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Development of New Sulphonyl Resin from Modification of Commercial Resin

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Summary

This article deals with the handy synthesis of sulfonyl resins, which were produced by the treatment of a commercial sulfonic resin (Lewatit VPOC1812®) based at divinylbenzene (DVB) and styrene (STY). The preliminary chemical modification was based on the reaction of the Lewatit VPOC1812® with thionyl chloride aiming to produce the sulfonyl chloride groups. The best conditions to obtain the sulfonyl chloride groups were: $SOCl_2/SO_3H$ (molar ratio) = 13 at 79°C during 72 h. The resin chlorinated was afterward treated with urea, thiourea or guanidine. The functionalized resins with urea, thiourea or guanidine were produced with 56, 68 and 93% yield, respectively. The commercial and modified resins were characterized by apparent density, swelling degree, elemental analysis (CHNS), FTIR, optical microscopy (OM) and scanning electron microscopy (SEM).

Introduction

Functionalized cross-linked resins have gained great importance in many fields of scientific research as well as for industrial applications, which go on increasing due to several possibilities of modifications on their chemical and physical properties [1,2]. Polymer sorbents with certain functional groups are able to complex with different metal ions and they are widely used as complex-forming sorbents. The possibility to modify the polymer sorbents binding additional functional groups enlarges the spectrum of their applications [3-6]. Organic and inorganic sorbents functionalized with complexing groups have been developed and reported in the literature [7-10]. Polymers bearing alkyl- or arylsulfonamide sites were so far obtained by two classical procedures: polymerization of the sulfonamide monomers [11-13] or the interaction of the polysulfonylhalogenides with ammonia or amines [14]. The polysulfonylhalogenides can be synthesized from crosslinked benzenosulfonic acid resin with thionyl chloride [15] or polystyrene-divinylbenzene resin with chorosulfonic acid [16]. All the techniques mentioned above involve multistage and sometimes laborious chemical modifications.

This article aims to report a handy methodology to produce two new derivatives of sulfonyl resins (urea or thiourea) as well as a more efficient procedure to obtain the functionalized resin with guanidine. [17].

Experimental part

Materials

Toluene, 1,2-dichloroethane, 1,4-dioxane, chloroform, sodium hydroxide, hydrogen chloride, nitric acid and potassium bromide were purchased from Vetec (Brazilian Co.) with P.A degree. Thionyl chloride (Merck), 1,2-dimetoxiethane (Fluka), guanidine hydrochloride (Acros Organics), urea (Reagen) and thiourea (Reagen) were adquirided with P.A. degree and Lewatit VPOC1812® (Bayer) with commercial degree. All reagents were used as received.

Resin characterizations

The presence of sulfonyl group was evaluated by infrared technique (FTIR – Perkin Elmer 1720x) in KBr pellets. The sulphur contents were measured by elemental analysis (CE Instruments, Mod. EA 1110 CHNS-0). Apparent density and swelling degree were determined using the graduate cylinder method [18]. The morphological characteristics were observed with a stereo optical microscope (Olympus SZ10) with magnification of 40x. Resins were also characterized at scanning electron microscope (Jeol JSM 5800LV). The beads were coated with gold and their external and internal parts were observed using 20 kV acceleration electron beam. The exchange capacities (EC) of the commercial and modified resins were determined by titulometric method using NaOH 0.1N [18].

Preparation of chlorinated sulfonyl resins

For these reactions, the following reagent ratio was employed: sulfonic resin 0.01 mol (2g), thionyl chloride 0.13 mol (10 ml). This procedure was carried out using resin without previous treatment as well as swelled Lewatit VPOC1812® resin with 30 ml of toluene or 1,2-dichloroethane for 24 h. The resin was transferred to a three-necked round bottom reactor (50 ml). This reactor was equipped with reflux condenser, mechanical stirrer and thermometer. Afterwards, thionyl chloride was slowly added under stirring. Latterly, the system was iced and the resins were filtered off using a sintered glass funnel. The resins were washed with chloroform. The reactions conditions (reaction temperature and time) were summarized on Table 1.

