

The removal of hardness of water using sulfonated waste plastic

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Abstract

The possibility of using waste polystyrene to remove the hardness of water has been investigated. Waste of polystyrene is consisting of white coffee cups and they were converted into adsorbent by heterogeneous sulfonation. Infra red technique has been used to confirm the sulfonation. Degree of sulfonation and cation exchange capacity have been determined by titration. Hard water has been prepared by dissolving Mg or Ca salts in distilled water. The modified polymer provides high purification of hard water comparable to conventional adsorbent.

1. Introduction

Polystyrene is an inexpensive and hard plastic, structurally; it's a long hydrocarbon chain with a phenyl group attached to every carbon atom. Polystyrene is produced by free radical vinyl polymerization from styrene. A large portion of polystyrene's production goes into packaging (cups, plates, bowls, trays, clamshells, meat trays, yogurt and cottage cheese containers) and

protective packaging (shaped and pieces used to ship electronic goods such as audio/visual cassettes). Unfortunately, only few amounts of waste polystyrene are recycled.

In fact, there are three main types of waste polystyrene recycling, that is; material recycling, thermal recycling and chemical recycling.

The material recycling is a simple method to reuse waste plastics, and which has been applied in the plastics processing industries. The thermal recycling is to get thermal energy by burning waste plastics, but this technique requires high

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calorie incinerator. Moreover, it produces harmful gases such as dioxin and hydrogen chloride gases while burning. The chemical recycling is to convert waste polystyrene into styrene or hydrocarbures [1–7]. Recently, a new technique of polystyrene recycling has been developed and which seems to be more efficient, this process's goal is to convert polymer waste into functional polymer with a new application and added value. It is well known that the sulfonation of polystyrene allows the obtaining of interesting product such as: cationic exchanger resin, polyelectrolyte and fuel cell membrane. Therefore, the new developed process is based on the sulfonation of waste polystyrene to produce a new functional polymer more valuable than virgin material or hydrocarbures. By using this method Inagaki et al. [8] have converted waste polystyrene which consists of video cassette into a polyelectrolyte, the process used is an homogenous sulfonation with fuming sulfuric (SO_3 , content 60 wt %). Simitzis [9] has converted waste consisting of foam polystyrene into a cation exchange resin by dissolving waste into styrene and then copolymerizing with a crosslinking agent, and sulfonating the mixture. These techniques have the disadvantage of being expensive, and very complicated for a laboratory experiment. For that reason, the first objective of the present research is to obtain a polymeric exchanger from common packaging waste polystyrene with a simple and less expensive procedure of sulfonation. The technique developed in our laboratory in front of this problem was to sulfonate polystyrene just on the surface and to keep the core of the material unmodified. This partial sulfonation, in the absence of solvent, keeps the new sulfonated polystyrene insoluble in water and attaches sulfonic groups to polymer chains and consequently it could be used as resin for ion exchange applications such as the softening of hard water.

On the other hand, water is a vital solvent which must be tasteless, colorless, and odorless. As water moves through soil and rock, it dissolved

Table 1

The classification of hardness of water

Classification	Ca and/or Mg (mg/L)
Soft	0–17.1
Slightly hard	17.1–60
Moderately hard	60–120
Hard	120–180

very small amounts of minerals and holds them in solution. Calcium and magnesium dissolved in water are the two most common minerals that make water “hard”. The degree of hardness becomes greater as the calcium and magnesium content increases.

Water hardness is classified in Table 1. To control the hardness of water, cation exchange resins are widely used. In this process, water passes through the resin, usually sulfonated polystyrene beads, and the hardness minerals attach themselves to the resin beads while sodium on the resin beads is released simultaneously into the water. In this paper, we present a technique of recycling waste polystyrene consisting of white coffee cups into a cation exchange resin and the use in the softening of hard water.

2. Experimental

2.1. Preparation and characterization

2.1.1. Preparation

White coffee cups were crushed till we obtained particles with the size of 0.2–0.3 cm², afterwards 5 g of dry material and 100 mL of dense sulfuric acid, 95%, were introduced to a flask and were left to react under agitation while time and temperature are varied. When the reaction period is complete, the slurry was filtered with a funnel and washed with 250 mL portions of distilled water, after the sixth washing a portion of filtrate was checked with pH paper to ensure the residual sulfuric acid has been removed from

the resin, and then the sulfonated resin was dried at 40°C for 30 min.

