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Use of polystyrene sulfonate produced from waste plastic cups as an auxiliary agent of coagulation, flocculation and flotation for water and wastewater treatment in Municipal Department of Water and Wastewater in Uberlândia-MG, Brazil

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Summary

In this paper, we demonstrated the viability of recycling waste plastic cups for synthesizing polystyrene sulfonate (PSS), which was used as an auxiliary agent of coagulation, flocculation and flotation in water and wastewater treatment plants. The study was carried out in the treatment plants of the Municipal Department of Water and Wastewater in Uberlândia-MG, Brazil. The polystyrene sulfonate, when compared with commercial polymers, presented promising results for treating water with turbidity above 30 NTU, and presented the best results on the wastewater treatment. However, for water treatment, a further study needs to be carried out considering the Brazilian legislation concerning the quality of the treated water.

1. Introduction

Polystyrene is a thermoplastic material obtained from styrene. Polystyrene presents, in general, good mechanical, thermic and electric resistance, and low density. Due to these properties, it is used to produce discardable materials such as cups and food trays. Polystyrene can be produced with distinct regularities: atactic, isotactic and syndiotactic. Most of the commercial polystyrene products are made with the amorphous polystyrene. Polystyrene may suffer diverse chemical reactions of substitution on the benzene ring, among which, the reaction of sulfonation is the one that presents more commercial applications. The reaction of sulfonation may be homogeneous or heterogeneous [1].

Recent papers about polystyrene sulfonate (PSS) may be divided in the following way: i) study of the chemical reactions of sulfonation of the commercial virgin polystyrene [2,3]; ii) study of the chemical reactions of sulfonation of recycled polystyrene for several uses, such as the production of admixtures for improving the workability and resistance to compression of concrete [4], production of ion exchange membranes [5]; and the production of polyelectrolytes, which may be used as auxiliary agents of coagulation on the treatment of industrial waters, i.e., presenting high turbidity [6,7].

The research about the production of alternative polyelectrolytes for water treatment is becoming more and more important since the subterraneous water supply is frequently inadequate for big demands. Superficial waters need to be treated even more carefully at the same time that the populational density keeps growing. Industries demand more and more water, as well as a better quality of their supplying sources. Rivers, natural supplying sources, keep receiving an increasing amount of domestic and industrial wastewater, demanding therefore, a greater attention for solving the problems that come from the inadequate wastewater treatments.

In water and wastewater treatment plants, the coagulation process is very important. This process allows removing colloidal particles that are present on these waters. The objective of using coagulation auxiliary substances is to decrease the dosage of the coagulation agent and accelerate the formation of flocs, thus accelerating the sedimentation process [6]. The polyelectrolytes that are used on water and wastewater treatment are not reusable, and for this reason, it becomes important, both from the environmental and economical point of view, to obtain them from polymeric residues.

We have recently began a study aiming at the application of waste polystyrene, chemically modified through the heterogeneous reaction of sulfonation, in water and wastewater treatment plants in Uberlândia-MG, Brazil [8].

In the present paper, we present a comparative study of the properties of polystyrene sulfonate (PSS), obtained from waste plastic cups, with the properties of other polymers on the water and wastewater treatment at Bom Jardim water treatment plant (Bom Jardim-WTP) and Aclimação wastewater treatment plant (Aclimação-WWTP), of the Municipal Department of Water and Wastewater of Uberlândia-Minas Gerais, Brazil.

2. Experimental

The used polyelectrolytes were: A3015® (polyacrylamide of high molecular weight, low anionic character, according to manufacturer specifications), A3040® (polyacrylamide of medium molecular weight, medium anionic character, according to manufacturer specifications), N3100® (polyacrylamide of high molecular weight, non ionic character, according to manufacturer specifications), furnished by DEGUSSA; Aqualex 360® (polyacrylamide of medium molecular weight, strong anionic character, according to manufacturer specifications) and W360® (polyacrylamide of high molecular weight and strong cationic character, according to manufacturer specifications), furnished by CHEMSEARCH. Aqualex 360® is used as coagulation auxiliary and W360® as flotation auxiliary, at Bom Jardim-WTP and Aclimação-WWTP, respectively. The sulfonated derivative was obtained through the sulfonation of Polystyrene with sulfuric acid, in agreement with references [7,8]. Zanatta® plastic cups were used as raw material. The obtained material was rubbery and swollen, presenting brown color. The polyelectrolyte was washed and filtered with water at 10ºC. The sulfonation of polystyrene was confirmed by Fourier

Transformed Infrared Spectroscopy (FTIR).Tablets of KBr pressed with polystyrene sulfonate were analyzed in a Perkin Elmer Infrared Spectrum 1000. 24 scans were perfomed, using 4 cm^{-1} resolution. The degree of sulfonation was calculated through volumetric titration with NaOH 0.10 M, using phenolphthalein as indicator. The produced material presented a degree of sulfonation of (60.3 ± 2.41)% and average viscometric molar weight of 126,000 g mol^{-1}, which was previously determined using an Ostwald viscometer in a thermostated bath at 25ºC and an aqueous solution of acetic acid 0.1M/sodium chloride 0.2M as solvent system, being [η] = 0.03441 (obtained through the Huggins relation), K= 3.29 10^{-6} gL^{-1}, a = 0.788, in Mark-Howink-Sekurada-Kuhn equation [4]).

