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A technique for purifying wastewater with polymeric flocculant produced from waste plastic

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Abstract

One of the most important treatment processes in surface water treatment is coagulation. Surface waters such as rivers and lakes contain suspended particles and turbidity. With the aid of coagulants, and by flocculation process, followed by sedimentation and filtration, these impurities can be removed from raw waters. Besides conventional chemicals such as alum and ferric chloride, polymers such as sulfonated polystyrene are getting common. In this study, we are interested in waste plastics; waste polystyrene-containing additives were converted into a polymeric flocculant by chemical modification. Specifically, waste polystyrene consisting of white coffee cups was sulfonated to produce a water-soluble polymer. The sulfonation was characterised by FTIR technique and the degree of sulfonation was determined by titration. The polymer provides high purification of the supernatant after flocculating a kaolin suspension. Moreover, the material provides a pure supernatant in the treatment of actual wastewater comparable to conventional polymeric flocculants. A new reclamation technology to convert waste plastic into a functional polymer is reported.

Keywords: Waster water treatment; Turbidity removal; Flocculant; Waste polystyrene

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1. Introduction

One of the natural pollutants in surface waters are suspended particles. The presence of these impurities will cause turbidity in waters. The usual source of turbidity is clay particles resulting from the erosion of soil in the catchments area. The size of colloidal particles is in the range of a few nanometers up to some hundred micrometers, usually colloidal particles in surface waters have sizes ranging from 0.001 up to 10 microns. The time of settling down of these particles ranges from half an hour up to 63 years [1]. The application of coagulation and flocculation is necessary for the removal and settlement of colloidal particles. Adding coagulants (such as sulphate of aluminium or ferric chloride) to the wastewater creates a chemical reaction in which the repulsive electrical charges surrounding colloidal particles are neutralized, allowing the particles to stick together creating clumps or flocs. Flocculants are then used to facilitate the agglomeration and decantation. Most of used flocculants consist of polyelectrolytes such as derivatives of polyacrylamide and polystyrene.

Nowadays, there has been interest in plastic recycling. Polystyrene is a plastic which has been extensively used in packaging. Various investigations have adopted chemical recycling of waste polystyrene into the corresponding monomers or hydrocarbons [2,3]. However, the process is not efficient because the cost of hydrocarbons and monomers is low compared to that obtained by recycling. Therefore, it is useful to find an efficient technique to recycle waste polystyrene. Recently, a new technique of polystyrene recycling has been developed which seems to be more efficient. The goal of this process is to convert polymer waste into a functional polymer with a new application and added value [4–8]. It is well-known that the sulfonation of polystyrene allows obtaining interesting products such as cationic exchanger resin, polyelectrolyte and fuel cell membranes. Therefore, the new process developed in our laboratory is based on the sulfonation of waste poly-

styrene to produce a polymeric flocculant and to use it for the removal of turbidity from wastewater.

2. Experimental

2.1 Preparation of flocculant from waste polystyrene

Waste polystyrene used was packaging consisting of white coffee cups. This waste was collected after verifying the ISI code of polystyrene (Fig. 1). It was cleaned and dried in the atmospheric environment; its principal additive is the oxide of titanium. The sulfonating agent used was sulphuric acid H_2SO_4 96% (purchased from Prolabo). The method used in our laboratory for the sulfonation of waste polystyrene is called “method of VINK” [9]. This method is an interfacial reaction of total post-sulfonation of polystyrene and it allows obtaining of sodium salt of sulfonated polystyrene (PSSNa) completely charged.

0.25 g of waste polystyrene was dissolved in 25 ml of cyclohexane. In parallel, in a bicol of 150 ml under agitation, and in an oil bath of 40°C, 3 g of phosphorous pentaoxyde (P_2O_5), a powerful dessicant agent, were slowly added to 50 ml of concentrated sulphuric acid (H_2SO_4). The solution was maintained under agitation for 30 min. Polystyrene dissolved in cyclohexane was added slowly to the acidic solution and it was maintained under agitation at 45°C for 2 h. The mixture was, then, transferred in a separating funnel. The separation consists in three phases: i) cyclohexane on the top, a clear phase; ii) polyacid PSSH in the centre, a turbid phase and iii) a yellow phase at

