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Synthesis and Utilization of New Flocculants from Waste Polystyrene by Modified Sulfonation

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Atık Polistirenden Modifiye Sülfolama ile Yeni Flokülant Sentezi ve Kullanımı

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Özet

Sunulan bu çalışmada çeşitli modifiye sülfolama denemeleri yapılarak elde edilen sülfolanmış polistiren flokülantların gerçek atıksu arıtımında etkinlikleri ortaya konmuştur. Dahası, bu flokülantların performansları klasik yöntemle elde edilen sülfolanmış polistiren ve konvansiyonel flokülant ile kıyaslanmıştır. Koagülasyon-flokülasyon işleminde sentezlenen flokülantlar ile bulanıklık ve KOİ giderim yüzdesi, plastiklerin yıkama atıksuyu türüne ve sentezlenmiş flokülantlara göre değişiklik göstermiştir. Sentezlenen flokülantlar ile en yüksek bulanıklık giderimi HDPE atıksuyunda gözlenirken, KOİ giderimi en fazla PP yıkama atıksularında elde edilmiştir. Dahası, sentezlenen flokülantlar arasında FSPS3, atık sulardan bulanıklık gideriminde daha iyi performans gösterirken, FSPS1 KOİ gideriminde daha başarılı olmuştur. Çamurda ise, FSPS3 diğer sentezlenmiş flokülantlara kıyasla çamur susuzlaştırma özelliklerinin geliştirilmesinde genellikle daha yüksek verimliliğe sahiptir.

Anahtar kelimeler: Sülfolama; Polistiren atık; Koagulasyon-flokülasyon; Atıksu arıtma çamuru

Synthesis and Utilization of New Flocculants from Waste Polystyrene by Modified Sulfonation

Abstract

The efficiencies of sulfonated polystyrene flocculants (FSPS) obtained in modified sulfonation experiments were revealed for real wastewater treatment. Moreover, their performances were compared with sulfonated polystyrene obtained by conventional method and conventional flocculants. Efficiency of turbidity and COD removal with synthesized flocculants in coagulation-flocculation process shown an alteration based on plastics' washing wastewater types and synthesized flocculants. While the highest turbidity removal efficiency with synthesized flocculants was obtained in HDPE, COD removal was found highest in PP washing wastewater. Moreover, while FSPS3 among synthesized flocculants shown better performance in turbidity removal from wastewaters, FSPS1 was better in COD removal. As for treatment sludge, FSPS3 usually had higher efficiency on enhancement of sludge dewatering properties compared to other synthesized flocculants.

Keywords: Sulfonation; Polystyrene waste; Coagulation-flocculation; Wastewater; Treatment sludge

1. Introduction

Polyelectrolytes are polymers which includes ionic centers in the monomers and opposite ions bound to the central ion as to provide electroneutrality. As for polystyrene sulfonic acid (PSSA), it is a compound that can be easily produced from polystyrene and is commonly used in polyelectrolyte chemistry [1]. Moreover, it attracts attention of researchers with properties of ion-exchanger and low-cost production [2,3]. Sulfonation of polystyrene (PS) is a topic that has been started in the 1960s [4] and has been rapidly spreading [5] since the Makowski [6] patent (US Patent no 3,870,841) [7].

The first PS sulfonation method in the homogenous phase was developed by Turbak [4]. In this method, triethyl phosphate and sulphur trioxide complexes in dichloroethane were reacted with PS. However, Makowski [6] used acetyl sulfate complexes for sulfonation in his patent. As for Vink method [1], it can be accepted as the basis of for today's studies and PSSA was prepared in inert cyclohexane by using Ag_2SO_4 or P_2O_5 as the catalysts. Additionally, PS sulfonation method in the heterogeneous phase was developed by Kucera and Jancar [5]. Although there are other studies, the most widely applied and/or studied method has been Vink method and many modifications of its have been developed in several studies in time [7-10].

The transformation of plastic wastes to different functional polymeric products and added- value have been taken an important place in recycling studies which increase after growing plastic waste problem. Nowadays, PS is widely used in packaging and in plastic plates, cutlery and some types of tea cups (e.g. disposable white plastic plates). In the developed processes, the PS waste material is separated by chemical treatment into monomers/hydrocarbons [11] or waste PS is sulfonated to produce new functional polymers more valuable than the original [12]. For instance, various products such as ion exchangers, resins, polyelectrolytes, fuel cell membranes were obtained with sulfonation of PS. Some methods in the literature used for production of flocculants by sulfonation were investigated and compared; consequently, it was observed that used methods have similar logic and are modified from Vink method [1,9,3,10,8,5,13,14].

