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Leaching Behavior of Sulfonated Polystyrene (SPS) from Recycled Styrofoam

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***Abstract*—The leaching behavior of the sulfonate group ($SO_3^-H^+$) and the heavy metals exchanged by the sulfonated polystyrene (SPS) were investigated using the Toxicity Characteristic Leaching Procedure (TCLP). The SPS used for the TCLP tests was prepared by the direct method of adding sulfuric acid to recycled Styrofoam and was then subjected to batch ion exchange test with ion-simulated wastewater. Experimental results from the TCLP tests yielded the following results: the heavy metals exchanged leached out with concentrations greater than the regulatory standards for wastewater; and the sulfonate group or the active site remained in the ion exchange material. The results suggest that the SPS from recycled Styrofoam will only slow down the release of heavy metals to the receiving environment and will act as a temporary holder of heavy metals. The SPS leached the heavy metals but the sulfonate group remained in the polystyrene unit making it available to trap heavy metals again.**

***Index Terms*— polystyrene, sulfonated polystyrene (SPS), Styrofoam, toxicity characteristic leaching procedure (TCLP).**

I. Introduction

The Toxicity Characteristic Leaching Procedure (TCLP) analysis simulates landfill conditions. Over time, water and other liquids percolate through landfills. The test was designed to model a theoretical scenario in which a waste is to be disposed in an ordinary sanitary landfill. Waste sample vary widely and may be completely solid or completely liquid, or contain both liquids and solids, such as sludge samples. If a waste contains less than 0.5% solids, only the filtered liquid needs to be tested and the complex leaching procedure does not need to be performed. A sample composed of both liquid and solid material must be filtered to separate any liquid. The liquid portion is saved for further testing. The remaining solid is then mixed with a slightly acidic extraction liquid equal to 20 times the weight of the original sample being tested. This sample and the extraction fluid are then placed into a tumbler and mixed for at least 18 hours. This tumbling simulates the leaching action of water seeping through waste in a landfill. After tumbling the sample for almost 18 hours, extraction fluid mixture is filtered to separate the solid material from the extraction fluid. The solid portion is discarded. The remaining extraction fluid is then analyzed using specific analytical procedures for various metals and chemical compounds. The concentrations of each constituent are reported, usually in milligrams per liter (mg/l), which is equal to parts per million (ppm). If the concentration of the constituent is greater than the TCLP limit, the waste is a "toxicity characteristic" hazardous waste [2], [5], [6]. The Environmental Protection Agency (EPA) Test Method 1131 or the TCLP test is the laboratory leaching procedure applied in the experiment. The reliability and comparison of the TCLP process with other leaching tests like the Multiple Extraction Procedure and the American Society and Testing Materials (ASTM) is beyond the scope of the study.

This study is part of the research on the potential application of sulfonated polystyrene (SPS) from recycled Styrofoam in the reduction of heavy metals from wastewater. The research was divided into three phases- sulfonation of the clean and contaminated polystyrene; ion exchange of the SPS with heavy metals in wastewater; and the leaching property of the SPS. The long-term application of the research is to minimize the contribution of the waste Styrofoam into the solid waste stream and use this waste as a component in a landfill liner that will temporarily trap the heavy metals from landfill leachate [4].

The general objectives of the laboratory leaching tests are to determine the ability of the SPS to trap the exchanged heavy metals and to evaluate the leaching property of the sulfonate group. The first part of the leaching experiment will identify if the concentration of heavy metals in the TCLP extract are within the regulatory standards for wastewater in the Philippines. The second part of the TCLP experiment is to verify if the sulfonate group or the active site of the ion exchange material are permanently attached to the styrene unit.

II. Methodology

The clean and contaminated polystyrene (PS) or Styrofoam samples used for the leaching tests had been sulfonated with the direct method of adding sulfuric acid and the time of sulfonation is two hours. The method of ion exchange used for the experiment is the batch process and the heavy metals used for the ion-simulated wastewater are – nickel (Ni^{+2}), cadmium (Cd^{+2}), chromium (Cr^{+3}), and lead (Pb^{+2}) [4].

The method applied for the TCLP process is the Toxicity Characteristic Leaching Procedure (TCLP) or the Environmental Protection Agency (EPA) Method 1131. This

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experiment was performed to investigate the ability of the SPS to capture or trap the heavy metals in the simulated wastewater and to test the leaching property of the sulfonate group or the ability of the sulfonate group ($SO3^-H^+$) to remain in the PS.