Water Treatment

Ideal pH test

The raw water of the treatment plant was put into 6 Jar Test flasks. Next, the polyelectrolyte and 7 to 10 ppm of aluminum sulfate was added to the flasks, according to the initial water turbidity. The mixture was stirred for 1 minute at 100 rpm and the Jar Test was turn off. A solution of $Ca(OH)_2$ (1.2 $g.L^{-1}$) was added to the flasks in increasing volumes, aiming at evaluating the pH in which bigger and denser flocs would be formed. The mixture was stirred for 20 minutes at 60 rpm. Next, the sedimentation process was observed in the flasks. After 30 minutes of decantation, the turbidity and the pH of the superficial water was measured. The ideal pH (ideal for the efficiency of the flocculation process) was chosen according to the lowest measured turbidity of the superficial water [8].

Tests of coagulation and flocculation

After testing the ideal pH, the coagulation and flocculation tests were performed in a Jar Test FlocControl II (PoliControl), with 6 flasks, 2 liters each, filled with raw water from the water treatment plant (Bom Jardim-WTP). The evaluated polyelectrolytes and 7 to 10 ppm of aluminum sulfate was added to raw water. The pH was corrected by adding $Ca(OH)_2$, up to the ideal flocculation pH. This mixture was stirred at 100 rpm for one minute, and then, at 60 rpm for 20 minutes. Next, it was decanted for 30 minutes, after which, a water sample was collected. Its turbidity was measured in a Hach turbidimeter 2100P, and the pH was measured in an Orion pHmeter 310.

Wastewater Treatment

This test was carried out using an adaptation of the coagulation and flocculation test that was used in the water treatment. However, besides waiting until the material decantation, it was also necessary to wait out the natural flotation due to the wastewater fermentation in the Jar Test flasks. One liter of raw wastewater from Aclimação-WWTP and 200 mgL^{-1} of an aqueous solution of ferric chloride were added into each Jar Test flask. The polyelectrolyte was added in varied concentrations in five of the six flasks. One of them was kept without the polyelectrolyte for comparison. The ideal dose of polyelectrolyte was 1 mgL^{-1} (dose routnely used by the Municipal Water and Wastewater Department of Uberlândia). Next, this mixtures were stirred at 100 rpm for one minute, and then, at 20 rpm for five minutes. The mixtures were decanted for 15 minutes, and a sample of the intermediate water, between the floated and the decanted mud. The turbidity and the pH were measured using the previously described equipment.

3. Results and discussion

3.1. FTIR

Figure 1 presents a FTIR spectrum for polystyrene after the sulfonation reaction. Attention must be given to the bands from 3000 cm^{-1} to 3500 cm^{-1}, which are attributed to the OH stretching of the $–SO_3H$ groups and absorbed water; and to the bands at the region from 1100 cm^{-1} to 1200 cm^{-1}, which are attributed to the symmetric and asymmetric stretching of the $R–SO_2–O$ group, respectively [5].

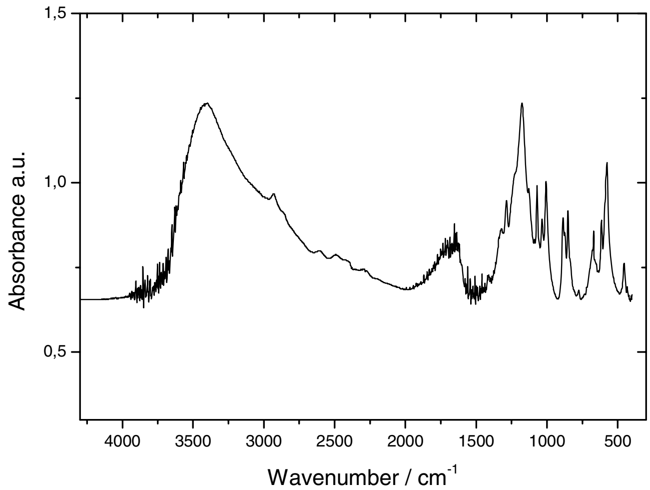

Figure 1. FTIR of polystyrene sulfonate (PSS) made of waste plastic cups.