Reaction of chlorinated sulfonyl resin with urea or thiourea

For these reactions, the following reagent ratio was employed: 0.01 mol of chlorinated sulfonyl groups, 0.03 mol (1.8g) of urea or 0.03 mol (2.2 g) thiourea as case. Hence, the resin was transferred to a three-necked round bottom reactor (50 ml). This reactor was equipped with reflux condenser, mechanical stirrer and thermometer. The previous heated solution (at $70^{\circ C}$) of urea or thiourea in 1,4-dioxane has added to the reactor. The system was maintained at constant stirring and then heated to 100°C during 24 or 48 h. Latterly, the system was iced and the resins were filtered off using a sintered glass funnel. Finally, the resins were washed with water and dried at 100°C for 24h.

Reaction of chlorinated sulfonyl resin and guanidine

For these reactions, the following reagent ratio was employed: 0.01 mol of chlorinated sulfonyl groups, 0.02 mol (2 g) of guanidine hydrochloride and 50 ml of 1,2-dimethoxyethane. Hence, the resin has transferred to a round bottom reactor (100 ml) containing three-neck equipped with reflux condenser, mechanical stirrer and thermometer. The previous heated solution (at 70°C) of guanidine hydrochloride in 1,2-dimethoxiethane was added to the reactor. The system was kept at constant stirrer. Then the reaction temperature was raised to 85°C during 24 h. Latterly, the system was iced and the resins were filtered off using a sintered glass funnel. The modified beads were washed with water and dried at 100°C for 24h.

Table 1: Experimental condition to chlorination of Lewatit VPOC 1812 with SOCl2

Reaction	T(ºC)	t (h)
R1	27	6
R2	40	6
R3	40	24
R4[a]	reflux	24
R5[b]	reflux	24
R6	reflux	12
R7	reflux	24
R8	reflux	48
R9	reflux	72

a. Swelled with 1,2-dichloroethane; b.Swelled with toluene

Results and discussion

The sulfonic resin named Lewatit VPOC1812® was used in this experiment as a starting material. This resin is based at divinylbenzene (DVB) and styrene (STY) containing -SO_3H groups. The resin sulfonation degree was evaluated by elemental analysis (CHNS) and exchange capacity using acid-base titrations. Both techniques had similar results (5.0 mmol/g and 4.8 mmol/g, respectively).

The swelling degree capacity of commercial resin was conducted using different solvents (Table 2). The determination of swelling degree was conducted using the dried resin at 100°C until the constant weight because the sulfonic resin presented a high percentual of water (90 %).

As it was expected for a gel-like resin with low porosity (microporous), the beads have presented different values of swelling degree. As chloform did not swell the beads this solvent is not appropriated to the next reaction step. In spite of toluene having a partial interaction with aromatic ring of resin, this solvent presented a low swelling degree (40 %) compared to the others. In according to the result, 1,4-dioxane produced an acceptable swelling degree. The swelling degree determination in water was measured focusing the knowledge the resin behavior in this middle, because it can be used to recovery ions of wastewater.

Table 2: Swelling degree of commercial resin Lewatit VPOC1812®

Solvent	Swelling degree (%)
Chloroform	0
Toluene	40
1,2-Dichloroethane	40
1,4-Dioxane	85
Water	120

The physic characteristics of Lewatit VPOC1812® were measured by determination of apparent density using a methodology described at literature [19]. The value obtained was 0.74 g/cm^3 which can be associated to a material with low porosity. This result was confirmed by optical microscopy (Figure 1). The optical micrograph shows that the beads present spherical shape and diaphanous. The almost transparency of beads is a feature of materials with small pores (microporous resin) or gel resin, as these materials do not produce light dispersion [20].

