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Analytical, Optical, and Thermal Study of Sulphonated Polystyrene Prepared from Some Industrial Polystyrene Waste

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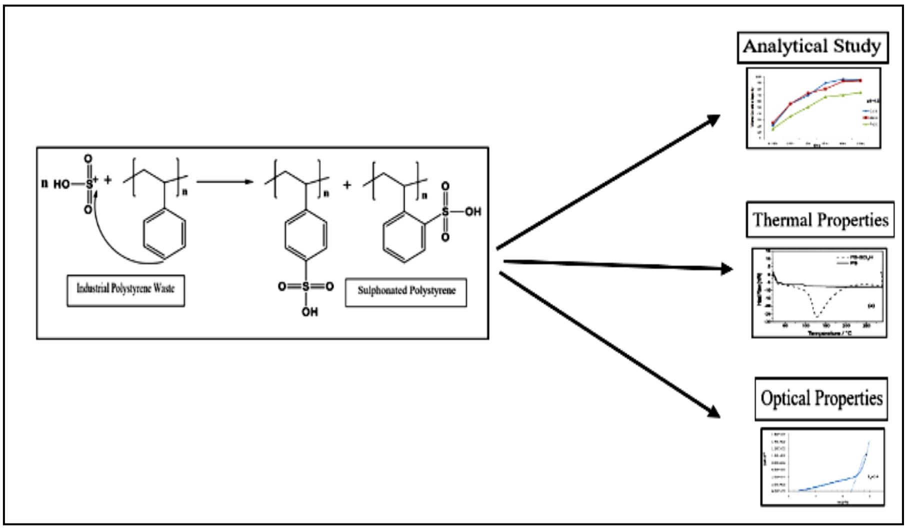
ABSTRACT

In this study sulfonated polystyrene (SPS) was prepared from some industrial waste polystyrene (PS). The degree of sulfonated and molecular weight were determined. An analytical study was evaluated for SPS to determine the efficiency of chelating some ions (Zn, Cu, and Pb). The binding capacity of the sulfonated PS toward metal ions was studied in different pH (2.5, 4.5, and 6.5) under continuous shaking for affixed time of 6 hours at laboratory temperature. Optical properties studied for this polymer and energy gap values culcalet of the polymer. Finally, some thermal parameter was calculated from the TGA thermogram to evaluate thermal stability of these polymers.

GRAPHICALABSTRACT



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Introduction

Heavy metal removal, heterogeneous catalysis, solid electrolytes, ion exchange membranes, ion-selective electrodes, and industrial waste purification are just a few applications for synthetic chelating ion exchange resins [1]. Chelating resins are an effective treatment for selective metal adsorption. The recovery of valuable compounds from industrial waste benefits both the economy and the environment [2]. Polystyrene (PS) waste chemical recycling is critical for the environment. One method for modifying the original chemical and physical properties of waste PS is sulfonation. The product with a low sulfonation degree can be used as membranes in fuel cells, a modern source of energy, to separate electrodes, and conduct protons. Sulfonation can also result in crosslinked and water-absorbing polymers that can be used as ion-exchange resins [3]. Ion exchange resins are widely used in separation, purification, and decontamination processes. Cross linking decreases the resin's ion-exchange capacity and lengthens the time required to complete the ion-exchange processes while increasing the resin's robustness. Specialized ion-exchange resins include chelating resins. Anion and cation resins are the two most common resins used in the ion exchange process. Cation-exchange resins replace cations with positively charged hydrogen ions, whereas anion-exchange resins replace anions with hydroxyls (negatively charged ions). When a solution containing magnesium and calcium ions comes into contact with the resin, the magnesium and calcium ions migrate preferentially out of the solution to the active sites on the resin, where they are replaced by sodium ions [3].

By washing the resin with a solution that has dissolved sodium ions in it at a high concentration, the resin can be recharged. Ion-exchange resins can be used, for example, to filter out heavy metals and toxic ions from contaminated water [4].

Heavy metal pollution may be linked to industrial processes such as ore smelting or metal refining, both of which transfer metals into the atmosphere, water, and soil. Heavy metals like copper, lead, and mercury are extremely dangerous.

Because cadmium and mercury are thought to be non-biodegradable and as a result accumulate in people and other living things, they can eventually lead to various health problems and illnesses [5-10].

Sulfonated polymers and copolymers are reportedly employed in severalapplications such as fuel cell membrane [11-13]. In continuation of our previous work, we want to make use of the plentiful polystyrene trash in an eco-friendly and cost-effective manner. As a result, the study will use sulphonated polystyrene, which is made from leftover industrial polymers, to chelate some divalent ions.

