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Sulphonation of expanded polystyrene waste with commercial sulphuric acid for potential use in removal of heavy metals from contaminated waters

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Polystyrene has been sulphonated using commercial sulphuric acid in order to obtain ion exchangers, which could be used to uptake some heavy metals from solutions. Reaction conditions which affect the sulphonation conversion, have been investigated such as: reaction time, reaction temperature and molar ratio of styrene: sulphuric acid. As expected, the reaction time leads to higher conversion. The reaction yield is also increased with increasing the temperature of the oil bath. The molar ratio plays an important role, the sulphonation occurs with a molar ratio (1 : 1, St : H₂SO₄), and the reaction conversion increases with increasing the molar ratio. The reaction conversion using pure sulphuric acid was insignificantly higher compared with the conversion using commercial sulphuric acid. In addition, polystyrene samples were irradiated with gamma rays prior to sulphonation; a higher sulphonation degree was obtained for the irradiated samples. The ability of sulphonated PS to uptake some toxic metal ions has been evaluated with respect to the sulphonation ratio: Cu²⁺, Co²⁺, Ni²⁺, Cr³⁺.

KEY WORDS:

expanded polystyrene waste

irradiation

removal toxic elements.

sulphonation

KLJUČNE RIJEČI

iradijacija

otpad od ekspaniranog polistirena

sulfonacija

uklanjanje otrovnih elemenata

Sulfoniranje pjenastoga polistirenskog otpada komercijalnom sumpornom kiselinom za potencijalno uklanjanje teških metala iz kontaminiranih voda

Sažetak

Polistiren je sulfoniran komercijalnom sumpornom kiselinom kako bi se dobio izmjenjivač iona primjenjiv za uklanjanje teških metala iz otopina. Istraživani su sljedeći reakcijski uvjeti koji utječu na konverziju sulfonacije: vrijeme reakcije, temperatura reakcije te molarni omjer stirena i sumporne kiseline. Prema očekivanjima, vrijeme reakcije povećava konverziju. Iskoristivost reakcije također raste s povišenjem temperature uljne kupke. Molarni omjer ima važnu ulogu i sulfonacija se javlja pri molarnom omjeru S:H₂SO₄ 1:1, a konverzija reakcije raste s povećanjem molarnog omjera. Konverzija reakcije uz korištenje čiste sumporne kiseline bila je znatno jača u usporedbi s konverzijom s pomoću komercijalne sumporne kiseline. Osim toga uzorci polistirena ozračivani su gama-zrakama prije sulfonacije. Zamijećeno je da ozračeni uzorci postižu viši

stupanj sulfonacije. Sposobnost sulfoniranog polistirena da preuzima neke otrovne metalne ione procijenjena je prema omjeru sulfonacije: Cu²⁺, Co²⁺, Ni²⁺, Cr³⁺.

Introduction

Global world production of plastics rose in the last decades from 204 M tons in 2002 to 288 M tons in 2012 (about 41%).¹ Polystyrene(PS), which is one of the most six common types of plastics, forms 7.3% of this production.² Polymer waste can be generally modified / treated differently depending on the chemical structure of the backbone chain. Polyesters or polyamides can be treated chemically in order to obtain valuable raw materials, which might account for different applications.³⁻⁷ Polystyrene, which is the subject of this work, has been recycled chemically in many ways. For instance, styrene and styrene dimer, trimer and oligomer were recovered from polystyrene by thermo-chemical treatment⁸ and by catalytic thermo-chemical treatment.⁹

Functionalizing of the benzene ring, which is a characteristic segment of the PS, supports the formation of new polymer derivatives having different behaviour and applications.¹⁰ Sulphonate group is one of these functions, and the sulphonation reaction has been studied by many researchers. Most of these studies have used sulphuric acid as sulphonating agent but they have dissolved polystyrene in many solvents¹¹ like halogenated hydrocarbon in order to carry on the reaction homogeneously¹²⁻¹⁷ while other studies have used silica sulphuric acid as sulphonating agent.¹⁷

Bekri-Abbes sulphonated the polystyrene waste, which consists of white coffee cups by sulphuric acid with a ratio PS : H₂SO₄ 1gr : 20mL (molar ratio was 1:36 styrene(St): H₂SO₄) then he used the sulphonated polystyrene to reduce the hardness of water.¹¹