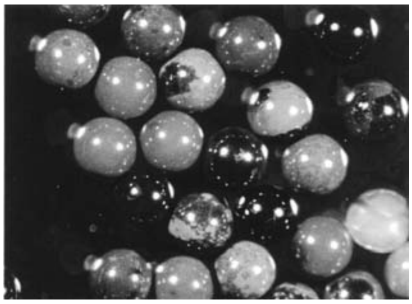

Figure 1: Optical microscopy of Lewatit VPOC1812® resin (magnification 40x)

Figure 2 shows the scanning electronic micrographs of the Lewatit VPOC1812® which confirm the small porosity of material. The micrographs were carried out with magnification of 45x or 13000x, which showed a smooth external surface with small rough (Figure 2b).

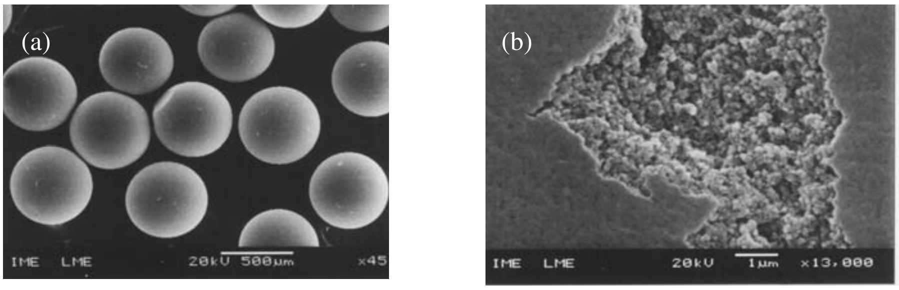

Figure 2: Scanning electronic micrograph (SEM) of internal (a) and external surfaces (b) of beads of commercial resin Lewatit VPOC1812®

The Lewatit VPOC1812® resin was chemically modified according to the general scheme (Figure 3). The first step reaction was the chlorination with $SOCl_2$ of sulfonic resin to obtain the sulfonyl chlorides [21-23]. The second step was the reaction of sulfonyl chloride with different amine derivatives, namely urea, thiourea and guanidine [24].

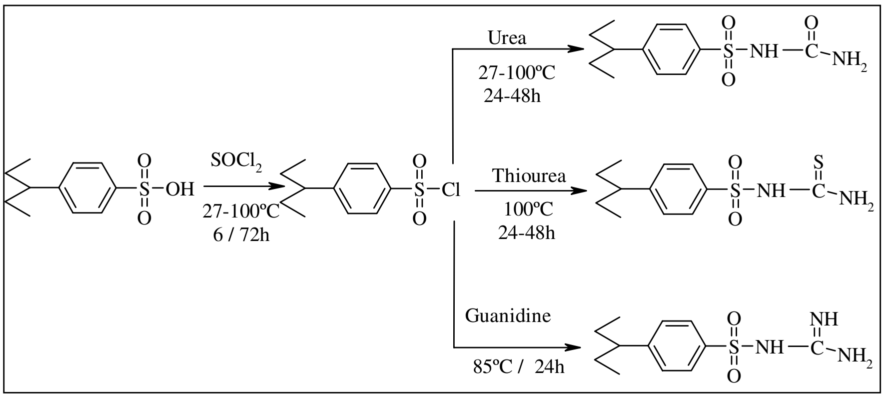

Figure 3: General scheme of reaction sulfonyl chloride with urea, thiourea and guanidine

Initially, the Lewatit VPOC1812® resin without any pre-treatment reacted with thionyl chloride at room temperature for 6 hours (R1, Table 1). This reaction was not succeeded since the FTIR analysis has not shown the characteristic bands of the chorosulphonate group at ~1410 cm^{-1} and ~1200 cm^{-1} [17, 23].

In the following, new experiments to promote the halogenation of Lewatit VPOC1812® were conducted at 40°C with reaction time of 6 h or 24 h (R2, R3 – Table 1). The molar ratio between $SOCl_2/SO_3H$ was 13. The FTIR spectra did not show the characteristic bands of sulfonyl group.