Materials and Methods

Material used

All the chemical and solvent used were of analytical grade, fuming sulphuric acid, chloroform, sodium hydroxide pellets, acetone, copper nitrate, lead nitrate, and zinc nitrate, while the polystyrene used was a waste of some industrial polystyrene.

FTIR spectrometer

The infrared spectra were obtained by Bruker, FTIR spectrum one using universal ATR sampling accessory (4000-500 cm^{-1}) as KBr disk.

ThermogravemetricAnalysis (TGA)

Approximately 10 mg of each sample was added to the ceramic crucible and heated from 30-700°C, at a heating rate of 10°C per min. in hydrogen atmosphere at a flow rate of 20 ml per min. (Aperkin-Elmer STA 6000) simultaneous thermal analyser.

Synthesis of Sulphonated Polystyrene

Typically, 20 g of waste polystyrene was heated in a vacuum oven at 100 °C to dry it, and then it was dissolved in 500 mL of chloroform with fuming sulfuric acid at room temperature while being vigorously stirred for 1 to 4 hours. The polymer solution was decanted into a considerable excess of ice-cold water while being mechanically stirred to stop the sulphonation reaction.The pH of polymer precipitate was neutralized by filtering and many washes with distilled water. The polymer was then dried for 8 hours at 25 to 50 °C under a vacuum. Titration was used to determine the degree of sulphonation; 1-2 g of sulphonated polystyrene was added to 0.5 M aqueous sodium hydroxide and left for 1 day. Back titrating the solution with 0.5 M hydrochloric acid while using phenolphthalein as an indication.

Results and Discussion

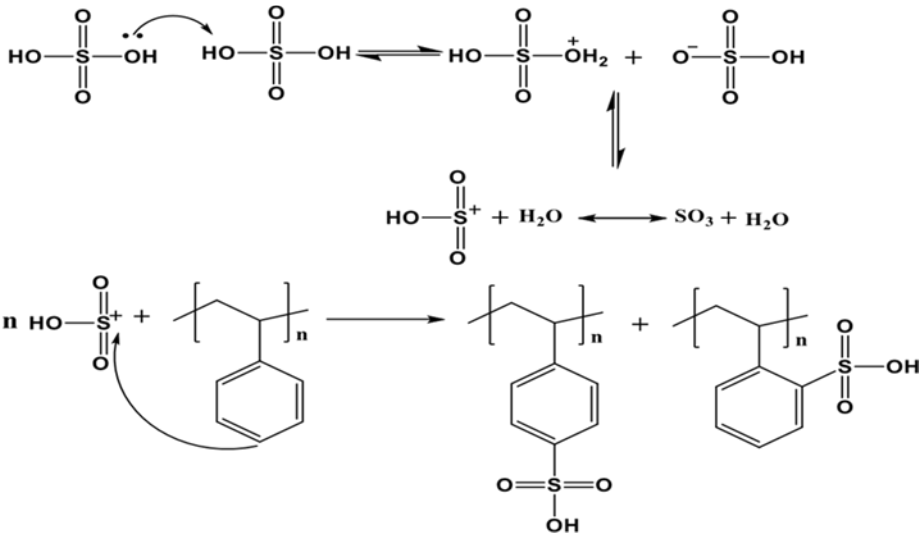
Sulphonation process

The molar ratio of polymer to the sulphonating agent has varied multiple times during the sulphonation process. The pathway of the sulfonation reaction towards the aromatic compound-containing polystyrene was expressed in Scheme 1. Three different sulfonated polystyrene (PSS1, PSS2, and PSS3) were made, and Table 1 lists the reaction conditions.

The value of the sulfonation degree will change as a result of the increase in SO_3H. According to viscosity measurments, the molecular weight of PSS2, the chelating polymer utilized in this work, was determined to be 9.1 × 10^4 $g.mol^{-1}$.

FTIR study

The sulphonation product was investigated using FTIR spectroscopy. Figure 1's spectrum demonstrates the typical peak at 1180 cm^{-1}, associated with SO_2's stretching vibration, which is a solid sign of sulphonation processes. In addition, further absorption bands at 3417 and 1068 cm^{-1}, respectively, wetre caused by the stretching of the O=S=O group and the vibration of the hydroxyl groups [14].