2.2. Neutralization

Neutralization has for objective the conversion of the resin into its Na⁺ form. It consists of a saturation of the polymer with Na⁺ ions by stirring the polymer for 2 h at 500 mL 1 M NaCl solution.

2.3. Material and characterization

Ca²⁺ and Mg²⁺ concentrations were obtained with an atomic absorption spectrometer (AAS Vario) equipped with a deuterium lamp, background correction, a hollow cathode lamp, and an air-acetylene burner.

2.3.1. Determination of the degree of sulfonation

The degree of sulfonation of the polymer was evaluated by titration; 0.3 g of sulfonated polymer is dissolved in about 30 mL of a toluene/methanol (9:1, V). A solution 0.1/5 N of sodium hydroxide in methanol is used to titrate the polymer solution with phenolphthaleine as indicator.

2.3.2. Determination of ion exchange capacity

The ion exchange capacity (with unit of mmol/g of dry polymer) of sulfonated polystyrene was determined by measuring the concentration of H⁺ that was exchanged with Na⁺ when acid-form of sulfonated polystyrene was equilibrated with NaCl solution. A known weight of dry polymer (for example 0.5 g) in the H⁺ form was placed 100 mL of 0.2 M NaCl solution and shaken occasionally for 2 h, the amount of H⁺ released by the polymer was determined by titration with 0.01 M NaOH.

2.4. Hard water preparation and softening

Hard water has been prepared by dissolving about 150 mg of Mg or Ca salt in one liter of distilled water. To test the ability of our resin on the softening of this hard water, 1 g of the prepared resin is placed in 50 mL of the previous solution and it allowed under agitation for 2 h at room temperature.

3. Results and discussions

3.1. Characterization

Commercial cation-exchange resin are network polymers, usually it consisted of crosslinked polystyrene. The crosslinking step is carried out in order to ensure the non solubility of polymer. In this experiment, we have limited to a partial sulfonation in order to obtain an ionomer insoluble in water having sulfonic ionic responsible of ion exchange properties. In Fig. 1, we have represented the waste coffee cups before and after crushing and immersion in hot sulphuric acid solution. It is important to observe that sulfonated crushed particles present brown colour similar to conventional cation exchange resins such as Lewatite S100.

The characterization of modified waste polystyrene by FTIR technique proves the success of reaction of sulfonation of waste polystyrene. In Fig. 2, we have represented the FTIR spectra of waste polystyrene before and after sulfonation at

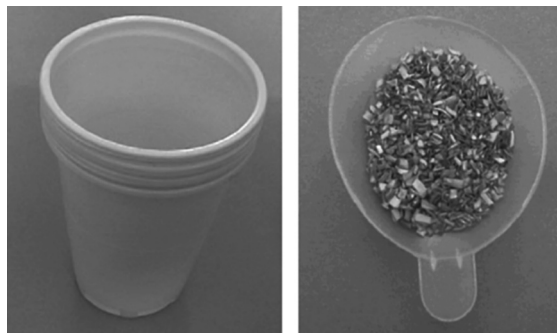


Fig. 1. Plastic coffee cups were transformed into crushed sulfonated particles.