Two new reactions (R4 and R5 – Table 1) were carried out employing higher temperature as well as swelled resin. In these cases, the resins were swelled with 1,2-dichloroethane (R4) or toluene (R5). Both reactions were performed at 79°C for 24h. The FTIR spectra of modified resins have displayed the sulfonyl bands at ~1410 cm^{-1} and 1200 cm^{-1} attributed to asymmetric and symmetric vibrations of SO_2Cl group, respectively [17, 23]. In spite of the chemical modification, the SEM analysis of resin beads shows that the morphological aspects were not preserved. The micrographs have evidenced that the resin beads has broken. Then, the next reactions were performed with mechanical stirring aiming to avoid the beads fragmentation.

Finally, the not swollen resin was modified with thionyl chloride at 79°C (reflux temperature) employing reaction times of 12, 24, 48 or 72 hours (R6, R7, R8, R9 – Table 1) under mechanical stirring. The morphological feature was preserved (this fact was demonstrated by microscopy). These reactions were carried out with the same reagent ratio ($SOCl_2/SO_3H$ = 13). The FTIR spectra showed characteristic bands of sulfonyl group in all reactions (Figure 4). As it could be noticed, these bands were more intense in the R9 resin, suggesting that this resin presented the best chloride group amount.

The second modification step was the treatment of R8 chlorinated resin with an urea solution in 1,4-dioxane during 24 h. This reaction has been carried out employing urea in excess (urea/SO_2Cl = 3) at 27ºC. The resin beads (RU1) were thoroughly washed with water and dried at 100ºC. Finally, the FTIR analysis (Figure 5) showed the characteristic absorptions of urea group [broad band at ~ 3300 cm^{-1} (NH_2 and NH), 1690-1650 cm^{-1}, ν (C=O); 1450-1400 cm^{-1}, ν (C-N)] [25].

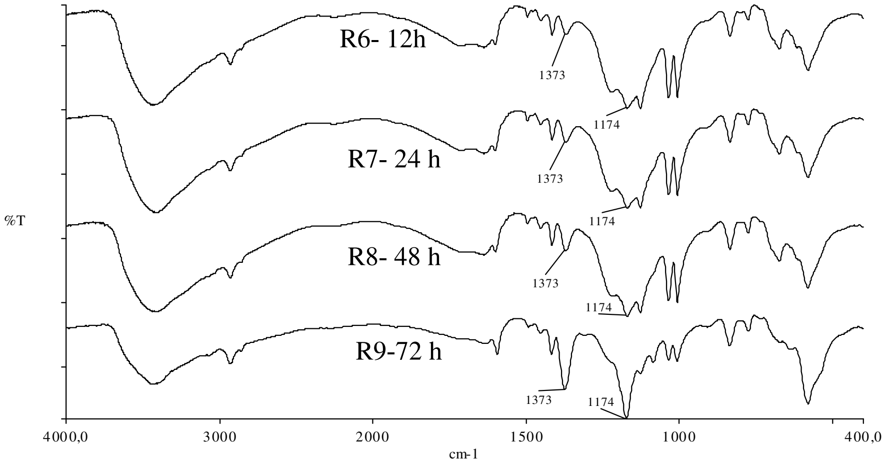

Figure 4: FTIR spectra of chlorinated resins employing different reaction times: R6 - 12h; R7 - 24 h; R8 - 48 h and R9 -72 h