Scheme 1: Pathway of sulfonation reaction of polystyrene

Table 1: Degree of sulphonation products

Product	Temperature (°C)	Sulphuric acid Wt %	Degree of Sulfonation
PSS1	25-30°C	5.0	35.07
PSS2	25-30°C	10	42.12
PSS3	25-30°C	15	48.71

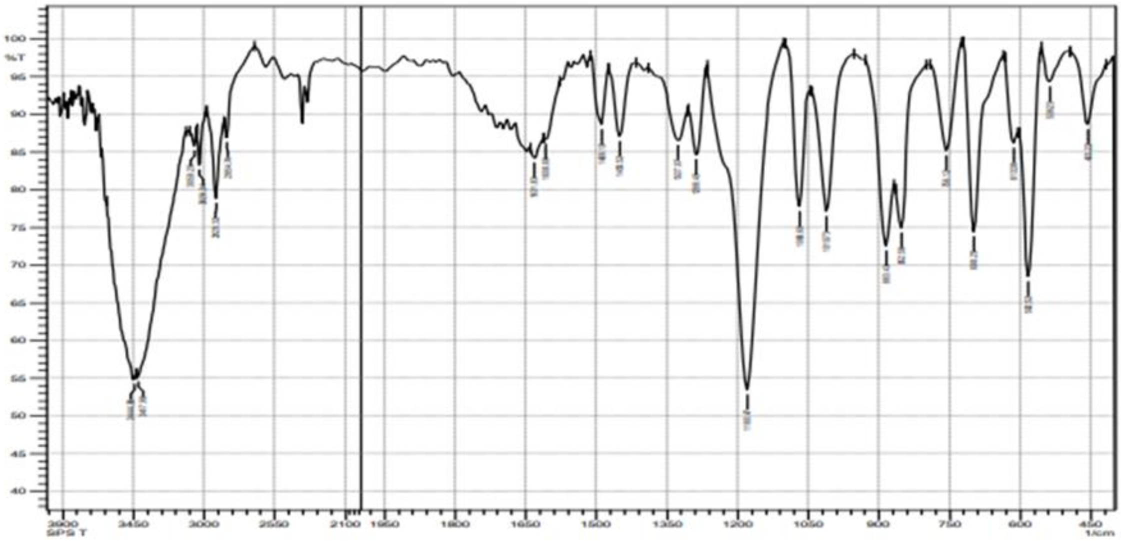


Figure 1: FTIR of PSS1

Thermal properties study

Using TGA, the thermal stability of PS and PS that has been sulfonated was investigated. According to this investigation, sulfonated PS exhibits less thermal stability than PS as a function of the concentration of sulfonic groups. The weight loss process is depicted in pure PS as beginning at 350°C At 200°C, sulfonated PS exhibits a weight decrease (Figure 2). The breakdown of sulfonated PS in a single step is well-depicted in Figure 3.

The DSC curves for polystyrene and sulfonated polystyrene are displayed in Figure 4. The glass transition temperature of polystyrene was 98 °C, while for sulfonated polystyrene, it was 138 °C. On the other hand, C_P for polystyrene was 1.17j /g.C^{-1}, while for sulfonated polystyrene was 0.87 J/g.C^{-1}. This behavior indicate that the sulfonated polystyrene was amorphous polymers and the presence of sulfonic group increase the structural rigidity of the materials [15].