The present work reports on the use of commercial sulphuric acid produced by the Syrian corporation for fertilizer production for the sulphonation of expanded polystyrene waste which is used in packaging stuff; then it was compared with pure sulphuric acid. The influence of the main three reaction conditions with commercial acid has been studied i.e. temperature, reaction time, and the molar ratio. Furthermore, polystyrene waste was irradiated before sulphonation to follow up any increase in the sulphonation ratio. Goulas et al. reported that the terms of mechanical strength of PS was slightly affected after 30 kGy,¹⁸ and also after 100 kGy.¹⁷

Experimental

Expanded polystyrene waste;

Commercial sodium hydroxide (*Niko Chem*, Volgograd, Russia);

Commercial sulphuric acid obtained from the *Syrian Company for Production of Fertilizers*.

Expanded polystyrene waste (PS) which is used in packaging was grated, and then heated at 100°C for two hours to reduce its volume. One gram of grated PS waste powder was placed with H₂SO₄ into a flask, and the flask was heated in oil bath (silicon oil) for desired time intervals. When the reaction was completed, the product was washed 3-4 times with 100 ml distilled water then filtered and washed with diluted solution of

sodium bicarbonate to ensure the removal of residual sulphuric acid. The ion exchange capacity (IEC) of the sulphonated polymer, expressed in meq g⁻¹, was determined by back-titration; titration of excess NaOH with standard hydrochloric acid solution of known normality.

The sulphonation degree, DS, is defined as the ratio of the moles of sulphonated PS units, N_{SPS} , to that of the total moles of sulphonated PS and un-sulphonated units of PS, N_{PS} , such that,

$$DS\% = \frac{N_{SPS}}{N_{SPS} + N_{PS}} \times 100$$

N_{SPS} was obtained from the IEC, such that

$$N_{SPS} = 10^{-3} \times W \times IEC$$

and N_{PS} from the expression,

$$N_{PS} = \frac{W - (M_{SPS} \times N_{SPS})}{M_{PS}}$$

where W was the polymer dried weight in g, M_{SPS} and M_{PS} were the molecular weights of the repeat units of sulphonated PS and PS, (183 and 102 g, respectively).¹⁹

Due to ion uptake, dry sulphonated PS was transferred into solutions of metal sulphate with a concentration of 1,000 ppm. The concentration of the solution was measured using a double-beam UV-VIS spectrophotometer (*Shimadzu*, type UV-1601). Solvated ions show an absorption band in visible range, or indicators/dyes might be added to get maximum adsorption. A calibration curve has been recorded as it is known in chemistry for every element; then the rest of ions retained in the solution were measured. The difference is the amount which was adsorbed by the prepared polystyrene sulphonates.

Results and discussion

The sulphonation of PS: the effect of experimental condition

The sulphonation of PS proceeds in concentrated sulphuric acid (96%) at high temperature to yield somewhat degraded but also crosslinked (due to sulphone formation) and colored products. In the absence of catalyst, the reaction proceeds rather slowly to yield an inhomogeneous, elastic gel, and if coarse, granular material is used, the particles are quickly coated with a gelatinous material, many coalesce, and an intractable mass is formed. Other conditions that would affect the sulphonation reactions are detailed in the following sections. The sulphonation reaction was followed by Fourier Transform Infrared (FTIR) Spectroscopy. Figure 1 shows the FTIR spectra of PS and SPS, from which changes in the structures of PS on sulphonation were deduced. These corresponded with the appearance of new absorption bands and the splitting of others, consistent with the presence of -SO₃H group on the aromatic ring. New absorption bands at 3,340, 1,250, and 1,078 cm⁻¹ were assigned to the stretching of the -OH in the -SO₃H group and to the asymmetric and symmetric stretching of the O=S=O group, respectively.

Effect of reaction temperature / Utjecaj temperature reakcije

Figure 2 represents the conversion of the PS sulphonation versus the temperature of the oil bath; other reaction conditions were kept constant as indicated. It can be seen that below the temperature of 100°C, the reaction was very slow, which may be attributed to the presence of water. Above the temperature of 110°C the sulphonation increases with the increase of the oil bath temperature.

