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SULFONATION OF CLEAN AND CONTAMINATED POLYSTYRENE (STYROFOAM)

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ABSTRACT

This study investigates the efficiency of the direct method of sulfonation or the addition of sulfuric acid to clean and contaminated polystyrene or Styrofoam and the comparison of the ion exchange capacity of clean and contaminated polystyrene.

The sulfonation process was divided into four sets of experiments. The first part was to determine the correlation between the time of sulfonation and ion exchange capacity (IEC) of sulfonated polystyrene(SPSusing clean polystyrene; the second part was to test the replicability of the sulfonation process using clean polystyrene; third part was to verify the calculated IEC and sulfonation degree by performing the regeneration process and the last part was the sulfonation of the contaminated polystyrene.

Experimental results from the sulfonation process yielded an average IEC value of $10.3 \pm 5.05 \times 10^{-4} \frac{mol}{gSPS}$ *for clean SPS as compared to* $15.0 \pm 7.61 \times 10^{-4} \frac{mol}{gSPS}$ *for contaminated SPS, and the degree of sulfonation, calculated as percent sulfonation has an average value of* $11.98 \pm 6.53\%$ *for clean SPS as compared to* $18.41 \pm 11.44\%$ *for contaminated SPS.*

These values indicate that the method of sulfonation employed was able to introduce sulfonatate groups both for the clean and contaminated polystyrene with apparent greater effectivity for the contaminated polystyrene.

I. INTRODUCTION

Sulfonation is defined as a substitution reaction used to attach the $-SO_3H$ group on the molecule of an organic compound via chemical bond to carbon. Generally, sulfonation of a polymer can be carried out as a heterogeneous reaction, i.e., the polymer and the sulfonating agent exist in different phases, or as a homogeneous reaction in hydrocarbons or chlorinated solvents. Compounds, such as H_2SO4 and SO_3 are commonly used as sulfonating agents for various polymers, including polystyrene (Martins, Ruggeri & De Paoli, 2003).

The first studies on sulfonation of high polymers such as polystyrene were published before World War II. polystyrene was first sulfonated in a homogeneous phase by a method developed by turbak via reacting polystyrene with complexes of triethyl phosphate and and sulfur trioxide in dichloroethane. Makowski et al also prepared lightly sulfonated polystyrene by using acetyl sulfate complexes as the sulfonating reagent in a solution of dichloroethane. in this reaction random ionic functionalities along the polymer chains were generated without significant degradation or crosslinking of the reaction product. Vink described preparation of polystyrenesulfonic acid (PSSA) in an inert cyclohexane solvent using Ag_2so4 or phosphorous

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pentoxide as an accelerator. the reaction was carried out at a slightly elevated temperature (40^0c) to prevent phase separation in the cyclohexane solution. in the method of Thaler, sulfonation was also carried out in cyclohexane solution, however, hydrocarbon-soluble acyl sulfates produced by reaction with sulfur trioxide and chlorosulfonic acid (for example lauric acid) were used as sulfonating agents (Kucera & Jancar, 1996).

Sulfonation is a versatile route to polymer modification that is especially suitable for aromatic polymers. It introduces sulfonic acid functionality, which aids in the transport of protons. It makes the polymers hydrophilic and hence it increases the solubility. Several methods of sulfonation have been described in literature. These include sulfonation by concentrated sulfuric acid, by chlorosulfonic acid, by pure or complexed sulfur trioxide, and by acetylsulfate (Zaidi, 2003). The sulfonation process is controlled by different variables – time of sulfonation, the concentration of the sulfuric acid, the volume of the sulfuric acid used and the sulfonating agent used. There are different established methods applied for the sulfonation process but for this particular study the method of sulfonation applied is the addition of concentrated sulfuric acid. Concentrated sulfuric acid (97%) is selected as the sulfonating agent because of the simple chemical reaction and is known to produce polymers free from degradation and cross-linking reactions that occurs at sulfonation with 100% sulfuric acid or with chlorosulfonic acid (Zaidi,2003; Martins, et al.,2003).

Sulfonated polymers are commonly used as fuel cell membranes. They are also considered as interesting membrane material for ultrafiltration, nanofiltration, reverse osmosis and ion exchange process. They exhibit good resistance properties to bio-, protein- and oily water fouling due to their hydrophilic nature and negative surface charge (Martins, et al., 2003).

The extent of sulfonation is measured by the degree of sulfonation or the ratio between the sulfonated polystyrene repeating units and the total styrene units. It can be controlled by the following parameters- the sulfonating agent, the concentration or the amount of the sulfonating agent, the time of sulfonation, pH and the temperature of the reaction.