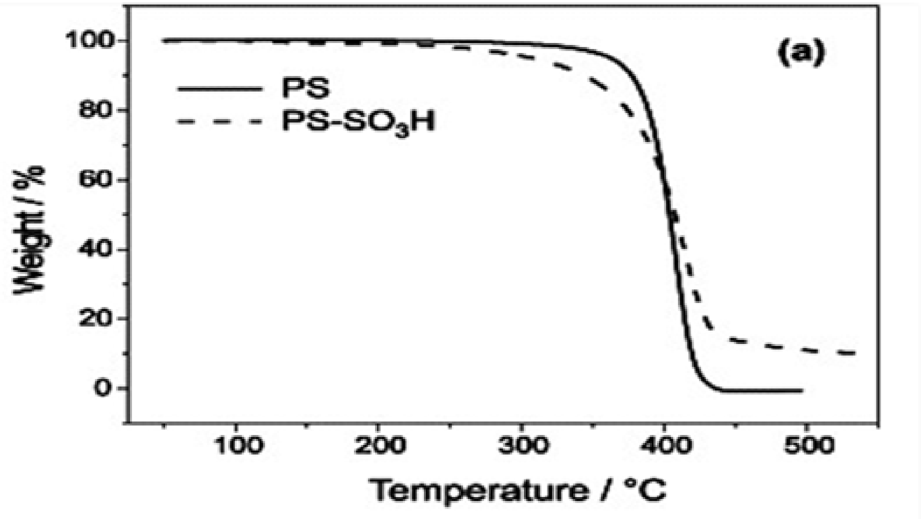


Figure 2: TGA thermogram of polystyrene and sulfonated polystyrene

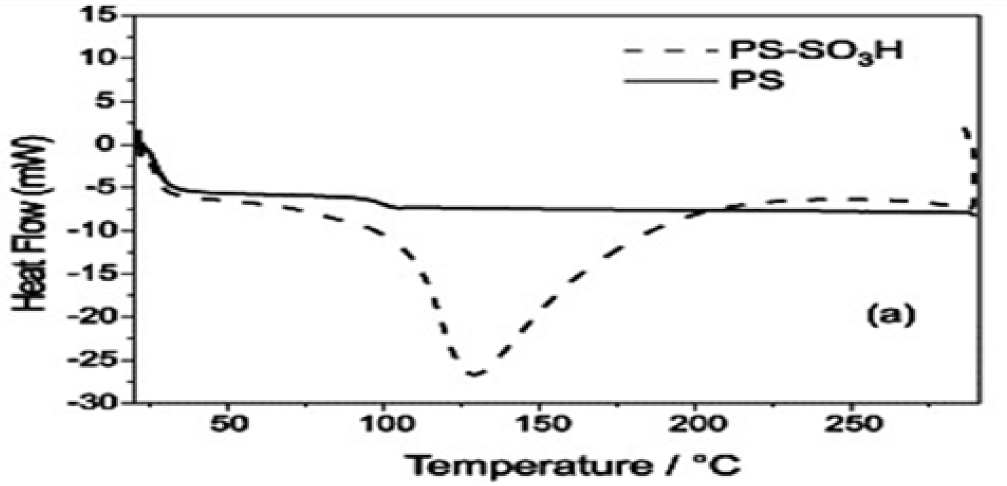


Figure 3: DSC thermogram of polystyrene and sulfonated polystyrene

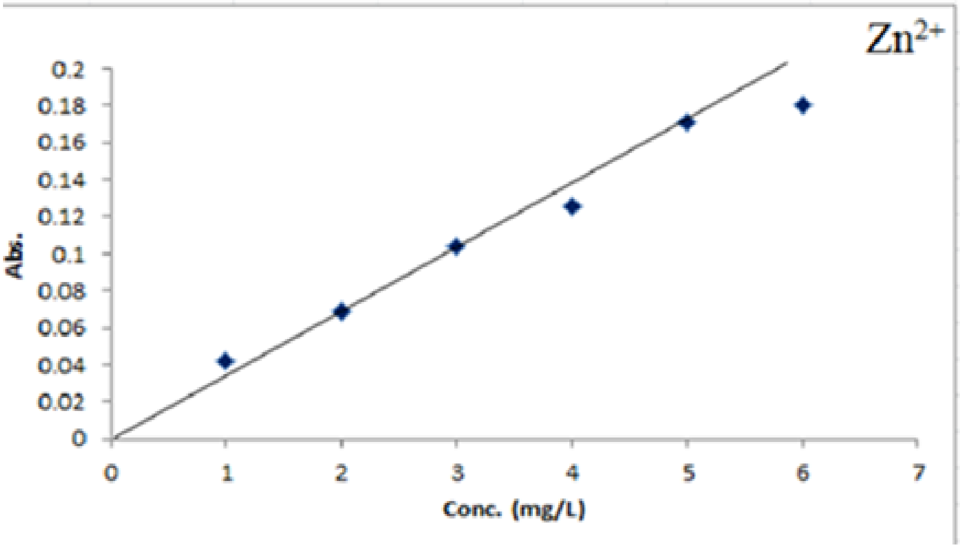


Figure 4: The calibration curve for Zn(II)

Evaluation of Chelating SPS

The metalsorption capacity of PSS was study by using the solution containing (100 ppm) of Zn^{2+}, Cu^{2+} and Pb^{2+} as nitrate salts. The batch method used in this study by treating (0.1 g) of sulfonated PS with 10 mL solution ions at different pH (2.5, 4, 5, and 6.5) and shaking time (15 min, 30 min, 1 h, 3 hrs., 6 hrs, and 24 hrs.).

The pH was adjusted by adding HCl (0.1 M) or NaOH (0.1 M) using pH meter. The atomic absorption spectrophotometer model (AI-1200) was used to determine the initial and final metal ions concentration in the solution. Metal sorption capacity was calculated by using this equation, % Metal sorption capacity in (mg ions/ g polymer) = (C_i-C_f) V/ W (%), where C_i and C_f are initial and final concentration, respectively, V refer to the volume of the solution, while W was the weight of polymer. The standard calibration curve for each ion was constructed by measuring the absorbance for a series of metals ions concentrations i.e. (1, 2, 3, 4, 5, 6, 7, and 8 ppm) of standard solution for each metal ion. These were illustrated in Figures 4, 5 and 6.