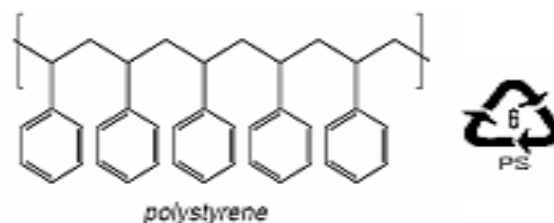


Fig. 1. Chemical structure and ISI code of polystyrene.

the bottom containing the acidic solution and P_2O_5 . The acidic solution is eliminated. 150 ml of water was then added slowly to dissolve the polymer. This operation is long because the polyacid is difficult to redissolve and sometimes it tends to foam (it is necessary to count from 15 to 30 min). After decantation, the aqueous phase was recovered. The neutralisation was carried out by adding NaOH pastilles until obtaining a basic pH. A yellow powder of the soluble polymer in the form PSSNa was obtained after distillation.

To evaluate the effect of dessicant on the reaction, sulfonation was carried out in the absence of dessicant in cyclohexane and acetone solution.

The sulfonic acid and the sulfonate groups in the sulfonated waste polystyrene were confirmed by Fourier transformation infrared spectrum (FT-IR) using a Nicolet spectrophotometer (model 560) with a scanning range between 400 and 4000 cm^{-1} . The samples were prepared as tablets diluted in KBr. The percentage of sulfonation was calculated by titration with NaOH solution against phenolphthalein indicator.

2.2 Preparation of polyelectrolyte solutions and jar-test studies

To evaluate the flocculating effectiveness of PSSNa, we used a synthetic wastewater, which was made of clay particles/water with an initial turbidity of 177 NTU. The flocculating effectiveness of PSSNa was evaluated by the jar-test studies using a four-beaker jar-test apparatus (Bio-block model 10408). The turbidity was measured using a turbidimeter (WTW Turb 555 IR). $Al_2(SO_4)_3 \cdot 18H_2O$ (Merck) was dissolved in distilled water to obtain a final concentration of 1 mg Al^{3+}/mL . A PSSNa polyelectrolyte solution was prepared using distilled water to achieve a concentration of 1 mg PSSNa/mL. Other PSSNa solutions with concentrations of 0.01 and 0.1 mg/mL were prepared by dilution. The study of the flocculation started after the determination of the optimum dose of the coagulant. In the four beakers of the jar-test apparatus, a constant dose of alum was

added to the liquid. The samples were mixed for 1 min at 200 rpm. Then various doses of polyelectrolytes were added using a micropipette. The samples were mixed at 45 rpm for 30 min. The solutions were allowed to settle for 15 min and the turbidity was measured.

3. Results and discussion

The reaction of sulfonation allows the attachment of sulfonic groups to the polymer chains as shown in Fig. 2. The mechanism of the reaction implies the preliminary formation of sulphur trioxide SO_3 starting from the sulphuric acid. This reaction proceeds in the interface organic solvent–sulphuric acid. The sulfonation of the phenyl cycles takes place in para position for steric reasons. The reaction is more efficient when a dessicant agent such as P_2O_5 is used. This agent allows sulphuric acid to be more concentrated in SO_3 . The neutralization of the sulphonic acid is a simple acid–base reaction, which allows obtaining sodium salt of sulfonated polystyrene as shown in Fig. 3.

The reaction proceeding in the absence of P_2O_5 did not permit obtaining completely charged polymer. Even if the waste contained an additive agent such as oxide of titanium, polystyrene could be sulfonated. Indeed, for wastes consisting of

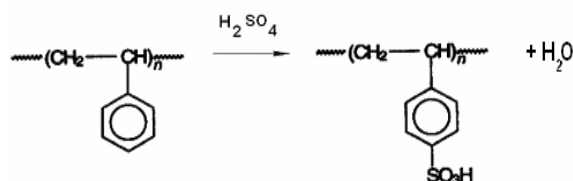


Fig. 2. The sulfonation reaction of polystyrene.