The product obtained in sulfonation process can have characteristics of water soluble or insoluble polymer depending on used solvent in the process of sulfonation. When PS is first dissolved in cyclohexane and then sulfonated with sulfuric acid, water-soluble polyelectrolyte, PSS-sodium salt is obtained [9]. Although these prepared resins and polyelectrolytes were tried in removal of water hardness and turbidity by the same authors; however, they have been not studied in real wastewater. Accordingly, in this study, the efficiencies of sulfonated PS flocculants obtained in various modified sulfonation experiments were revealed for real wastewater treatment and their performances were compared with sulfonated polystyrene (SPS) obtained by conventional method and conventional flocculants. In the study, wastewaters obtained in washing process of plastic wastes, which have an important place in plastic recycling studies, has been used as wastewater. Additionally, the effects of different characteristics in different types of plastics' washing wastewaters on treatment efficiencies were compared.

2. Materials and Methods

Firstly, sulfonated polystyrene (FSPS) was synthesized by using classical literature methods from PS supplied from the waste collection center [1,7,9] (Table 1). Literature studies [1,9,3,10,8,5,13,14] revealed that although the main logic of synthesis method appears to be same, some details in the methods have an effect on the structure of synthesis material and/or its efficiency in usage area. Therefore, in this study, some modifications were applied (Table 1) and 3 alternative synthesis materials were obtained. FTIR analysis was conducted for characterization of synthesized polymers.

2.1.Plastic Waste Washing and Washing Wastewater Characterization

HDPE, LDPE, PET, PP and PS thermoplastic used in the study were obtained from the municipal solid waste separation center. Firstly impurities (such as paper, glass, etc.) were removed from wastes and then they were ground with blade system to obtain particle size less than 8 mm. Ground thermoplastic wastes were washed with NaOH in completely mixed reactor. Waste washing was carried out in 3 stages. In the first stage, washing was carried out by using 42% NaOH [15]. 126 g of NaOH was dissolved in 300 mL of water and complete to 1500 mL. 250 g plastic waste was washed in this solution. The first stage of the washing process was finished after boiling the mixture at 90°C for 10 minutes. Finally, wastes were filtered and plastic wastewater was obtained. For second stage, plastic wastes were boiled at 90°C for 10 minutes after addition into 1500 mL of water and then filtered. In the third stage, the same process was carried out with the second stage. The wastewaters obtained in washing processes were accumulated and they were characterized.

Table 1. Applied synthesis modifications in the study

Short name	Form	Reference	Method
FSPS1	Solid-powder 	Bekri-Abbes et al.[9]; Vink [1]	It was produced from waste PS plates. Method was applied without any modifications. ➢ Mixing 50 mL H_2SO_4 + 11 g P_2O_5, cooled to 40°C ➢ Dissolve 1.5 g PS + 75 mL cyclohexane separately and mixed them (while mixing one, other is added gradually) ➢ Wait by mixing at 40°C for 30 min. ➢ Wait 1 hour without mixing ➢ Cooled suddenly with 25 g ice and generate 3 phases ➢ Take adhesive phase in the middle, add 150 mL of pure water, dispose obtained solvent phase ➢ Dry
FSPS2	Liquid 	Modified from Sulkowski et al. [13,14]	It was produced from waste PS foam (extended PS) materials. 1,2 g PS foam + 0,05 g Ag_2SO_4 + 20 mL H_2SO_4 Firstly, it was stirred at 80 °C in the top-cooled system. Then, pink and sticky phase formed after addition of 20 mL deionized water was disposed. 30 mL deionized water was added to dissolve; after that, 12 g Na_2CO_3 was added to form precipitate. Remained liquid after precipitation, which is wastewater, was kept and used in experiments.
FSPS3	Solid-powder 	Modified from Sulkowski et al. [13,14]	This is similar method to FSPS2; however, PS plates were used in this method. It was precipitated with $CaCO_3$ and precipitate was used as powder after drying. Mixing 1 g PS + 20 mL H_2SO_4 at 60-80˚C for 4 hours. 20 mL of deionized water was added to the dark brown slurry substance. After that, formed sticky material was dissolved with 30 mL deionized water. Finally, $CaCO_3$ was added gradually by mixing and generated yellow precipitation was filtered and dried at 40˚C.