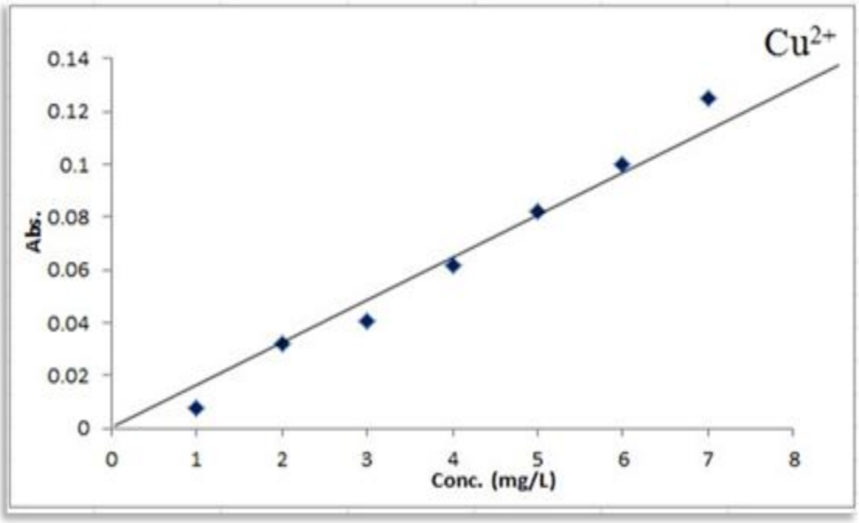


Figure 5: The calibration curve for Cu (II)

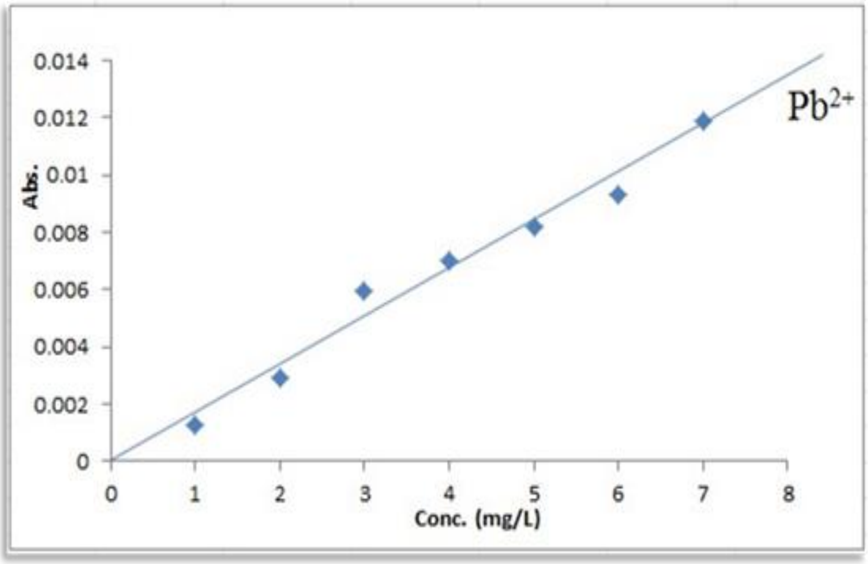


Figure 6: The calibration curve for Pb(II)

Effect of time on metal sorption

The factor of contact time is important in esteeming the adsorption ability, which assistances the rate of maximum removal of solutes [16]. The sorption of various divalent metal ions (Cu , Zn, and Pb) on sulfonated PS was studied as a function of contact time. The results were shown in Figures 7, 8 and 9. The result indicate that the loading capacity was increased by increasing time and a steady state was reached within 6-24 hours. According to multiple studies [14, 15], the type of active sites in the polymers, the number of repeating units, and structural characteristics of the polymers like (porosity, surface area, size, and molar mass) have an impact on the adsorption of metals in various chelating polymers. Likewise, the metal ion concentration and the separated mixture. The metals behave in this steady-state uptake from polymer in the following order: Cu ion > Zn > Pb, i.e. the polymer has the largest capacity for uptake of Cu ions and the lowest for Pb ions. The adverse steric effect on coordination with the chelat group in the polymer can be used to explain this outcome. The result of metal sorption capacity are presented in Tables 2, 3 and 4.