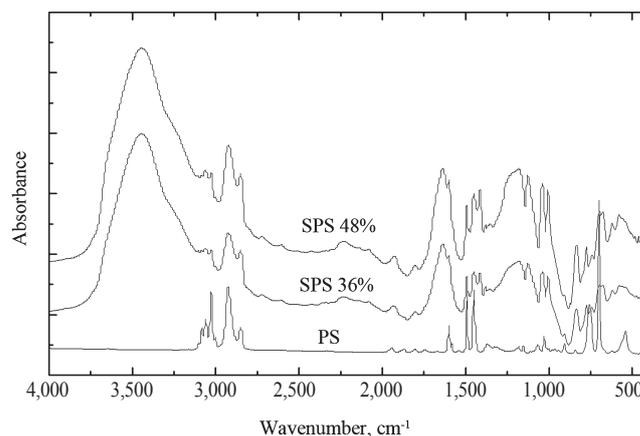


FIGURE 1 – IR spectra of polystyrene (PS) and sulphonated polystyrene (SPS)

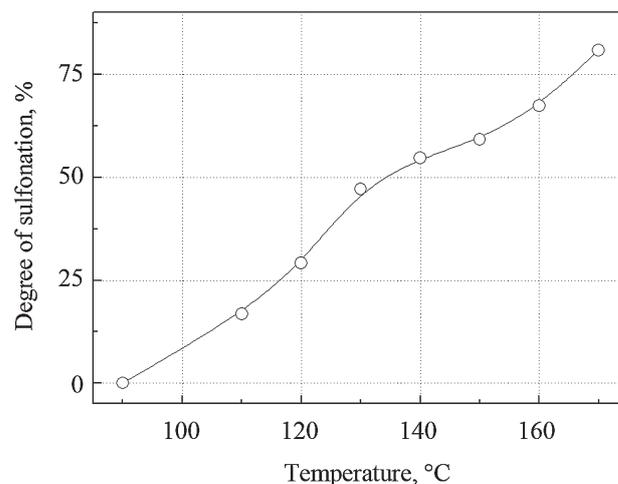


FIGURE 2 – Sulphonation conversion versus the temperature of the oil bath; molar ratio 1:2 St: H₂SO₄(1g:1.1mL); reaction time 1.5 h

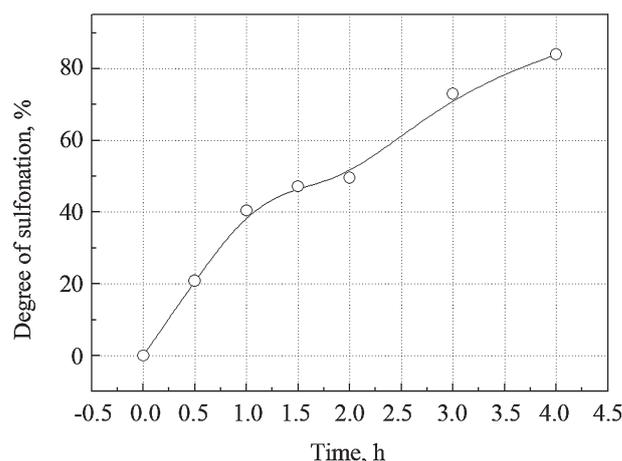


FIGURE 3 – PS sulphonation versus the reaction time, the reaction parameters are: the temperature of the oil bath 130°C; molar ratio 1:2, St: H₂SO₄ (1g : 1.1mL)

Effect of reaction time

Figure 3 shows the conversion of the PS sulphonation versus the reaction time, while other reaction conditions were kept constant as indicated. It can be seen clearly that the sulphonation yield increases with longer reaction time as expected; it rises rapidly to 40% in the first hour. Almost 5 hours were needed to achieve a complete conversion, but the colour of the

product became brownish to black indicating the oxidation of the polymer. The rapid increase in sulphonation degree during the first hour indicates that the reaction was not diffusion controlled. This may be attributed to the fact that PS was present in the rubbery state (its glass transition temperature above 100°C) which has a positive effect on the sulphonation reaction.