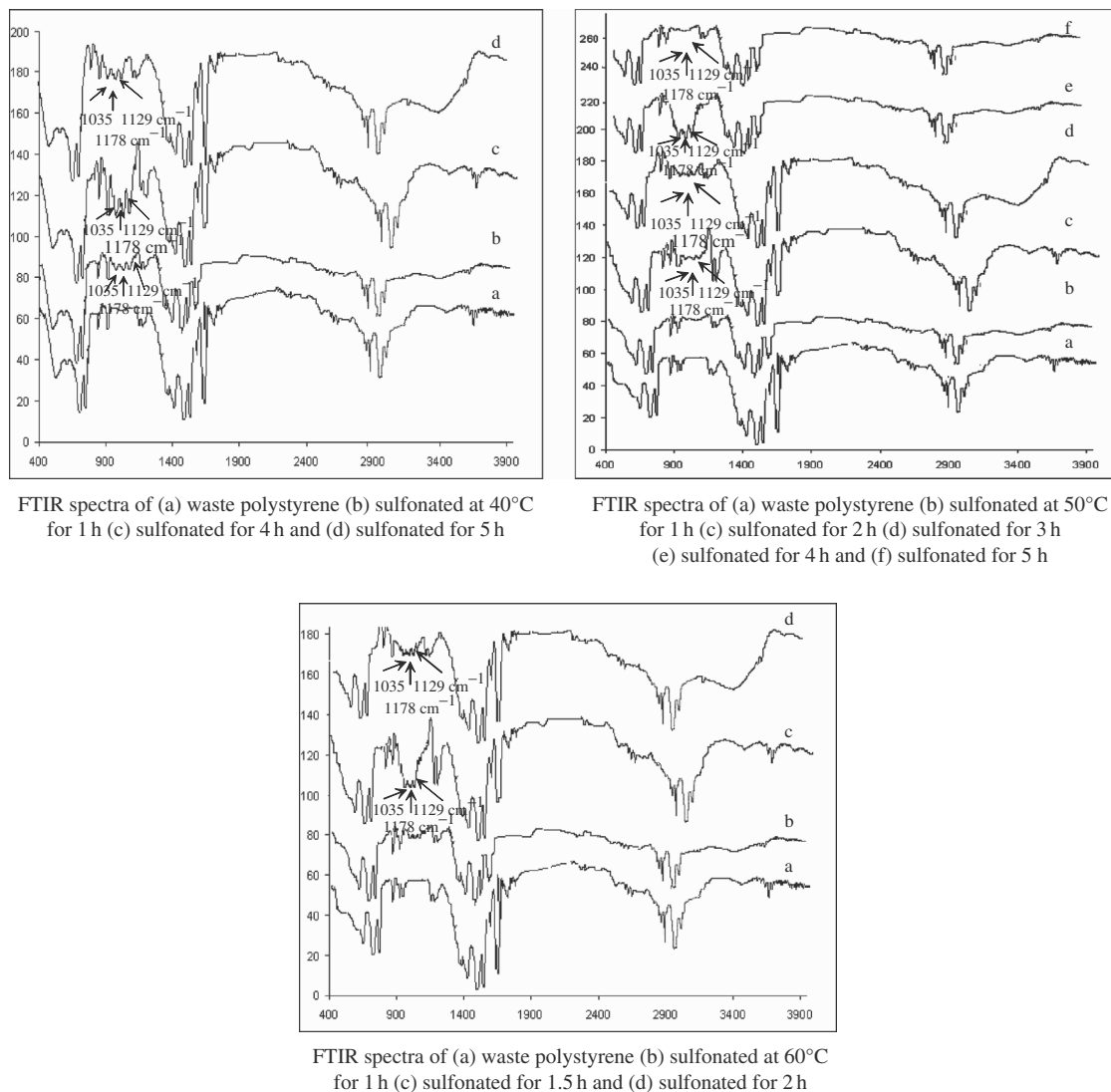


Fig. 2. FTIR spectra of samples sulfonated at different temperatures and periods.

40, 50 and 60°C for various periods of reaction. It can be seen the presence of sulfonic group bands (at 1178, 1129 and 1035 cm^{-1} [10]) in the FTIR spectra of sulfonated polystyrene.

The degree of sulfonation gives mole percentage of the styrene units sulfonated. Degree of sulfonation has been determined using the previous equation and best values have been obtained for samples treated at 40°C for 4 h and 60°C for 1.5 h

(respectively 16 and 17%). The influence of other reaction conditions (such as, dimension of samples and rate of stirring) on degree of sulfonation and have been also reported in our previous work [11]. It was shown that degree of sulfonation increased extensively when dimension of particles decreased. In fact, by decreasing the dimension of particles, the efficiency of the contact between the polystyrene and the sulfonating