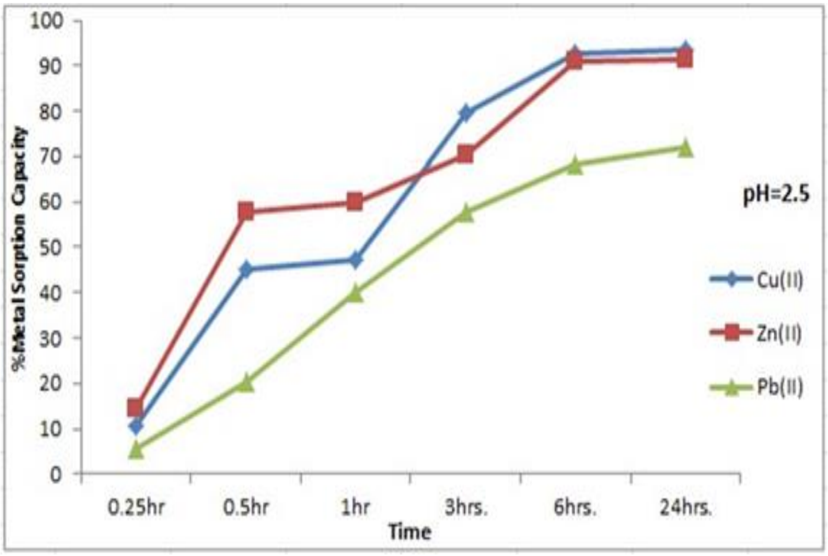


Figure 7: Percentage of metal sorption capacity at pH 2.5 by resin as a function of contact time

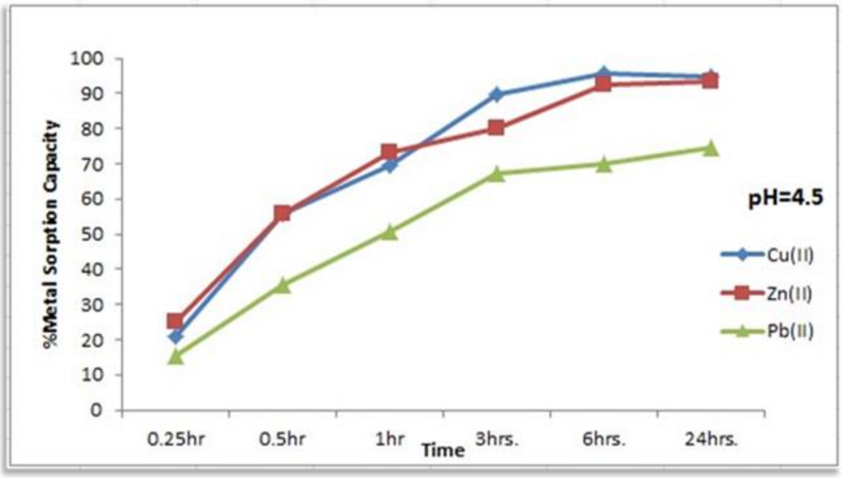


Figure 8: Percentage of metal sorption capacity at pH 4.5 by resin as a function of contact time

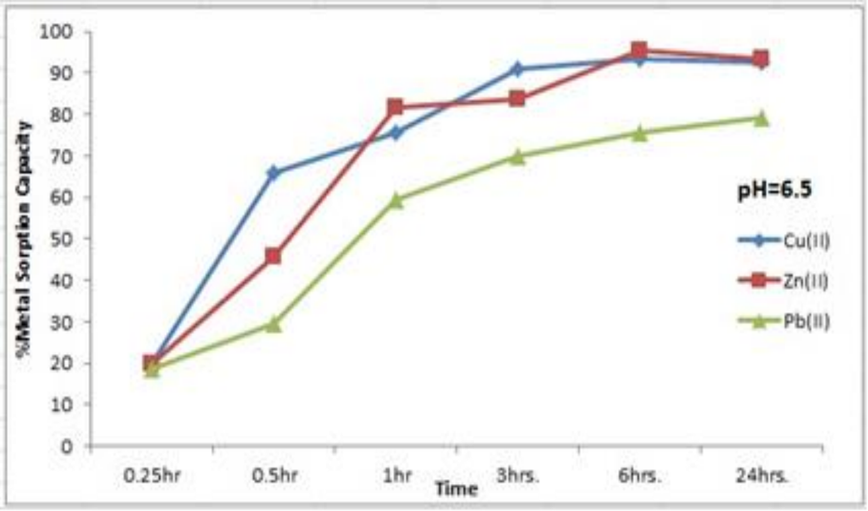


Figure 9: Percentage of metal sorption capacity at pH 6.5 by resin as a function of contact time