3.2. Evaluation of PSS made of waste plastic cups in water treatment

For evaluating the use of the produced PSS in water treatment, it was initially compared to Aqualex 360® (commercial polyelectrolyte), which is used in the water treatment plant where the bench tests were performed. Table I shows the performed tests.

The first test was performed in a raw water sample of low turbidity (Water 1 (A) – 4.80 NTU). Using only aluminum sulfate, a 1.50 NTU diminishing in the water turbidity was observed. The use of polyelectrolytes, after the treatment with aluminum sulfate, changed the final water turbidity very little. As water presents low turbidity, the effect that should be observed when using polyelectrolytes is not very significant. As flocculation depends on the particles collision, the formation of flocs will be less efficient in low turbidity systems.

Since the initial turbidity of raw water was low in the first experiment, a second experiment was performed to evaluate the polyelectrolytes efficiency in systems of higher turbidity raw water (Water 2 (B) – 33.0 NTU). In this case, a 22% increase in the removal efficiency was observed with the use of both the polyelectrolyte (PSS) and the aluminum sulfate, in contrast with the use of the latter alone. The same increase in efficiency was observed when using AQUALEX 360®. The removal efficiency was nearly the same when the polyelectrolyte (PSS) dosage was reduced, table 1 water 2(C). This result is interesting because it allows controlling the amount of flocculant agent, avoiding high residue doses in the treated water.

Table 1. Tests that were performed in raw water of the water treatment plants*

Raw water	Agents of treatment	Average Turbidity (NTU)	Average pH
Water 1 (A) Average Turbidity = 4.80 NTU, pH = 6.20	$Al_2(SO_4)_3$: 7.00 mg.L^{-1}	1.50	6.30
	$Al_2(SO_4)_3$:7.00 mg.L^{-1} PSS: 0.50 mg.L^{-1}	1.43	
	$Al_2(SO_4)_3$:7.00mg.L^{-1} AQUALEX360®:0.50 mg.L^{-1}	1.65	
Water 2 (B) Average Turbidity = 33.0 NTU, pH = 6.20	$Al_2(SO_4)_3$: 10.00 mg.L^{-1}	4.50	6.30
	$Al_2(SO_4)_3$: 10.00 mg.L^{-1} PSS: 0.50 mg.L^{-1}	3.50	
	$Al_2(SO_4)_3$: 10.00 mg.L^{-1} AQUALEX 360®:0.50 mg.L^{-1}	2.97	
Water 2 (C) Average Turbidity = 33.0 NTU, pH = 6.20	$Al_2(SO_4)_3$: 10.00 mg.L^{-1}	4.50	6.30
	$Al_2(SO_4)_3$: 10.00 mg.L^{-1} PSS: 0.25 mg.L^{-1}	3.45	
	$Al_2(SO_4)_3$:10.00 mg.L^{-1} AQUALEX 360®:0.25 mg.L^{-1}	3.25	

*In the treatment station the turbidity of raw water changes according the seasons.

Figure 2 presents the performance of the polyelectrolytes evaluated for raw water with initial turbidity of 13.0 NTU. The coagulation and flotation of the disperse particles in the water to be treated depends very much on the dosage of aluminum sulfate and polyelectrolytes, as well as the kind of the employed polyelectrolyte, its molecular weight and kind of ionic charge.

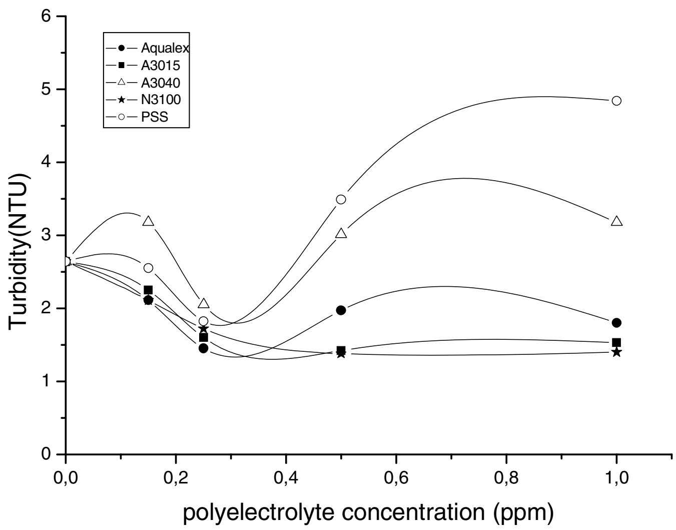

Figure 2. Final turbidity of decanted water in function of the polyelectrolyte concentration.