Some of the initial studies on the sulfonation process of waste polystyrene membrane using sulfuric acid showed that the percent sulfonation and ion exchange capacity is directly proportional to the time of sulfonation at constant volume of sulfuric acid and temperature (Ching, Fernandez, Fermin &Santiago, 2006); the ion exchange capacity initially increases with time up to a point of maximum ion exchange capacity and then it will slowly decrease with time if silver sulfate (Ag_2SO_4) was used as a catalyst (An, Shin & Chase, 2006); and a 0.8 meq/100 g polystyrene or 16% sulfonation degree resulted in a 90-minute reaction time between waste polystyrene and concentrated sulfuric acid (Abbes, Bayoudh & Baklouti, 2006). The studies of Ching et al and An et al focused on the sulfonation of waste polystyrene membrane or the methodology involved the dissolution of polystyrene prior to the sulfonation process. On the other hand, the study of Abbes et al used infrared spectrometer in verifying the sulfonate group in the polystyrene and focused on the morphology and characterization of the polymer like glass transition temperature, infrared spectra and differential scanning calorimetry. The study will not incorporate the dissolution process and will use the titration method in the determination of the ion exchange capability of sulfonated polystyrene.

This study is part of the research on the potential application of sulfonated polystyrene from waste Styrofoam in the reduction of heavy metals in wastewater. The long term application of the study is to minimize the contribution of waste Styrofoam into the solid waste stream and use this waste as a component in a landfill liner that will act as an ion exchange material that will temporarily trap the heavy metals from landfill leachate.

The general objectives of the sulfonation experiments are to determine if the direct method of sulfonation or addition of sulfuric acid at room temperature to polystyrene will be able to introduce sulfonate groups to the polystyrene units and to compare the ion exchange capacity and degree of sulfonation of clean and contaminated or waste polystyrene.

II. Materials and Methods

The method of sulfonation applied was the addition of concentrated sulfuric acid (97-98%) at room temperature. The simple reaction of adding sulfuric acid was chosen for the following reasons- polymers are free from degradation and cross-linking reactions that occurs at sulfonation with 100% sulfuric acid or with chlorosulfonic acid; the possibility of desulfonation is eliminated because the reaction occurs at room temperature; concentrated sulfuric acid is less hazardous to handle in the laboratory as compared to other form of sulfuric acid such as chlorosulfonic acid and sulfur trioxide and lastly the waste acid can be reused by treating it with oleum. The procedure used was detailed below and Figure 1 and 2 show the sulfonation experiment and the process for the determination of ion exchange capacity, respectively.

Procedure:

1. Measure 5.0 g of polystyrene (PS) (cut into squares, dimension is approximately 1 cm x 1 cm x 0.4 m).
2. Add 300 mL concentrated sulfuric acid (97-98%) ensuring that all PS are completely soaked or submerged in the acid solution[1].
3. Let the sulfuric acid react with the PS at variable time of sulfonation.[2]
4. After sulfonation, wash the polystyrene with distilled water to remove excess sulfuric acid adhering to the surface of the PS.
5. Air dry the SPS overnight or until completely dried.
6. Measure the mass of the dried SPS.
7. Add 200 mL of 1.0M NaCl to the dried SPS and continuously stir the solution for 1 hour using a magnetic stirrer.
8. Filter the SPS from the NaCl solution.
9. Get the pH of the solution after the reaction with the SPS.
10. For the determination of the ion exchange capacity, titrate the NaCl solution with 1.0M NaOH solution using phenolphthalein as an indicator (endpoint is when a faint pink color was observed in the solution).

The chemical equations for the sulfonation process are:

Sulfonation:

$$C_6H_5C_2H_3 \quad + \quad H_2SO_4 \quad \leftrightarrow \quad C_2H_3C_6H_4SO_2OH + H_2O$$

Polystyrene + sulfuric acid sulfonated polystyrene + water

Sulfonated polystyrene with the salt solution:

$$RSO_3H + \quad Na^+ \leftrightarrow (RSO_3^-)(Na^+) \quad + \quad H^+$$

Acid-base reaction of the hydrogen ions with sodium hydroxide:

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[1] Since sulfuric acid is denser the water and the tendency of the PS is to float in the acid solution, a device with a piston-like material was used for the sulfonation process.

[2] For the first batch of experiment, time of sulfonation is from 10min-48h, but for the replication, 2h sulfonation time was used.