A. Leaching Property of the SPS or Ability of the SPS to trap the heavy metals

The EPA method 1131 or the TCLP process was applied to the SPS after the ion exchange process. The samples were considered 100% solid and size reduction was not necessary on the assumption that the exchange of ions is limited only to the surface of SPS. Acetic acid solution with a pH of 2.88± 0.05 was used as the leachant or extraction fluid over liquid to solid ratio of 20:1 and tumbling in an end-over-end fashion for 18 hours. The filtered liquid extract was then brought to an accredited laboratory for the metal analysis using Atomic Absorption Spectrophotometry (AAS) [6].

B. Leaching Property of the Sulfonate Group

The second part of the experiment was conducted to verify the leaching property of the sulfonate group. TCLP test was applied to both clean and contaminated SPS (i.e. the SPS samples were not used in the ion exchange process).
Procedure:

1. Sulfonate the clean and contaminated polystyrene samples for two hours.
2. Divide the sulfonated polystyrenes into two groups – sample A and sample B.
3. Determine the ion exchange capacity (IEC) of sample A.
4. Perform a TCLP test on sample B.
5. Perform a regeneration process for sample B using hydrochloric acid.
6. Determine the IEC of sample B after the regeneration process.
7. Compare the IEC of samples A and B.

III. Results and Discussion

A. Leaching Property of the SPS or Ability of the SPS to trap the heavy metals

The results of the TCLP tests are shown in Table I.

TABLE I. AVERAGE TCLP RESULT FOR THE CLEAN AND CONTAMINATED SPS

Metal	TCLP extract, ppm		Regulatory[a] Standards
	Clean SPS	*Contaminated SPS*	
Cd(II)	10.35	52.10	0.01
Cr(III)	4.99	14.29	0.05
Pb(II)	13.67	46.79	0.05
Ni (II)	5.86	37.77	-

a. Based on the Department of Environment and Natural Resources Administrative Order No. 34.

From the results of Table I, The SPS leached out the heavy metals sorbed from the batch ion exchange tests with the ion-simulated wastewater. The concentrations of the heavy metals are greater than the regulatory standards for wastewater in the Philippines. This only implies that the SPS will temporarily trap the heavy metals and will slow down their release to the receiving environment.

B. Leaching Property of the Sulfonate Group

The second part of the experiment was to verify if the sulfonate group will leach out together with the metal or will remain in the polystyrene.

Both the clean and contaminated SPS were subjected to the TCLP test, regenerated and treated with sodium chloride for the determination of the ion exchange capacity.
Two possible scenarios for this process:

Case 1:

IEC before TCLP >>> IEC after TCLP:
This means that the sulfonate group leached out with the heavy metals after the TCLP test.

Case 2:

IEC before TCLP ≅ IEC after TCLP:
This means that the sulfonate group remained in the polystyrene after the TCLP test.

The result for the leaching property of the sulfonated group is shown in Table II.

TABLE II. LEACHING PROPERTY OF THE SULFONATE GROUP IN SPS

SPS	IEC, mole/g SPS		% sulfonation	
	Before TCLP	After TCLP	Before TCLP	After TCLP
Clean	7.35×10^{-4}	8.04×10^{-4}	8.12	9.37
Contaminated	1.17×10^{-3}	1.15×10^{-3}	13.45	13.16
p-value for the mean				0.18
p-value for the variance				0.81

From the results in Table II, the IEC before TCLP (and its corresponding percent sulfonation) for clean and contaminated SPS were numerically less than the values after the TCLP process. But, the p-values from the statistical analysis show that there is no significant difference between the IEC before and after the TCLP process. This only means that the sulfonate group remained in the polystyrene unit.

IV. Conclusion

In the TCLP experiment, the concentration of the extracts did not pass the regulatory standards for wastewater in the Philippines. This implies that waste SPS will only temporarily trap the metals but will eventually release it to the receiving environment. The waste SPS leached the heavy metals but the sulfonate group remained in the polystyrene unit making it available to trap heavy metals again.

Based from the results of the experiments, waste SPS has the potential to be a component material (a liner) in a sanitary landfill. The waste SPS will continuously trap the heavy metals from landfill leachate since the sulfonate groups remained in the polystyrene and will lessen the impact of the heavy metals concentration released to the receiving environment.

V. Recommendations

The study is only an initial attempt for the leaching property of the sulfonate group, it will still be further improved and refined if the following areas of research will be continued and investigated: the effect of the regeneration process on the ion exchange capability of contaminated polystyrene and a comprehensive study on the kinetics of the trapping and releasing of heavy metals by the waste SPS.

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