Table 2: The capacity of metal sorption at pH 2.5

% Metal sorption capacity						pH=2.5
24 hrs	6 hrs.	3 hrs.	1 hr	0.5 hr	0.25 hr	Ions
93.7	92.5	79.6	47.2	45.3	10.5	Cu(II)
91.5	91.2	70.3	59.8	57.8	14.3	Zn(II)
72.1	68.2	57.9	40.2	20.5	5.73	Pb(II)

Table 3: The capacity of metal sorption at pH 4.5

% Metal sorption capacity						pH=4.5
24 hrs.	6 hrs.	3 hrs.	1 hr.	0.5 hr	0.25 hr	Ions
94.7	95.5	89.6	69.5	55.6	20.7	Cu(II)
93.5	92.4	80.3	73.2	55.8	24.9	Zn(II)
74.6	70.2	67.3	50.6	35.5	15.3	Pb(II)

Table 4: The capacity of metal sorption at pH 6.5

% Metal sorption capacity						pH=4.5
24 hrs.	6 hrs.	3 hrs.	1hr	0.5 hr.	0.25hr	Ions
92.7	93.4	91.2	75.8	65.9	19.9	Cu(II)
93.6	95.3	83.9	81.8	45.9	19.9	Zn(II)
79.4	75.5	69.9	59.5	29.4	18.6	Pb(II)

Effect of pH on metal sorption

The binding capability of the sulfonated PS toward metal ions was investigated at various pH values (2.5, 4.5, and 6.5) with constant shaking for a predetermined period of 6 hours at room temperature. Figure 10 displays typical pH-binding capacity profiles. The outcome demonstrated that when the medium's pH value increased, so did the metal sorption capacity. This behavior can be explained by the weak acid nature of the sulfonated groups presented at the polymer's chain and by the protonation, which has a significant negative impact on the polymer's propensity to bind ions.

Optical properties study of SPS

Scientists and engineers of all disciplines have been interested in studying optical properties, as this study effectively helps in understanding and evaluating the properties of materials in an accurate manner, and knowledge of these properties contributes to helping to activate them by designing devices with high specifications and excellent accuracy, and optical constants are among the most important of those optical properties. One of the important factors affecting the optical properties of thin film is the materials from which the film is made, its thickness and the condition surrounding the preparation of the film on a substrate of glass, quartz, or other materials depending on the nature of study [17, 18]. In this study thin film of SPS was prepared by dissolving the polymer in dichloromethane and then spin coating on the glass substrate to form a homogeneous thin film. The UV-Visible spectrum of SPS was done in the range (200-900) nm, and the spectrum was depicted in Figure 11.

On the other hand, the absorption coefficient was calculated by Equation (1), and drawn as a function of the energy of the photon. Figure 12 shows this relationship.

$$\alpha = 2.303(A|t) \qquad (1)$$

Where, α is the absorption coefficient, A is the absorption, and t is the polymer film thickness in cm.