$H^+ + OH^- \leftrightarrow H_2O$

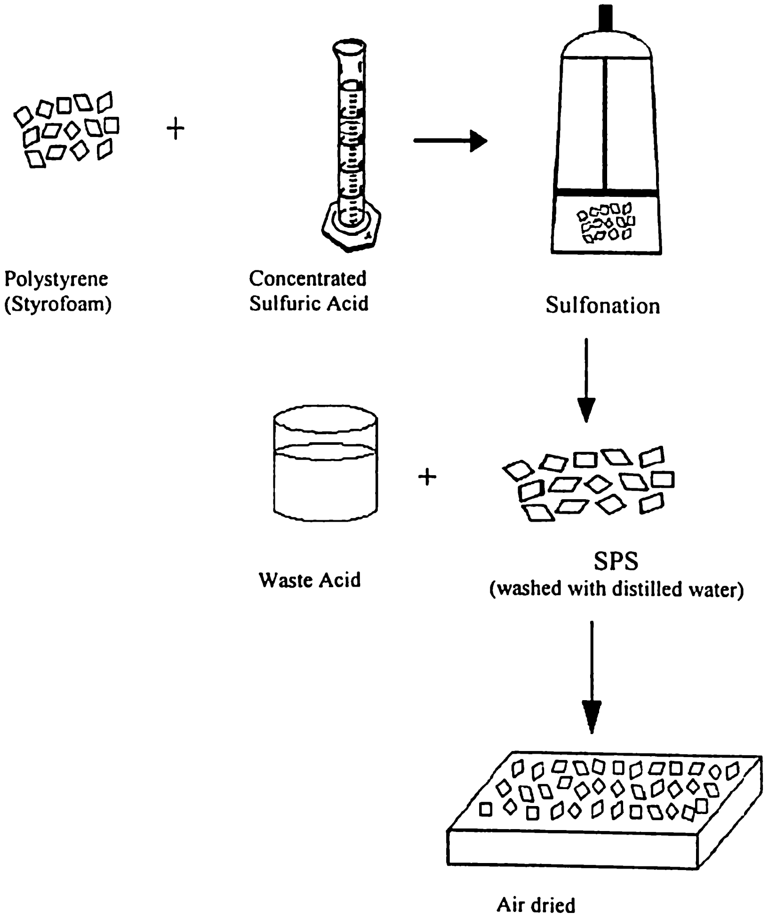

Figure 1. Sulfonation experiment

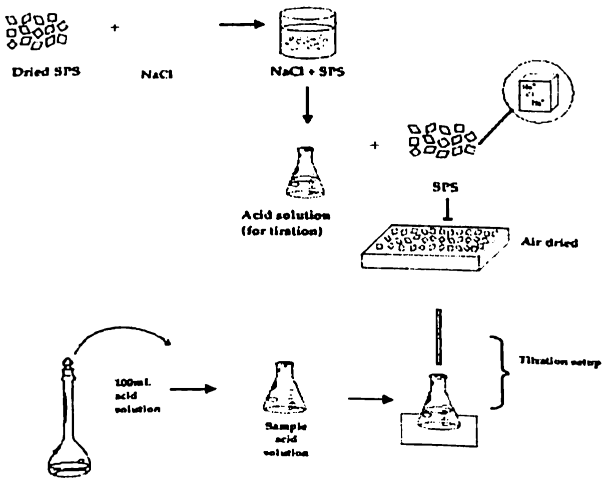

Figure 2: Process for the determination of ion exchange capacity (IEC)

III. Results and Discussion

The sulfonation process was divided into four sets of experiments. The first part was to determine the correlation between the time of sulfonation and ion exchange capacity (IEC) of SPS using clean polystyrene; the second part was to test the replicability of the sulfonation process to clean polystyrene; third part was to verify the calculated IEC and sulfonation degree by performing the regeneration process to the SPS and the last part was the sulfonation of the contaminated[3] polystyrene.

3.1. Correlation Between the Time of Sulfonation and Ion Exchange Capacity

In the first part of the experiment, clean polystyrenes were sulfonated at room temperature for different reaction times ranging from 10 minutes to 48 hours. The experimental results for the sulfonation process at different reaction times are summarized in Table 1.

Table 1:
Correlation between the time of sulfonation and ion exchange capacity (IEC)

Time of Sulfonation, min	IEC, mol/g SPS	% sulfonation[4]
10	1.20×10^{-3}	13.74
30	5.23×10^{-4}	5.68
45	4.44×10^{-4}	4.79
60	5.07×10^{-4}	5.50
90	8.45×10^{-4}	9.43
120 (2h)	2.77×10^{-3}	37.16
183 (3h)	9.38×10^{-4}	10.55
361 (6h)	7.23×10^{-4}	7.98
730 (12h)	6.88×10^{-4}	7.58
1081 (18h)	1.11×10^{-3}	12.63
1444 (24h)	8.01×10^{-4}	8.91
2883 (48h)	8.91×10^{-4}	9.99
Temperature: 25-27^{0}C Volume of sulfuric acid: 300mL Mass of sample: 5.0 g		

The linear regression results and the scatter plot for the time of sulfonation and ion exchange capacity are shown in Table 2 and Figure 3 respectively.