Effect of molar ratio

The conversion of the PS sulphonation is illustrated in Figure 4 with respect to the molar ratio H_2SO_4 : St. Other reaction conditions were constant as indicated. The graph shows that the sulphonation conversion increases with higher molar ratio of H_2SO_4 . This is due to the increase in the activity of sulphuric acid which is proportional to its concentration. The results suggest the use of a molar ratio of 1:3.5 St: H_2SO_4 (1g : 1.1mL) for the sulphonation reaction.

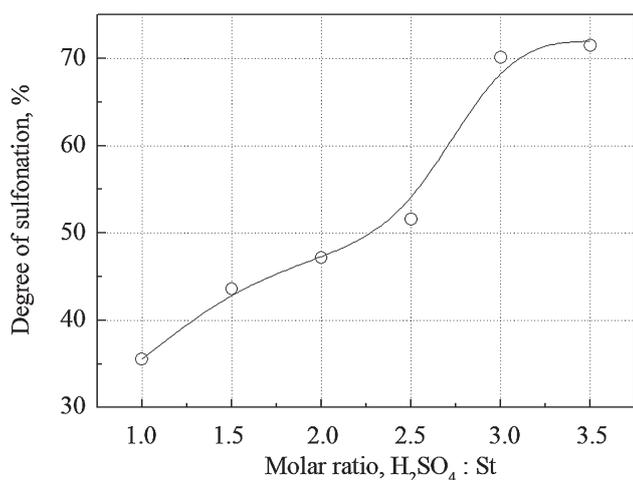


FIGURE 4 – PS sulphonation versus molar ratio; other reaction parameters were: reaction time = 1.5 h; temperature of the oil bath = 130°C

Effect of Gamma irradiation

PS samples were irradiated prior to sulphonation, using a Russian⁶⁰Co gamma facility (Type *ROBO*) for absorbed doses of 100, 300 and 500 kGy at a dose rate of 10 kGy/h. Figure 5 shows the conversion of the sulphonation reaction with respect to the radiation dose. The polymer was

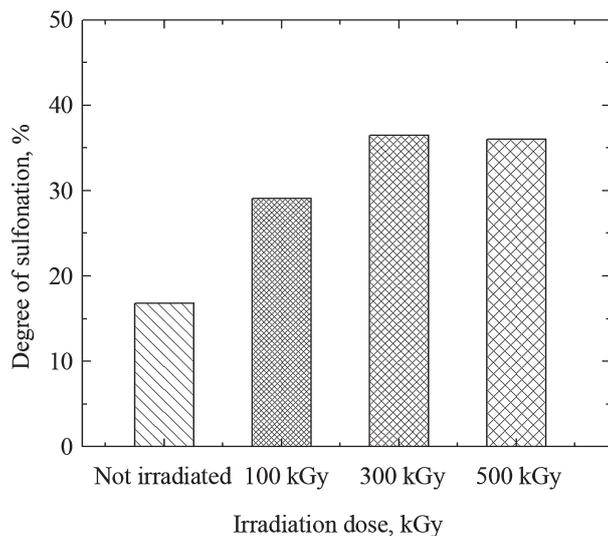


FIGURE 5 – Conversion of PS sulphonation for three gamma irradiated samples for 100, 300, 500 kGy. The conditions of sulphonation reaction were: molar ratio = 1:2 Styrene: H_2SO_4 (1g:1.1ml); reaction time = 1.5 h.; temperature of the oil bath = 110°C

sulphonated under the following conditions: molar ratio was 1:2 Styrene : H_2SO_4 (1g : 1.1ml); reaction time was 1.5 h; the temperature of the oil bath was 110°C.

It can be noticed that the irradiation of polystyrene waste before sulphonation has a good effect on the sulphonation reaction. It is known that the exposure of plastic materials to ionizing radiation leads to the building of radicals, which could enhance the sulphonation reaction. It can also be observed that the increase in the irradiation dose from 300 kGy to 500 kGy does not show a significant effect.

The end groups such as hydroxyl introduced by irradiation increases the yield of sulphonation of the irradiated PS compared with the original materials. This is consistent with other reported study of irradiated PEEK sulphonation. The decrease in the sulphonation yield above 300 kGy may be attributed to the increasing number of crosslinks and the further constraint introduced to the structure of PS for the diffusion of sulphuric acid molecules.²⁰⁻²¹

Effect of acid purity

Figure 6 shows the conversion of the PS sulphonation using commercial and pure sulphuric acid. The conditions of sulphonation reaction were: molar ratio was 1:2, St.: H_2SO_4 (1g : 1.1mL); reaction time was 1.5 h; the temperature of the oil bath was 110°C. It can be seen that the use of pure acid does not show a big difference in the sulphonation conversion of PS compared with the commercial acid; this result suggests the use of the commercial sulphuric acid because of its very low price.