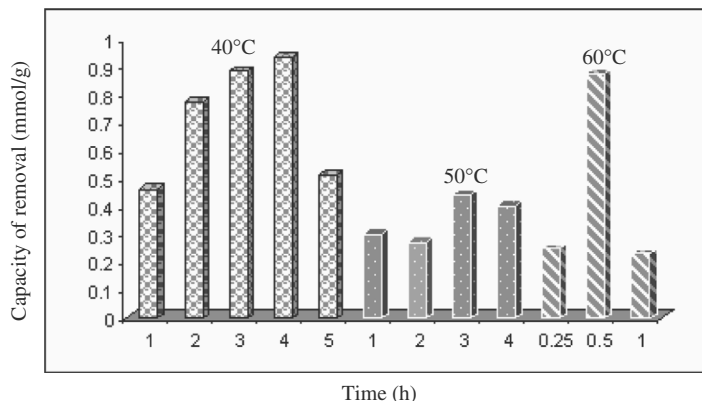


Fig. 3. Capacity of removal of calcium ions for samples sulfonated at different temperature and time.

agent can be remarkably increased. Furthermore, in order to increase the efficiency between polystyrene beads and the sulfonating agent, it is important that the shearing force must be moderate.

The exchange capacity of the sample treated at 60°C for 1.5 h was 0.8 meq/g of the resin. This value is acceptable with respect to common ion exchangers (Amberlite IR: 3–5 meq/g), because this adsorbent is a modified waste plastics and inexpensive as well.

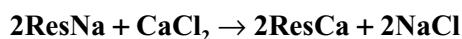
3.2. Application in the removal of hardness from water

In Figs. 3 and 4, we have represented respectively the capacity of removal of ions magnesium

and calcium ions for samples sulfonated at different temperature and time.

It can easily be seen (Fig. 3) that the capacity of removal of Ca ions at different temperature and time varies from 0.22 for sample treated at one hour for 60°C to 0.93 for that treated for 4 h at 40°C. These values are close to the exchange capacity of membranes, slightly higher than natural inorganic exchangers such as smectite clays and lower than the commercial organic exchange resin.

The reaction of exchange is as follows:



By the same way, we have determined the capacity of removal for the ion magnesium. It

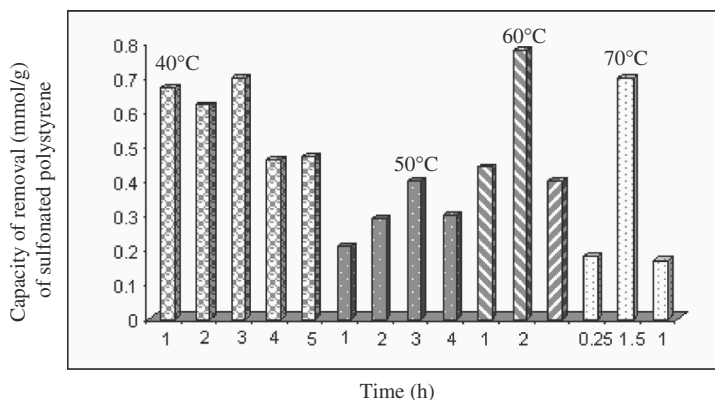
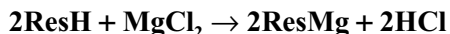


Fig. 4. Capacity of removal of magnesium ions for samples sulfonated at different temperature and time.

varies from 0.17 mmol/g for sample sulfonated for one hour at a temperature of 70°C to 0.78 mmol/g for that treated for 2 h at 60°C.

The corresponding reaction of exchange is as follows:



It is interesting to note that the capacity of exchange for the ions, Mg^{++} and Ca^{++} increases from magnesium to calcium. This order coincided with the selectivity of common exchange resins.

4. Conclusion

This paper gives a technique to recycle waste polystyrene which have been mass produced and hence is very beneficial for the protection of global environment. It allows the preparation of cation exchanger resin from waste and its application in the softening of hard water.

The application sulfonated waste plastics for the softening of water with a hardness of about 150 mg/L in ion calcium or magnesium has been tested. For calcium ions, the capacity of exchange varies from 0.22 for sample treated at one hour for 60°C to 0.93 for that treated for 4 h at 40°C while for magnesium ions, it reaches its maximum for waste polystyrene sulfonated for

2 h at 60°C (0.78 mmol/g). It is important to note that the exchange capacity of resins show the same trend of the variation of sulfonation.

Finally, we intend to study in further research the possibility of regenerating the resin after exchange.

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