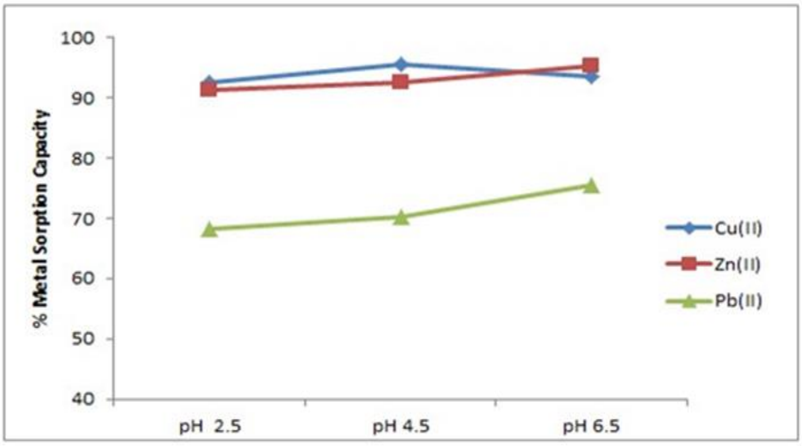


Figure 10: Percentage of metal sorption capacity by resin as a function of pH

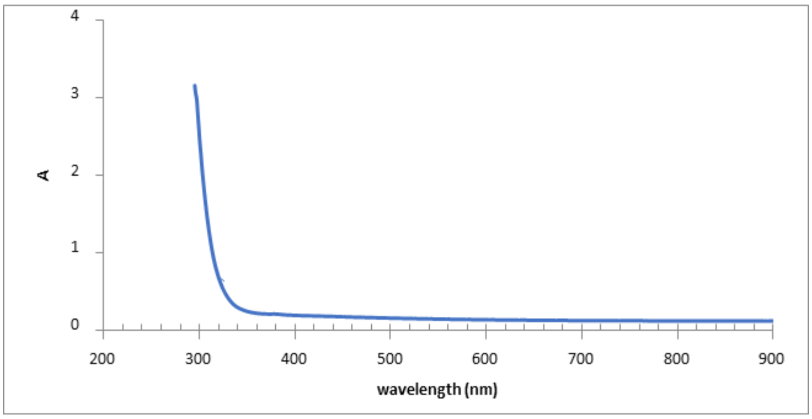


Figure 11: UV-Visible spectrum of SPS thin film

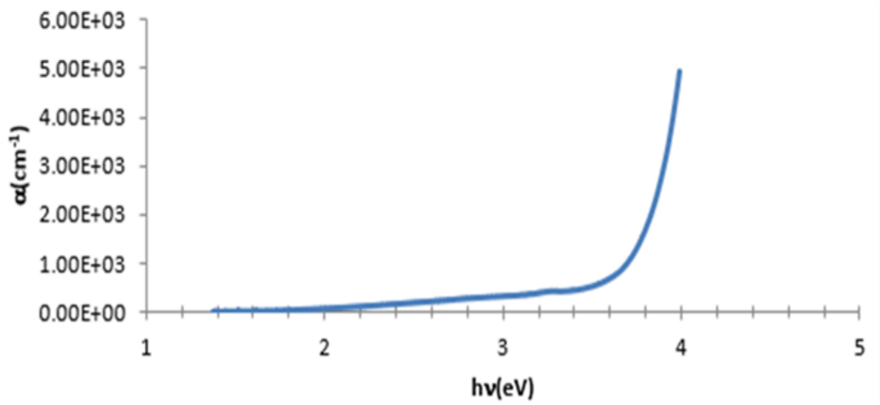


Figure 12: Absorption coefficient as a function of photon energy

Likwise, from this study, the optical energy gap was calculated based on the value of the absorption coefficient according to the equation of indirect electronic transitions, and by drawing the relationship between 1/2 (αhv) in terms of the photon shot, we find that the tangent to the straight part of the curve cuts the photon energy axis at αhv) 1\2 = 0)] and this represents the energy gap of SPS value of the indirect electronic transition. As demonstrated in Figure 13, the Eg was 3.4 which is less than the energy gap values of the polymer before the sulfonation process, due to the presence of the (SO_3H^-) group along the backbone of the polymeric chains that increase the hydrophilicity which adds a kind of polarity (polarly charged) [19].

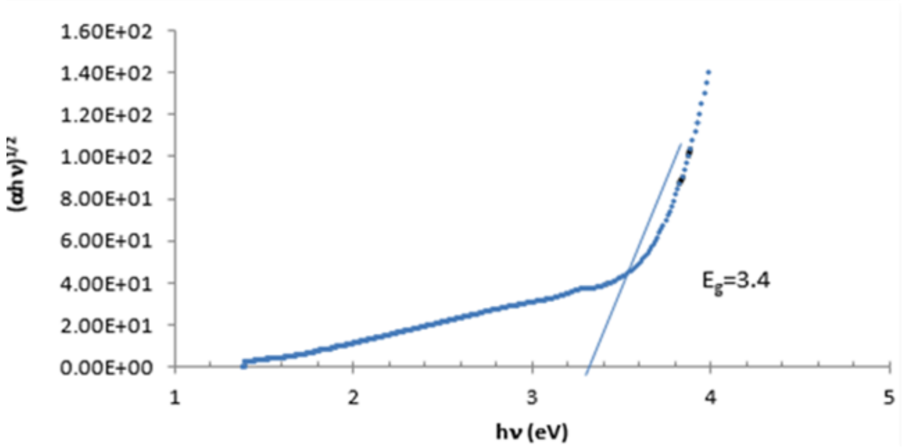


Figure 13: Energy gap for indirect electronic transition of SPS

Conclusion

Sulfonation of polystyrene was carried out and characterized by FTIR and TGA. The FTIR spectra sulfonated PS containing a functional groups of *o*-SO_3H and *p*-SO_3H. This polymer was used as chelating polymer for some divalent ions (Zn, Cu, and Pb) using a batch process, the results indicate the good ability of this resin towards ions. On the other hand, thermal properties of this resin were studied using TGA and DSC, the result shown from the DSC thermogram the T_g of the sulfonated PS was 138 °C compared with PS alone 98°C, while the TGA thermogram showed that the decomposition temperature of sulfonated PS was more than 350 °C. The addition of sulfonate groups to the prepared polymer improved its optical properties by increasing the polarity.

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Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

We have no conflicts of interest to disclose.

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