Table 2:
Regression analysis for the time of sulfonation and IEC

Parameter	10 min-48 h	30-90 min
R^2	0.004	0.83
equation of the line	$-5.0 \times 10^{-8}x + 0.0009$	$9.0 \times 10^{-6}x + 9.0 \times 10^{-5}$
p- value for the slope	0.84	0.01
p-value for the y-intercept	0.0015	0.45
% confidence interval	95	95

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[3] The degree of contamination was not measured in the experiment but the procedure was standardized so that all samples have more or less the same amount of contaminants (See Section 3.4).

[4] The degree of sulfonation calculated as % sulfonation is a derived quantity or calculated from the ion exchange capacity.

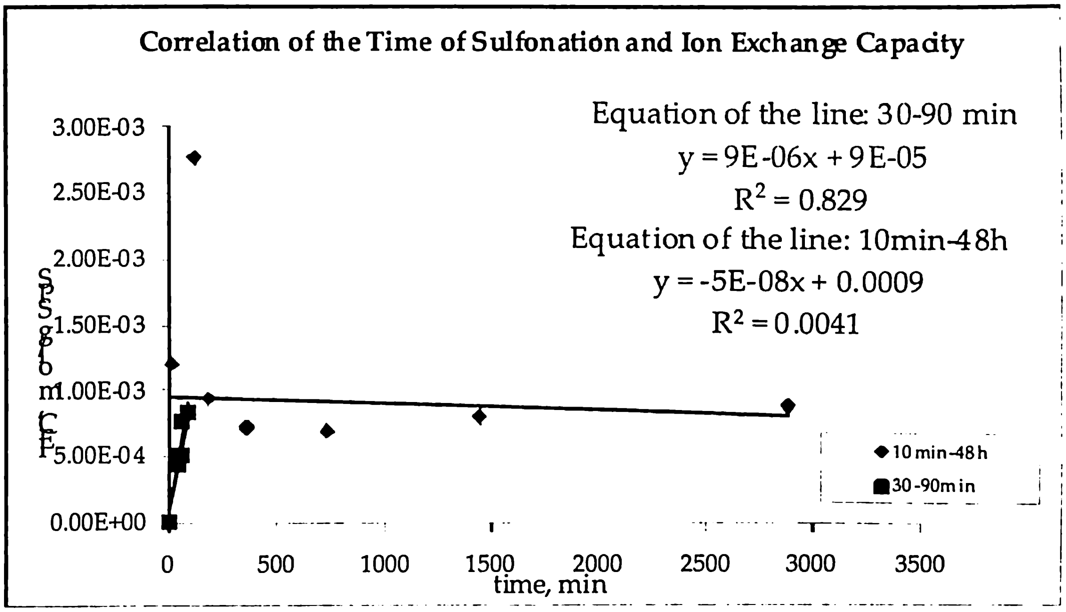

Figure 3. Scatter plot for the time of sulfonation and IEC using linear regression

The parameter r^2 is the coefficient of correlation, which describes the strength of the relationship between the time of sulfonation and the ion exchange capacity. The result obtained by using all the data points (10min-48h) implies that there is a very weak correlation between the time of sulfonation and ion exchange capacity but the r^2 value for the initial data points (30-90min) shows a strong positive correlation. The p-values for the slope and the y-intercept were used to test the null hypothesis that there is no linear relationship between the variables and that the y-intercept is equal to zero. The p-value for the slope of all the data points is greater than 0.05, which means that the null hypothesis will not be rejected and the slope is equal to zero or all data points can be represented by a straight horizontal line[5]. The p-value for the y-intercept of all the data points is less than 0.05, which means that the null hypothesis will be rejected and the y-intercept is not equal to zero. A y-intercept value of not equal to zero, implies that the regression line is not a correct representation of data (i.e. it is not possible to have sulfonated the polystyrene at zero time).

On the other hand, performing a linear regression analysis on the initial data points (30-90min) and forcing the y-intercept to be equal to zero, the p-value of the slope is less than 0.05, which means that the null hypothesis will be rejected and the slope is not equal zero and there is indeed a positive correlation between the time of sulfonation and ion exchange capacity.

The two sets of linear regression analysis show that from 30 to 90 minutes, the ion exchange capacity is increasing with time and it starts to level off or approaches a constant maximum value. This observation is consistent with the preliminary study of Kucera and Jankar on the sulfonation process of polystyrene.