2.2.Treatability of Plastic Wastes' Washing Wastewaters

Coagulation-flocculation treatment experiments of washing wastewaters were carried out by using synthesized sulfonated polymerized materials Also, same experiments were conducted by conventional flocculant polyelectrolyte (PEL) for comparison.

Coagulation-flocculation experiments:

Process experimental configuration was shown in Figure 1 [16]. Experiments were conducted in Jar-test device and glass beakers. $FeCl_3$ was used as coagulant at fixed dosage of 1000 mg/L since it was found more efficient in pretesting experiments [17]. PEL and 3 different FSPS synthesized in this study were used as flocculant. 1000 mg/L coagulant and flocculants with various dosages were added respectively to characteristically known wastewater at its own pH. Finally, coagulation and flocculation process were conducted as shown in Figure 1.

2.3 Analyses

FTIR (Fourier Transform Infrared) analysis: In this study, Bruker model FTIR spectrophotometer was used to obtain information about organic matters' structure by IR spectrum having 400-450 cm-1 wavelength.

Analysis for raw and treated wastewater: COD (mg/L), turbidity (NTU) and pH analysis were performed for both raw and treated wastewater samples. While COD was measured by 5220C and 5220D Standard Methods [18], turbidity was decided in spectrophotometer at 375 nm wavelength. As for pH, it was measured with Hach model pH meter.

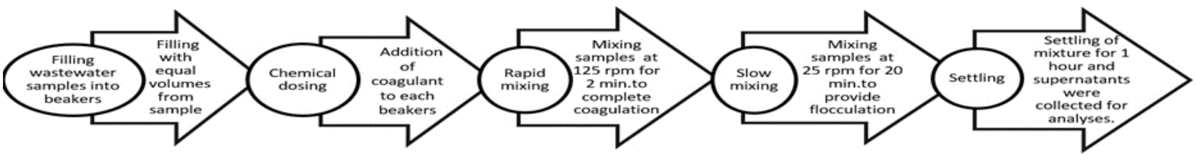

Figure 1. Experimental configuration of coagulation-flocculation process

Treatment sludge analysis: Sludge density, solid content and specific cake resistance analysis were performed for the samples having sludge production. While sludge density was calculated by division of weight to the volume, solid contents of sludges were found by gravimetric method of Standard Methods [18]. As for specific cake resistance of sludge, firstly R^2 values of filtered water volume (V) vs. time/volume (t/V) graph was calculated by linear regression and specific cake resistance was found by using these slope values in Reynolds [16].

3. Results and Discussions

3.1 The Structures of Synthesized Flocculants

The FTIR spectrums of the synthesized flocculants were given in Figure 2. For FSPS1, it was obtained bands which belong to aromatic C-H in-plane bending at 1082 cm^{-1}, disubstitue benzene at 855 cm^{-1} and sulfonic acid S-O strain at 608 cm^{-1} (Figure 2a). The bands of O-H stretching at 3326 cm^{-1}, C = C stretching of the alkene at 1638 cm^{-1}, sulfonate group SO_2 asymmetric stretching at 1379 cm^{-1}, aromatic C-H in-plane bending at 1092 cm^{-1} and sulfonic acid SO_2 symmetrical strain at 1037 cm^{-1} were observed in FSPS2 FTIR spectrum (Figure 2b). The bands of O-H stretching at 3523 and 3399 cm^{-1}, aromatic C=C stretching at 1620-1453 cm^{-1}, sulfonate SO_2 stretching at 1113 cm^{-1}, disubstitue benzene at 853 cm^{-1} and S-O strain at 700-600 cm^{-1} were obtained in FSPS3 FTIR spectrum (Figure 2c).

3.2 The Effect of Flocculants on the Treatment of Plastic Washing Wastewater with Coagulation-Flocculation

Firstly, COD and turbidity values were evaluated (Table 2) since although the main purpose of coagulation process is turbidity removal, it is well known fact that some organic compounds can also be removed with settled flocs.