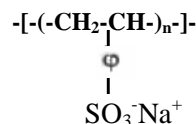


Fig. 3. Chemical structure of sodium salt of sulfonated polystyrene.

transparent coffee cups (which do not contain oxide of titanium as additives), there is no significant change in structure. Probably the presence of additives has an influence on the sulfonation. The presence of additives such as black of carbon has been reported to accelerate the degree of sulfonation and to favor obtaining water soluble polymer [4]. 1,2-dichloroethane (EDC) solvent is generally used for sulfonation [4]. Since EDC is not good for the environment compared to cyclohexane, we have chosen in this study to use cyclohexane as solvent.

Waste sulfonated in acetone solvent at 40°C for 2 h is not completely soluble in water. Only 10% of initial polystyrene is converted into a soluble polymer. This is due to the fact that acetone does not completely dissolve polystyrene, it just allows the polymer chains to move and flow freely.

Fig. 4 shows the spectra of unmodified and sulfonated polystyrene. Polystyrene without sulfonation (a) shows the following groups: OH (at 3400–3200 cm^{-1}), unsaturated aromatic C–H

tretching vibrations (at 3025 cm^{-1}), CH_2 bending vibration (at 2921 and 2846 cm^{-1}), aromatic ring (at 1492 cm^{-1}), CH_2 (at 1451 cm^{-1}), various substitution of benzene ring between 900 and 770 cm^{-1} (at 905; 837; 754 cm^{-1}). The characteristics of infrared absorbance of sulfonated polystyrene have been studied [10]. The spectrum of sulfonated polystyrene shows the following groups: OH (very strong at 3420 cm^{-1}) $-\text{SO}_2-\text{O}-$ (at 1178 cm^{-1}). The symmetric stretching vibration of SO_3H groups and the absorption at 1129 cm^{-1} result from a sulfonate anion attached to a phenyl ring.

The result of the flocculation of a clay suspension with an initial turbidity of 177 NTU using sulfonated waste polystyrene is shown in Fig. 5. This figure is a photo taken after 15 min after adding variable quantity of NaPSS. Sample 1 in Fig. 5 had no polymeric flocculant and did not change. However, for water treated with NaPSS, these samples were flocculated. The result indicates that SPS from waste polystyrene can be used as a polymeric flocculant in a clay suspension.

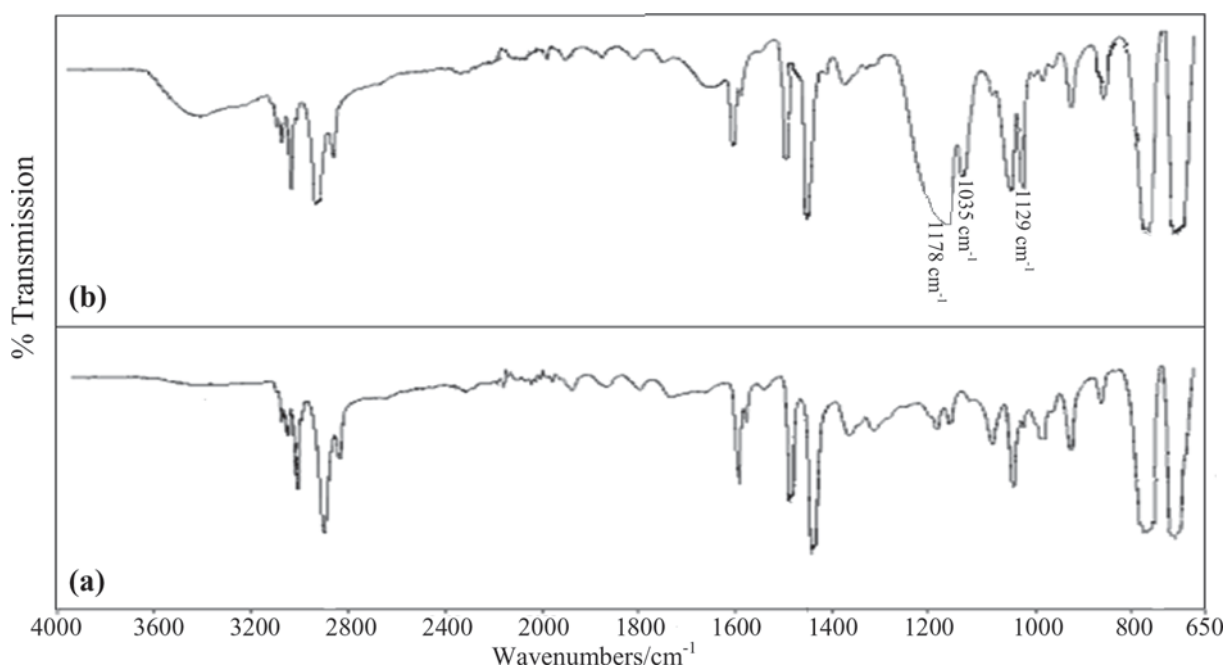


Fig. 4. FTIR spectra of a) waste polystyrene and b) sulfonated polystyrene.