Based from the result of the regression analysis, all data points can be divided into two groups- points wherein the ion exchange capacity is increasing with time and the group of data

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[5] The scatter plot is generated by the Megastat software and the conclusion that all data points can be represented by a horizontal line (which is not quite evident in the scatter plot) was based on the calculated p-values.

points wherein the ion exchange capacity approaches a constant maximum value. Data points will be modeled using the equation

$$y = k\,(1 - e^{-at})$$

$$where\,y = IEC$$

$$k = asymptote\ constant\ value,\ \frac{mol}{g\,SPS}$$

$$t = time$$

$$a = constant,\ \frac{1}{time}$$

The value of k and *a* are 8.0 x 10^{-4} and 2.8 x 10^{-2} respectively. The scatter plot for the above equation is shown in the figure below[6].

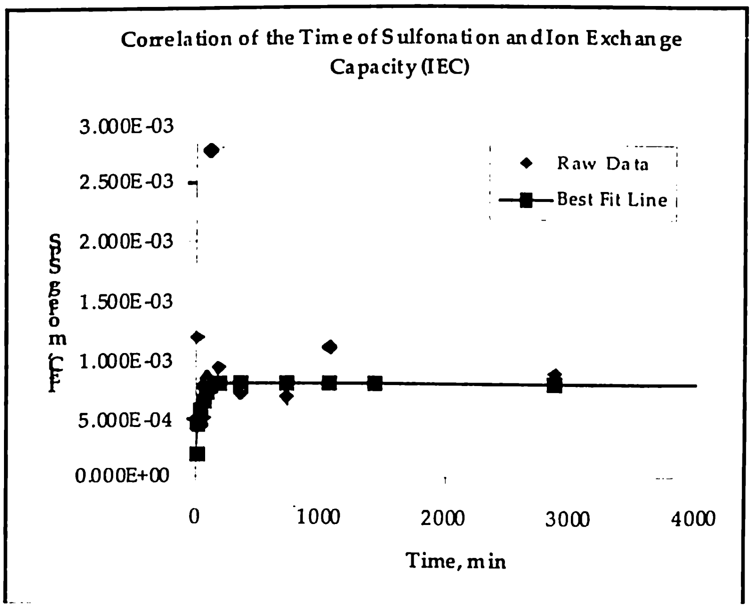

Figure 4. Correlation between the time of sulfonation and IEC using exponential function

3.2 Batch Sulfonation

The next part of the experiment was to test the replicability of the calculated ion exchange capacity and its corresponding percent sulfonation. Different batches of sulfonation were performed in order to determine the average value of the ion exchange capacity and % sulfonation. Time of sulfonation used was 2 hours.

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[6] In the determination of the value for the constants (k and a), the outliers (10-min and 2-h) data were not included.

Table 3 summarized the result of the different batches of sulfonation process.

Table 3:
IEC and % sulfonation for batch sulfonation (clean PS)

Batch Code	IEC	% sulfonation
12-29A	1.42×10^{-3}	16.62
12-29B	1.43×10^{-3}	16.84
12-29C	1.28×10^{-3}	14.81
12-29D	5.34×10^{-4}	5.80
12-29E	4.59×10^{-4}	4.95
02-05A	7.91×10^{-4}	8.23
02-05B	8.08×10^{-4}	8.99
02-05C	6.09×10^{-4}	6.66
02-09A	1.30×10^{-3}	15.08
02-09B	1.02×10^{-3}	11.54
02-09C	1.45×10^{-3}	17.05
02-09D	1.49×10^{-3}	17.66
02-13	1.30×10^{-3}	15.06
02-14A	1.51×10^{-3}	17.80
02-14B	2.38×10^{-3}	30.59
02-14C	5.36×10^{-4}	5.82
02-14D	5.58×10^{-4}	6.07
02-14E	5.97×10^{-4}	6.52
02-15A	7.35×10^{-4}	8.12
02-15B	4.94×10^{-4}	5.34
Temperature: 25-27°C Ratio of Sulfuric Acid to mass of PS: 300mL: 5.0g Time of Sulfonation: 2h		

The first column or the batch code represents the date of sulfonation while the second and third column represents the calculated ion exchange capacity (IEC) and its corresponding % sulfonation.

The tabulated data shows a wide range of values, from 4.59×10^{-4} to 2.38×10^{-3} $\frac{mol}{g}\ SPS$ for the ion exchange capacity (IEC) and from 5.80 to 30.57% for the percent sulfonation. Compared to the first batch of sulfonation, the values calculated are significantly different from the 2-h sulfonation in Table 1[7].

A descriptive statistical analysis was applied for the interpretation of data. The table below summarized the result of the descriptive statistical analysis.

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[7] The sample used for the big batch sulfonation process are from the same population of Styrofoam.