The first remarkable finding in Table 2 is that pH values did not change excessively with flocculants for all wastewaters and raw wastewater pH was always higher than treated wastewaters. These results showed that although synthesized flocculants decreased raw wastewaters' pH values due to their acidic nature, their impacts on pH values was not too much since raw wastewaters initially were washed with excessive quantity of NaOH (Table 2). Turbidity removal shown an alteration based on raw wastewater and synthesized flocculants' types. While the highest turbidity removal efficiency was obtained by FSPS3 for HDPE, LDPE, PET, PS and mixed wastewater, FSPS1 had highest performance in terms of turbidity removal for PP wastewater. Turbidity removal percentages for LDPE, PET, PS, Mixed and PP wastewater was found between 70%-83%, it was obtained as 86% for HDPE wastewater. Although all synthesized flocculants had effects on COD removal for all wastewater, the highest removal performance mainly was achieved with FSPS1 (Table 2). Especially for PP wastewater, 82.6% COD removal efficiency was achieved by FSPS1 flocculant. However, FSPS2 flocculant shown better performance in term of COD removal with 70% removal efficiency for PET wastewater.

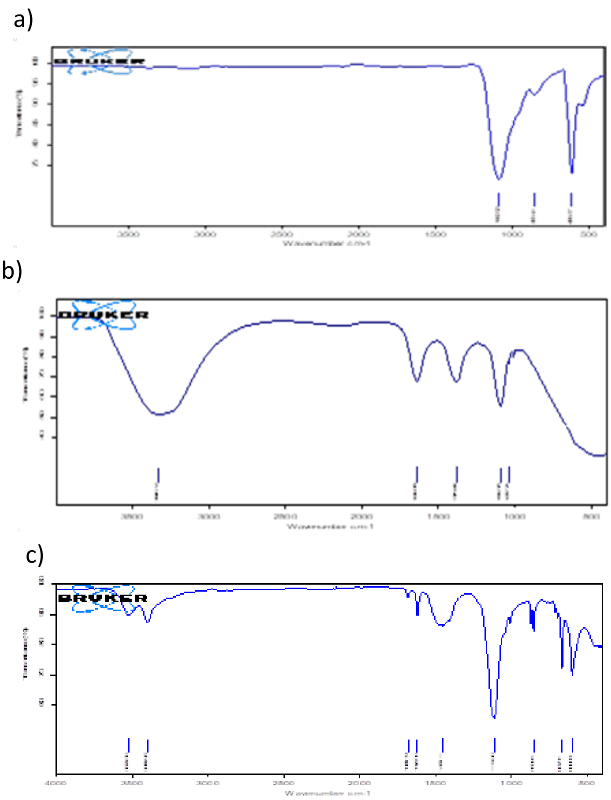

Figure. 2. (a) FSPS1 (b) FSPS2 (c) FSPS3 flocculants FTIR spectrums

Table 2. Turbidity and COD removal performance of flocculants

Parameters	Raw wastewater	FSPS1	FSPS2	FSPS3	PEL
HDPE					
pH	13.94	13.03	13.06	13.14	13.31
Turbidity, NTU	1664	245	233	223	230
COD, mg/L	2202	1504	1805	1705	1153
LDPE					
pH	13.76	13.12	13.13	13.13	13.11
Turbidity, NTU	560	199	169	151	142
COD, mg/L	768	802	1303	702	451
PET					
pH	13.87	13.2	13.2	13.15	13.26
Turbidity, NTU	883	215	199	187	169
COD, mg/L	3021	2807	902	2707	1654
PP					
pH	13.75	13.21	13.23	13.25	13.27
Turbidity, NTU	989	221	228	237	212
COD, mg/L	2304	401	1003	802	1554
PS					
pH	13.69	13.26	13.23	13.18	13.22
Turbidity, NTU	3323	714	733	553	671
COD, mg/L	4864	3008	3108	3108	4562
Mixed					
pH	13.67	13.17	13.15	13.1	13.19
Turbidity, NTU	1955	578	577	577	579
COD, mg/L	2918	1504	1905	1955	1654

Moreover, although turbidity removal efficiency was found close for synthesized flocculants and PEL in all wastewaters, synthesized flocculants usually had higher efficiency of COD removals compared to PEL (Table 2). For instance, while 70% COD removal was obtained by FSPS2 for PET wastewater, only 45% COD removal was achieved with PEL. Similarly, 82.6% and 32% COD removal was obtained with FSPS1 and PEL respectively for PP wastewater. Therefore, it can be emphasized that although FSPS2 and FSPS3 flocculants were synthesized by using similar methods having small differences, the least effective synthesized flocculant was FSPS2 for both COD and turbidity removal. This can result from both materials used in the methods (PS foam for FSPS2, PS plates for FSPS3) and precipitant chemicals (Na_2CO_3 for FSPS2, $CaCO_3$ for FSPS3) (Table 1).

