of NaOH on the floatability of the four plastics was studied. It was verified that NaOH solutions had a strong influence on PET floatability, medium influence on PVC and PMMA and limited effect on PS. The contact angle measurement confirms the dropping of flotation recovery of PET is ascribed to a sharp decline of contact angle, which implies PET surface becomes hydrophilic. The flotation recovery of PET, PMMA and PVC decreased with increasing NaOH concentration, temperature, and treatment time.

Sodium hydroxide treatment shows superior selectivity for PET plastic. Therefore, development of a selective flotation separation technology for PET/PS and PET/PVC mixtures can be successfully achieved. The best result was obtained in the PET/PS mixture separation. PET recovery in the sunk was about 98%, with a grade of 100%; and PS recovery in the floated was 100% with a grade of about 98%, with the following pretreatment conditions: 10% NaOH concentration, temperature at 80 °C, and treatment time of 30 min. For this mixture, the two size fractions (+2-2.8 mm and +2.8-4 mm) presented similar results. PET/PPMA mixture provided inadequate flotation and efficient flotation was obtained with PET/PVC. For these two mixtures, the quality of separation worsened slightly with the increase of the particles size as a consequence of the decrease of the recovery of PMMA and PVC in the floated for the coarser particles.

One particular advantage of the sodium hydroxide pretreatment is that in the flotation stage none wetting agents are used, and only a frother is required.

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