Table 4:
Statistical analysis of the IEC and its corresponding percent sulfonation (Clean PS)

Parameter	Value	
	IEC mole/g SPS	% sulfonation
Mean	1.03×10^{-3}	11.98
Sample standard deviation	5.05×10^{-4}	6.53
Minimum	4.59×10^{-4}	4.95
Maximum	2.38×10^{-3}	30.59
Range (Max-Min)	1.92×10^{-3}	25.63
standard error of the mean	1.13×10^{-4}	1.46

From Table 4, the average value of the IEC is 10.30 ± $5.05 \times 10^{-4}\ \frac{mol}{g}{}_{SPS}$ and the percent sulfonation was 11.98 ± 6.53%. The statistical analysis of the values on the ion exchange capacity and percent sulfonation shows a high dispersion or variation. The wide dispersion on the calculated values is an implication that the styrene units are randomly distributed to the samples resulting in a random distribution of the sulfonate groups.

Furthermore, the value of the average IEC was greater than the calculated theoretical value for the ion exchange capacity of $6.35 \times 10^{-8}\ \frac{mol}{g}{}_{SPS}$[8]. The implications of a higher value of IEC are - sulfonation process did not only occur at the surface of the polystyrene and the calculated average ion exchange capacity (from the experiment) includes the amount of sulfuric acid adhering to the surface of the polystyrene.

3.3 Regeneration Process

The purpose of the regeneration process was to verify the correctness and accuracy of the calculated ion exchange capacity (IEC). That is, the accounted sulfonated groups in the average value of IEC did not include the sulfuric acid adhering to the surface of the polystyrene. In the regeneration process, two batches of clean polystyrene have been sulfonated, treated with sodium chloride, air-dried and regenerated using concentrated hydrochloric acid. Table 5 shows the result of the regeneration process.

Table 5
Regeneration process

Batch	**A-clean**		**B-clean**	
Parameters	**Sulfonation**	**Regeneration**	**Sulfonation**	**Regeneration**
IEC, mole/g SPS	1.43×10^{-3}	1.38×10^{-3}	1.5×10^{-3}	1.42×10^{-3}
% sulfonation	16.84	16.19	17.68	16.71
p-value for the mean	0.04		0.41	
p-value for variance	0.44		0.50	

From the table, the IEC from the regeneration process are relatively less than the IEC from the sulfonation process, which is in accordance from literature. This only means that some sulfuric acid adhered on the surface of the polystyrene. But based on the calculated p-values of

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[8] The calculation of the theoretical value was based on stoichiometry and geometry of the sample used which is discussed in another study conducted by the authors.

variance, the difference is only very small and insignificant. Therefore, the calculated average value of IEC can be use to represent the IEC of the clean SPS.

3.4 Sulfonation of the Contaminated Polystyrene (PS)

The last batch of experiment was the sulfonation of the contaminated polystyrene in order to compare the ion exchange capability (IEC) of the clean and contaminated SPS. The same method of sulfonation was applied to the contaminated polystyrene. The time of sulfonation used was 2 hours.

The polystyrenes were contaminated by spaghetti sauce so the contaminants are tomato sauce, oil and grease. The contaminants were controlled and limited in order to have a baseline data on the general effects of contaminants on the sulfonation process (i.e. a decrease or increase in the calculated ion exchange capacity). The contaminated polystyrenes were washed with distilled water to remove all solid materials.

The results on the calculated ion exchange capacity and its corresponding sulfonation degree are shown in Table 6

Table 6

IEC and % sulfonation for batch sulfonation (contaminated PS)

Batch Code	IEC	% sulfonation
02-15A	1.17 x 10^{-3}	13.45
02-15B	9.71 x 10^{-4}	10.95
02-21	1.38 x 10^{-3}	16.14
03-09A	2.06 x 10^{-3}	25.68
03-09B	3.17 x 10^{-3}	44.13
03-14A	1.16 x 10^{-3}	13.32
03-14B	9.45 x 10^{-4}	10.63
03-14C	1.14 x 10^{-3}	12.99
Temperature: 25-27^{0}C Ratio of Sulfuric Acid to mass of PS: 300mL: 5.0g Time of Sulfonation: 2h		

The first column or the batch code represents the date of sulfonation while the second and third column represents the calculated ion exchange capacity (IEC) and its corresponding percent sulfonation.

The data also shows a wide range of values from 9.45 x 10^{-4} to 3.17 x 10^{-3} $\frac{mol}{g}_{SPS}$ for the IEC and 10.63 to 44.13 for the percent sulfonation. A descriptive statistical analysis was also applied for the interpretation of data. The table below summarized the result of the descriptive statistical analysis.