Properties of sludges obtained from treatment by using both synthesized flocculants and PEL were given in Table 3. It can be concluded from literature researches that all SCR values were at the recommended levels for coagulation sludges which dewatered well [19]. The sludge properties obtained in each of the syntheses for the same type of plastic wastewater are similar, but they differ from the sludges obtained with PEL (Table 3). Although PEL usually had higher efficiency in terms of sludge volume, TS and solid percentages of the treatment sludges, synthesized flocculants' impacts were better on dewatering of sludge compared to PEL (Table 3). This result can be explained by generation of gel-like characteristics of treatment sludge in the case of PEL usage. Moreover, FSPS3 had usually higher efficiency on enhancement of sludge dewatering properties compared to other synthesized flocculants.

Table 3. Properties of treatment sludges obtained by synthesized flocculants

Plastic	Flocculant	Sludge volume, mL	TS, mg/L	Density, g/cm^3	Solid, %	SCR, m/kg
HDPE	FSPS1	20.6	6520	1.088	0.60	6.66E+13
	FSPS2	20.8	6660	0.980	0.68	2.04E+13
	FSPS3	30	6820	1.005	0.68	2.47E+13
	PEL	17	10010	1.024	0.98	3.89E+13
LDPE	FSPS1	20.6	4510	1.010	0.45	2.86E+13
	FSPS2	20	4390	1.001	0.44	4.05E+13
	FSPS3	20	4350	0.974	0.45	3.41E+13
	PEL	13	5860	0.998	0.59	4.64E+13
PET	FSPS1	17.5	8610	0.980	0.88	2.21E+13
	FSPS2	19.5	8290	0.983	0.84	2.89E+13
	FSPS3	19	7710	1.022	0.75	1.89E+13
	PEL	15.5	5160	1.009	0.51	4.77E+13
PP	FSPS1	20.5	8690	1.014	0.86	2.91E+13
	FSPS2	21	8900	1.012	0.88	2.89E+13
	FSPS3	20.5	9110	1.015	0.90	1.76E+13
	PEL	18.5	9210	1.000	0.92	2.55E+13
PS	FSPS1	21.5	11110	1.016	1.09	6.87E+13
	FSPS2	17.5	12910	1.028	1.26	3.61E+13
	FSPS3	19.5	11440	1.006	1.14	5.70E+13
	PEL	19	12500	1.005	1.24	7.22E+13
MIXED	FSPS1	18.5	7870	1.006	0.78	4.56E+13
	FSPS2	20	7240	0.990	0.73	2.72E+13
	FSPS3	16.5	7960	0.994	0.80	2.69E+13
	PEL	17	8890	1.002	0.89	4.61E+13

4. Conclusion

In this study, the efficiencies of sulfonated PS flocculants obtained in various modified sulfonation experiments were revealed for real wastewater treatment and their performances were compared with SPS obtained by conventional method and conventional flocculants. The presence of aromatic and sulfonate groups' bands in all flocculants shows that the sulfonation of the PS was achieved.

Efficiency of turbidity and COD removal with synthesized flocculants in coagulation-flocculation process shown an alteration based on plastics' washing wastewater types and synthesized flocculants. The highest turbidity removal efficiency with synthesized flocculants was obtained in HDPE, PS and PET wastewater respectively at pH 13, which is the original pH value for all wastewaters. As for COD removal, the highest efficiency was achieved in PP wastewater in coagulation-flocculation process by synthesized flocculants. Moreover, while FSPS3 shown better performance in turbidity removal from wastewaters, FSPS1 was better in COD removal. The sludge properties obtained in each of the syntheses for the same type of plastic wastewater are similar, but they differ from the sludges obtained with PEL. Although PEL usually had higher efficiency in terms of sludge volume, TS and solid percentages of the treatment sludges, synthesized flocculants' impacts were better on dewatering of sludge compared to PEL. Especially FSPS3 usually had higher efficiency on enhancement of sludge dewatering properties compared to other synthesized flocculants. To conclude, all wastewaters studied in this study were treated at different levels with synthesized flocculants and the lowest treatment efficiency usually was obtained in FSPS2 among synthesized flocculants. This lower efficiency can be due to foam used in synthesis. Moreover, it can be highly recommended that different pH values for wastewaters and different $FeCl_3$ dosages should be studied to obtain most optimum conditions for synthesized flocculants in future studies.