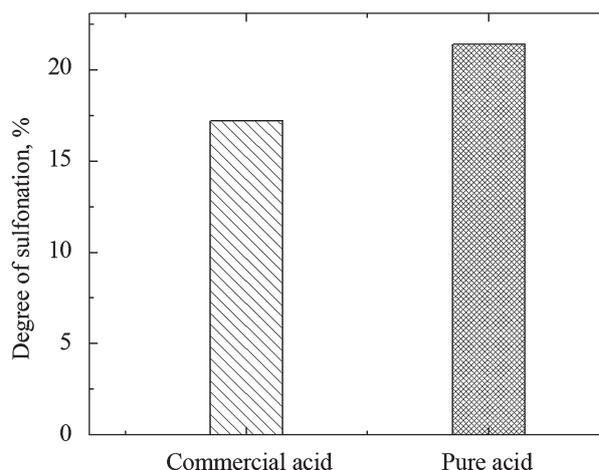


FIGURE 6 – Conversion of PS sulphonation by commercial and pure sulphuric acid. The conditions of sulphonation reaction were: molar ratio = 1:2 Styrene: H_2SO_4 (1g:1.1mL); reaction time was = h; temperature of the oil bath = 110°C

Removal of Cu^{2+} , Co^{2+} , Ni^{2+} , Cr^{3+} ions

The ability of the sulphonated PS waste has been investigated. Figure 7 represents the uptake / removal of some metal ions with regard to the sulphonation ratio: Cu^{2+} , Co^{2+} , Ni^{2+} , Cr^{3+} .

The sulphonated PS samples in their sodium salt form were mashed in distilled water for three hours, then they were transferred to a solution of Cu^{2+} of known concentration for 24 hours. Then the solution was completed to 25 ml and the rest concentration of the metal ion in the solution was measured in order to calculate the ions uptake. The procedure was repeated for each of the other ions (Co, Cr, Ni). Figure 6 illustrates the ion uptake with regard to the sulphonation ratio. It is obvious that the ion uptake rises with increasing the sulphonation ratio. Furthermore, it is clear that the samples with a sulphonation degree of 47% demonstrate the highest uptake of the metal ions and consequently the removal efficiency.

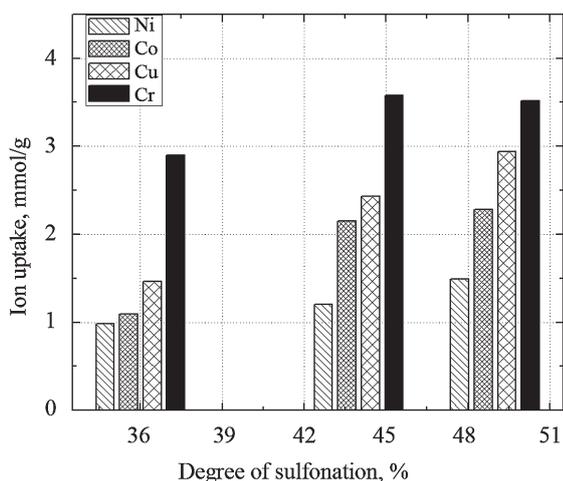


FIGURE 7 – Ion uptake vs. sulfonation degree

Conclusion

Expanded polystyrene waste has been sulfonated successfully using commercial sulphuric acid. The use of commercial acid reveals a lower reaction conversion compared with pure sulphuric acid but the price of the commercial acid overcomes the difference of the conversion. The reaction conditions of the sulfonation were optimized such as: reaction time, reaction temperature and molar ratio of styrene : sulphuric acid.

The gamma irradiation of polystyrene waste before sulfonation leads to higher sulfonation yield up to 300 kGy.

The modified polystyrene waste demonstrated good ability to remove some metal ions from contaminated waters: Cu^{2+} , Co^{2+} , Ni^{2+} , Cr^{3+} .

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