Table 7

Statistical analysis of the IEC and % sulfonation (contaminated PS)

Parameter	Value	
	IEC	% sulfonation
Mean	1.50x10-^{3}	18.41
sample standard deviation	7.61x10-^{4}	11.44
Minimum	9.45x10-^{4}	10.63
Maximum	3.17x10-^{3}	44.16
Range	2.22x10-^{3}	33.5
standard error of the mean	2.69x10-^{3}	4.04

From Table 7, the value of the IEC is $15.0 \pm 7.61\ \mathrm{x}10^{-4}\ \frac{mol}{g}_{SPS}$ and its corresponding percent sulfonation is 18.41 ± 11.44 %. The statistical analysis of the values on the ion exchange capacity and its corresponding percent sulfonation shows a high dispersion or variation.

Table 8 shows the comparison of the ion exchange capacity (IEC), percent sulfonation and statistical result of the clean and contaminated SPS.

Table 8

Comparison of the IEC, % sulfonation and statistical results for clean and contaminated SPS

Parameter	**Clean**	**Contaminated**
IEC, mole/g SPS	**1.03 x 10-^{3}**	**1.50 x10-^{3}**
Standard Deviation for IEC	**5.05 x 10-^{4}**	**7.61 x10-^{4}**
Range of IEC	**1.92 x 10-^{3}**	**2.22 x10-^{3}**
Median of IEC	**1.42 x 10-^{3}**	**1.17 x10^{-3}**
% sulfonation	**11.98**	**18.41**
Standard Deviation for % sulfonation	**6.53**	**11.44**
Range of % sulfonation	**25.63**	**33.50**
Median of % sulfonation	**10.26**	**13.39**
p-value of the mean (based on IEC)		**0.15**
p-value of the variance (based on IEC)		**0.15**

The IEC and percent sulfonation of the contaminated SPS were relatively higher than those of the clean SPS. The possible reasons for a higher value of IEC and percent sulfonation of contaminated polystyrene are – the clean polystyrene has a coating material that limits or blocks the polystyrene unit to be sulfonated while the contaminants removed or minimized the coating material; the contaminants in the polystyrene acted as catalyst in the sulfonation process.

The statistical analysis of the result using contaminated SPS shows a much wider spread or dispersion of the data. This possible reason for this is that the contaminants were also randomly distributed on the polystyrene sample in addition to the random distribution of the styrene group in the polystyrene.

3.5 Summary of results

Table 9

Summary of Results on the sulfonation process of clean and contaminated PS

PARAMETERS	**Values**
Ion Exchange Capacity , meq/ g SPS	
Estimated Theoretical Value	$6.35x10^{-5}$
Experimental data for clean PS	1.03
Experimental data for contaminated PS	1.50
Related Studies	0.008
Commercial/Industrial value for Cation exchange resin	4.4-4.8
% sulfonation	
Clean PS	11.98
Contaminated PS	18.41
Related Studies	16.00

STATISTICAL ANALYSIS	
Standard Deviation of the IEC-clean PS	$5.05 x 10^{-4}$
Standard Deviation of the IEC-contaminated PS	$7.61 x 10^{-4}$
Range of Values-clean PS	$1.92 x 10^{-3}$
Range of Values-contaminated PS	$2.22 x 10^{-3}$
Correlation between the time of sorption and IEC	$y = k\left(1 - e^{-at}\right)$

The sulfonation method of adding 97-98% sulfuric acid at room temperature introduced sulfonate groups to clean and contaminated polystyrene, with the contaminated polystyrene showing greater ion exchange capability (IEC) and degree of sulfonation. The experimental average value of the IEC of clean SPS is $10.3 \pm 5.05 \times 10^{-4} \frac{\text{mol}}{\text{g SPS}}$ as compared to the $15.0 \pm 7.61 \times 10^{-4} \frac{\text{mol}}{\text{g SPS}}$ for contaminated SPS. However, statistical tests showed no significant difference in the calculated IEC between the clean and contaminated SPS. The experimental average IEC value of $15.0 \pm 7.61 \times 10^{-4} \frac{\text{mol}}{\text{g SPS}}$ for the contaminated SPS is greater than the sulfonation experiment of Abbes et al on waste PS which is $0.08 \times 10^{-4} \frac{\text{mol}}{\text{g SPS}}$. Also, the average experimental values of IEC (clean and contaminated) when compared to the theoretical estimation of the available exchangeable site suggest that sulfonation did not only occur on the surface of the polystyrene. Apparently, the acid was able to diffuse into the layers of the polystyrene unit.