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5.References

[1] Vink, H., 1981. A New Convenient Method for the Synthesis of Poly(styrenesulfonic acid), Macromolecular Chemistry and Physics,182, 279-281.

[2] Bozkurt, A., 2002. Dielectric and Conductivity Relaxations in Quaternary Ammonium Polymer, Physics and Chemistry of Solids, 63, 685-690.

[3] Bozkurt, A., 2005. Anhydrous Proton Conductive Polystyrene Sulfonic Acid Membranes, Turkish Journal of Chemistry, 29, 117–123.

[4] Turbak, A. F., 1962. Polymer Sulfonation without Cross Linking. The Sulfur Trioxide-Phosphate System, Ind. Eng. Chem., Prod. Res. Dev. 1, 275-278.

[5] Kucera, F., Jancar J., 1996. Preliminary Study of Sulfonation of Polystyrene by Homogeneous and Heterogeneous Reaction, Chemical Papers, 50, 224—227.

[6] Makowski, H. S. andLundberg, R. D., 1981, Process for controlled gelation of polymeric solution, Google Patents.

[7] Bekri-Abbes, I., Bayoudh, S., Baklouti, M., 2008. The Removal of Hardness of Water Using Sulfonated Waste Plastic, Desalination, 222, 81–86.

[8] Vandervoorde, C.A., 1996. Amphiphilic Star Polymers as Solubilizing Agents for Environmental Separations, PhD Thesis, Massachusets Institute of Technology, USA.

[9] Bekri-Abbes, I., Bayoudh, S., Baklouti, M., 2007. A Technique for Purifying Wastewater with Polymeric Flocculant Produced from Waste Plastic, Desalination, 204, 198–203.

[10] Holley, D.W., 2009. Synthesis and Characterization of Branched Polyelectrolytes: Star-branched NaPSS, PhD Thesis, University of Tennessee, USA.

[11] Sato, Y., Koder, Y., Goto, J. and Matsui, Y., 2002. Effect of Polystyrene Addition on the Monomer Recycling of Phenol Novolac, Polymer Degradation and Stability, 78, 315–322.

[12] Inagaki, Y., Kuromiya, M., Noguchi, T. and Watanabe, H., 1999. Reclamation of Waste Polystyrene by Sulfonation Langmuir, 15, 4171-4175.

[13] Sulkowski, W.W, Wolinska, A., Szoltysik, B., Bajdur, W.M., Sulkowska, A., 2005. Preparation and properties of flocculants derived from polystyrene waste, Polymer Degradation and Stability, 90, 272-280.

[14] Sulkowski, W.W., Wolinska, A., Pentak, D., Maslanka, S., Sulkowska A., 2006. The Influence of the Chemical Additives in Polystyrene on the Features of Flocculants Obtained during Sulphonation of the Polystyrene, Macromol. Symp. 245–246, 621–627.

[15] Santos, A.S.F, Teixeira. B.A.N., Agnelli J.A. 2005. Characterization of Effluents Through a Typical Plastic Recycling Process: An Evaluation of Cleaning

Performance and Environmental Pollution Resources, Conservation and Recycling, 45,159-171.

[16] Reynolds, T.D, Richards, P.A., 2005. Çevre Mühendisliğinde Temel işlemler ve süreçler, 2. baskıdan çeviren: Ülker Bakır Öğütveren, Efil Yayınevi, çeviri: 2011.

[17] Özdemir, N.C., Sogancioglu, M., Yel, E., 2017. Waste LDPE and HDPE Washing Wastewaters Physico-Chemical Treatability with Sulphonated Polystyrene (SPS), 2nd IWA Regional International Symposium on Water, Wastewater and Environment (IWA-PPFW2017), Proceedings, 22-24 March, 2017, Izmir-Turkey.

[18] APHA/AWWA/WEF, 2005. Standard Methods for the Examination of water and Wastewater, 21st ed. American Public Works Association/American Water Works Association/ Water Environment Federation, USA

[19] Casey, TJ, 2006. Unit Treatment Processes in Water and Wastewater Engineering, AQUAVARRA Research Limited, Dublin, Chapter 16, 169-183.