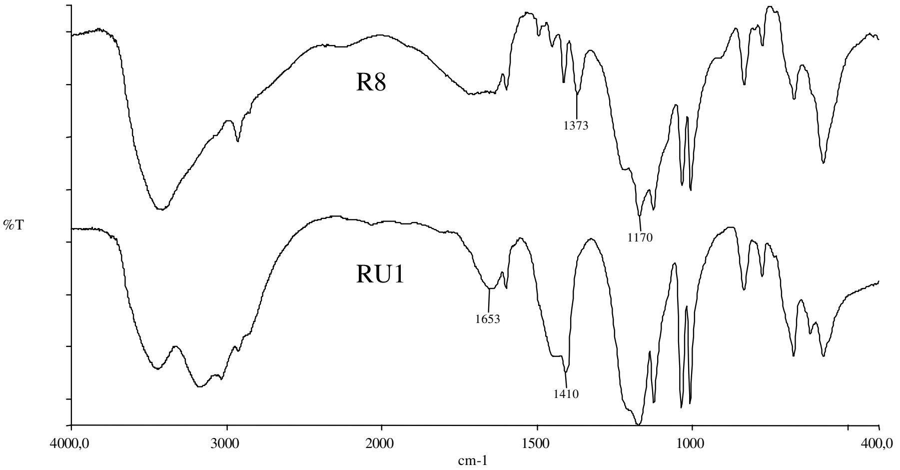

Figure 5: FTIR spectra of R8 chlorinated resin and modified resin with urea (RU1)

New reactions were performed focusing to improve the reaction extension. Hence, these reactions were conducted with the obtained chlorinated resins - R7, R8, R9 (Table 1) - have been treated with urea solution during 24 h at 100°C (RU2, RU3, RU4 respectively – Table 3). In same time, the R8 resin was treated in a condition employing reaction time of 48 h (RU5). The FTIR spectra of resins (RU2, RU3, RU4 and R5) presented the characteristic bands for urea group (Figure 6).

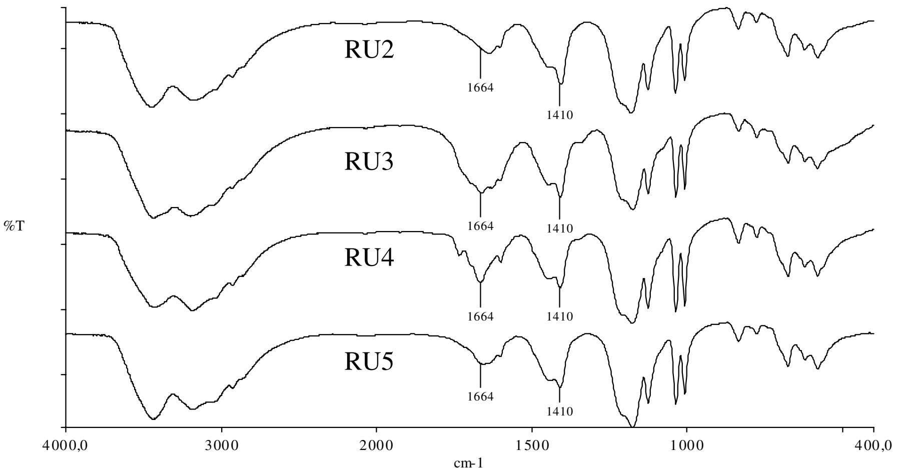

Figure 6: FTIR spectra of modified resins with urea and different chlorinated resins (R7, R8, R9, R8 respectively)

The Table 3 presented the yields of resin (RU2, RU3, RU4 and RU5) determined by elemental analysis (CHNS) based on the presence of nitrogen in relation to sulphur contents and the exchange capacity using acid-base titrations. These results shown on Table 3 demonstrated the extension of reaction time of second step (RU3 and RU5) did not produce an increasing of yield. These results demonstrated that the all NH_2 groups of urea were free into the resin (EC of commercial resin was 4.8 mmol g^{-1}).