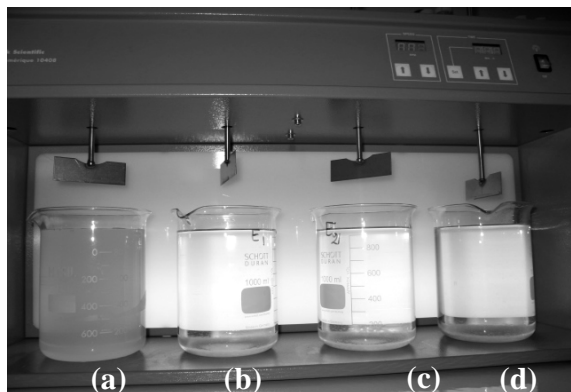


Fig. 5. Comparison of flocculation of a) initial water without flocculant b) 0.05 ppm of flocculant c) 0.08 ppm of flocculant and d) 0.1 ppm.

The study of the flocculation process was started after selection of an optimum dose of the coagulant and next of the flocculant. It was found that an optimum dose of coagulant was 66 mg/dm^3 of aluminium sulphate. For comparison, similar studies of the flocculation process were also conducted using the alkaline commercial Praestol 2515 polyelectrolyte synthesised from polyacrylamide. From the results obtained (Fig. 6) it could be concluded that the synthesised flocculant is

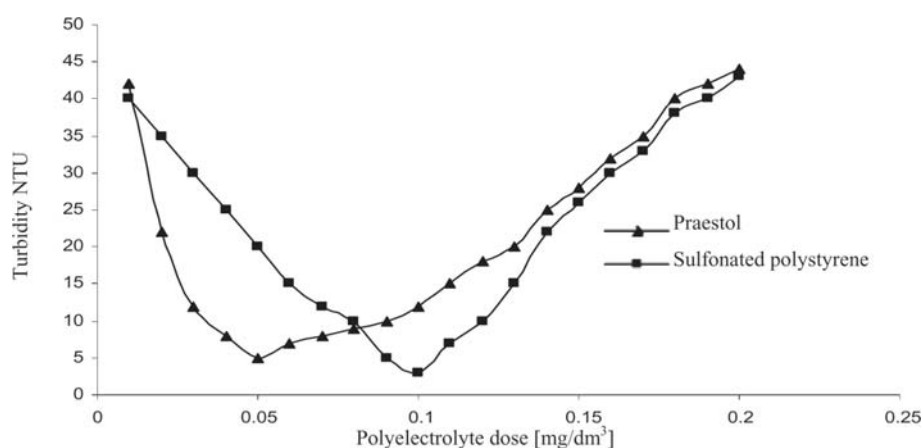


Fig. 6. Dependence of turbidity on polyelectrolyte dose (sodium salt of sulfonated polystyrene and praestol 2515 in a synthetic waste water having initial turbidity of 177 NTU, coagulant dose of 66 mg/dm^3 and $\text{pH} = 7$).

comparable to that of commercial Praestol 2515. The larger decrease of turbidity was observed for 0.1 ppm dose of polyelectrolyte synthesised from waste polystyrene. For this dose of flocculant, the percentage of turbidity removal reaches 98%.

4. Conclusions

In this paper, we have suggested a new technique to purify wastewater with high turbidity by coagulation and flocculation process using modified waste polystyrene. From experimental study it was concluded that

1. Waste polystyrene containing additives can be sulfonated to get a water-soluble polymer.
2. The polymer works as a polymeric flocculant in clay suspension.
3. The polymer is comparable to a conventional polymeric flocculant in purification of the supernatant after flocculation.

We suggest a new reclamation to convert waste polystyrene into a functional polymer. We believe that this technique will be of benefit for reusing waste polystyrene and purifying wastewater.

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