As observed in Figure 2, the initial water turbidity drops from 13.0 NTU to 2.64 NTU in the first step when aluminum sulfate is used (no polyelectrolyte had been added up to this point). This occurs because in these starting conditions suspense particles predominantly present negative charges, which are probably due to the adsorption of hydroxyl ions. Therefore, suspense particles in water are initially coagulated with $Al_2(SO_3)$, aiming the neutralization of superficial negative charges. These particles now have Al^{3+} ions on their surface which could interact easier with anionic polylectrolytes.
Then it was possible to reduce even more the turbidity by using the polyelectrolytes, reaching a limit value of approximately 1.50 NTU when using Aqualex 360®, A3015® and N3100®. When using PSS and A3040®, the limit values for the turbidity are approximately 1.75 NTU and 2 NTU, respectively. These values were observed for an ideal concentration of 0.25 mg·L^{-1} for Aqualex 360®, PSS and A3040®. The results also show that N3100® (non ionic character, according to manufacturer) and A3015® (low anionic character, according to manufacturer), both of them having high molecular weight, in accordance to manufacturer specifications, presented nearly the same efficiency for dosages higher than 0.25 mg·L^{-1}. Besides, even though the turbidity was kept constant with the increase of the dosage of these two polyelectrolytes, the formed flocs were the biggest (visual observation). When the results of these two polyelectrolytes are compared, the flocs that were formed when using N3100® are even bigger than those formed with A3015®. This may be attributed to a possible bridging effect caused by the high molar weight, in accordance to manufacturer specifications, of these polyelectrolytes [10].

For electrolytes having a more accentuated ionic character, PSS and A3040®, increasing the dosage besides 0.25 mg·L^{-1} causes an increase in turbidity; when using 1.00 mg·L^{-1} the PSS gives the highest turbidity. The increase in turbidity may be explained by a possible predominance of an electrostatic repulsion effect caused by the presence of a high concentration of polyelectrolyte, leading to a phenomenon of particle dispersion that impedes the coagulation process.

3.3. Evaluation of the use of the produced PSS in wastewater treatment

Table 2 presents the results of tests performed at Aclimação-WWTP for the distinct polyelectrolytes at 24ºC.

Table 2. Turbidity and pH for the use of the distinct polyelectrolytes in wastewater treatment.

Raw water (wastewater)	Treatment agents	Average Turbidity (NTU)	Average pH
Average Turbidity = 200 NTU, pH = 5.80	Ferric chloride: 200.00 mgL^{-1}	10.20	5.88
	Ferric chloride: 200.00 mg.L^{-1} PSS: 1.00 mgL^{-1}	5.64	
	Ferric chloride: 200.00 mg.L^{-1} AQUALEX: 1.00 mgL^{-1}	6.64	
	Ferric chloride: 200.00 mg.L^{-1} W360: 1.00 mgL^{-1}	8.07	

When using ferric chloride, a removal efficiency of 95% was observed. This value increases to 97% when using PSS as auxiliary, in addition to the ferric chloride. The presented results in table 2 show that the anionic polymers (PSS and Aqualex) are more efficient than W306®, the cationic polymer that is usually used at the wastewater treatment plant. This may be due to the prevalence of positive charges of iron ion complexes in pH lower than 6. Thus, as the positive charges increase due to the cationic polymer, there is the predominance of electrostatic repulsion. An opposite effect is observed with anionic polymers. At these conditions, the polymer that presented the best results was the PSS produced from waste plastic cups. This result may be attributed mainly to its strong anionic character.

4. Conclusion

Results showed that the studied polyelectrolytes (A3015® (polyacrylamide of high molecular weight, low anionic character), A3040® (polyacrylamide of medium molecular weight, medium anionic character), N3100® (polyacrylamide of high molecular weight, non ionic character), and PSS) behaved similar to Aqualex360®, a polyelectrolyte that is normally used in the water treatment plant at Bom Jardim-WTP. When used in wastewater treatment at Aclimação-WWTP, PSS presented better results thatn W360®, the polyelectrolyte that is normally used at this plant. Results also showed that the chemical recycling, through the heterogeneous reaction of sulfonation, of PS from waste plastic cups, is a viable alternative for the production of auxiliary agents of coagulation, flocculation and flotation for water and wastewater treatment plats in Uberlândia-MG. However, further studies need to be made before using these polyelectrolytes can be used to treat the water that is served to the population. However, in high turbidity waters, such as wastewater, the PSS that was produced from the chemical recycling of waste PS cups may be an efficient material to replace the commercial polyelectrolytes, thus contributing to preserve the environment.

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