Some contaminants in the polystyrene may have served as a catalyst in the sulfonation process. The removal of the surface protective coating in waste polystyrene which otherwise blocks the attachment of the sulfonate group to the styrene units enhances the degree of sulfonation. The values calculated also show a wide range of ion exchange capacity (both for the clean and contaminated) for the same batch of polystyrene, which is an indication of the random distribution of the styrene units in the polystyrene sample.

In the sulfonation experiment, the simple, easy, straightforward and relatively less hazardous method of soaking the PS to sulfuric acid is a good alternative method compared to the established procedure of sulfonation like the use of chlorosulfonic acid and 100% sulfuric acid.

IV. Conclusions and Recommendations

The sulfonation method of adding 97-98% sulfuric acid at room temperature introduced sulfonate groups to clean and contaminated polystyrene, with the contaminated polystyrene showing greater ion exchange capability (IEC) and degree of sulfonation. The experimental average value of the IEC of clean SPS is $10.3 \pm 5.05 \times 10^{-4} \frac{\text{mol}}{\text{g SPS}}$ as compared to the $15.0 \pm 7.61 \times 10^{-4} \frac{\text{mol}}{\text{g SPS}}$ for contaminated SPS. However, statistical tests showed no significant difference in the calculated IEC between the clean and contaminated SPS. The experimental average IEC value of $15.0 \pm 7.61 \times 10^{-4} \frac{\text{mol}}{\text{g SPS}}$ for the contaminated SPS is greater than the sulfonation experiment of Abbes et al on waste PS which is $0.08 \times 10^{-4} \frac{\text{mol}}{\text{g SPS}}$. Also, the average experimental values of IEC (clean and contaminated) when compared to the theoretical estimation of the available exchangeable site suggest that sulfonation did not only occur on the surface of the polystyrene. Apparently, the acid was able to diffuse into the layers of the polystyrene unit.

Some contaminants in the polystyrene may have served as a catalyst in the sulfonation process. The removal of the surface protective coating in waste polystyrene which otherwise blocks the attachment of the sulfonate group to the styrene units enhances the degree of sulfonation. The values calculated also show a wide range of ion exchange capacity (both for the clean and contaminated) for the same batch of polystyrene, which may be an indication of the random distribution of the styrene units in the polystyrene sample.

In the sulfonation experiment, the simple, easy, straightforward and relatively less hazardous method of soaking the PS to sulfuric acid is a good alternative method compared to the established procedure of sulfonation like the use of chlorosulfonic acid and 100% sulfuric acid.

Based from the results of the experiments, waste SPS has the potential to be used as an ion exchange material.

During the conduct of this study, the following areas of research have been identified for possible future work:

1. Refinement and improvement of the methodology (i.e. change other variables in the sulfonation and batch ion exchange process) to increase the ion exchange capacity of waste PS.
2. The synergistic effect of different contaminants on the IEC of waste polystyrene must be studied.
3. A comprehensive research on the optimization of the sulfonation process of the clean and contaminated polystyrene (i.e. effect of temperature, volume of sulfuric acid, form and surface area of the PS sample) may be undertaken.
4. To investigate the effect of the regeneration process on the ion exchange capability of the SPS (contaminated only).
5. To investigate the ability of the SPS to trap heavy metals in simulated wastewater.

V. REFERENCES

1. C. Martins, G.Ruggeri and M.De Paoli, *J. Braz. Chem Soc*, **14(5)** 797-802 (2003)
2. H.S. Makowski, G.H. Singhal and R.D. Lundberg, *U.S.pat,* **3(870)**, 841 (1975)
3. F. Kucera and J. Jancar, *Chem. Papers*, **50(4)**, 224-227 (1996)
4. S. Zaidi, The Arabian Journal for Science and Engineering, **28 (2B)**, 183-194 (2003)
5. A. Ching, E. Fernandez , R.Fermin and A. Santiago , B.S. Chemical Engineering Thesis, University of the Phillipines (2006)
6. H. An, C. Shin, G. Chase, *Journal of Membrane Science*, **283**, 84-87 (2006)
7. I.Abbes, S.Bayoudh, and M. Baklouti, *J Polym Environ,* **14**, 249-256 (2006)
8. I.Abbes, S.Bayoudh, and M. Baklouti, *Desalination,* **204**, 198-203 (2006)
9. D. Lind, W. Marchal and S. Wather "Basic statistics for business and economics", Mc Graw Hill (2006).
10. Nalco Corporation Technical Bulletin Printed 1-98

Nomenclature

Symbol	Description	Units
a	constant in the modelled equation for sulfonation	[1/h]
IEC	ion exchange capacity	[mol/g SPS]
k	asymptote constant value in the modelled equation	[mol/g SPS]
SD	sulfonation degree expressed as percent sulfonation	[%]
SPS	sulfonated polystyrene	[-]
t	time	[h]