Table 3: Elemental analysis results of modified resins containing urea groups

Resin	Chlorinated resin	EC ($mmolg^{-1}$)	C (%)	H (%)	N (%)	S (%)	Modification (%)[a]
RU2	R7	n.a.	45.72	6.10	6.12	15.31	46
RU3	R8	2.4	46.55	6.11	6.76	15.20	51
RU4	R9	n.a.	47.77	6.06	7.18	15.07	55
RU5	R8	2.3	47.80	6.41	6.44	14.85	50

[a]Modification (%) = [N(%) x 100 / (14 x 2)] / S(%) / 32
n.a: not avaliable

Then, the reaction for incorporating the group thiourea was developed the same way. The R8 resin was treated with thiourea solution in 1,4-dioxane at 100°C. The reagents molar ratio was similar to reactions with urea. Figure 7 shows that the FTIR spectra of RT1 modified resin displayed the characteristic absorptions of thiourea group [broad band at ~ 3300 cm^{-1}, ν (NH_2 and NH), 1450-1400 cm^{-1}, ν (C-N)] [25].

Two new reactions were performed employing the R8 and R9 chlorinated resins, which were treated with thiourea 1,4-dioxane solution at 100°C during 48 h (RT2) and 24 h (RT3), respectively. The FTIR spectra of RT2 and RT3 resins showed the characteristic absorptions of the thiourea group (Figure 8).

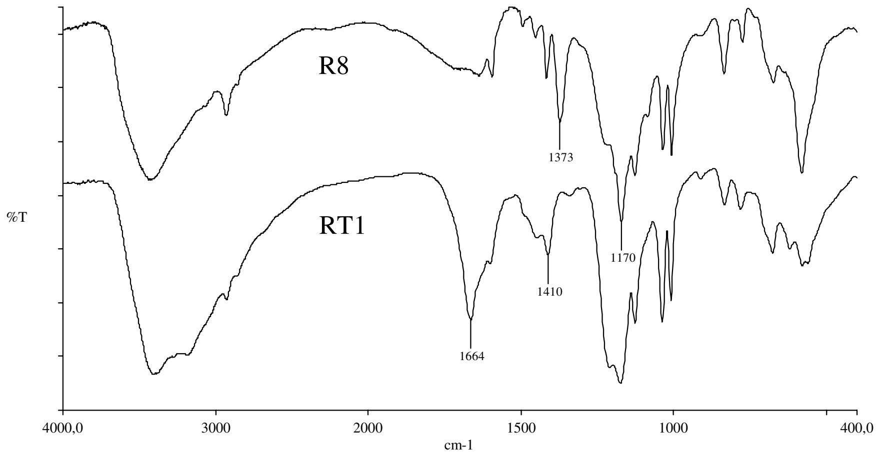

Figure 7: FTIR spectra of resins: R8 chlorinated and RT1 modified with thiourea

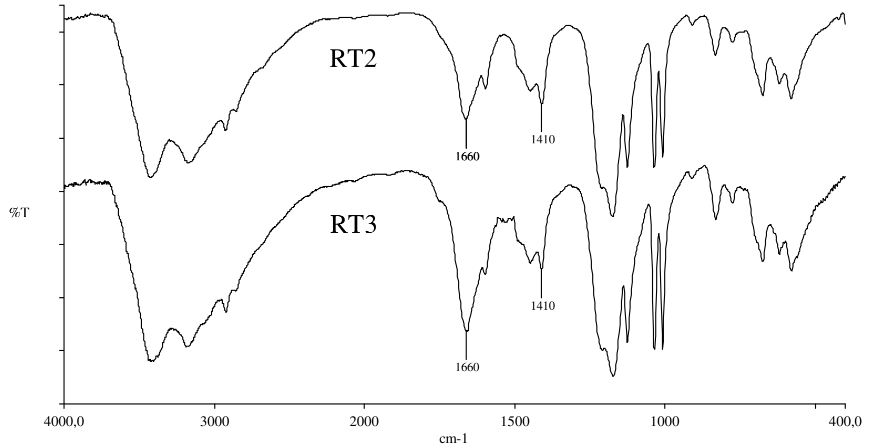

Figure 8: FTIR spectra of resin modified with thiourea and different chlorinated resins (R8 and R9 respectively)

The modified resins RT1, RT2 and RT3 were analyzed by elemental analysis (CHNS) to quantify the thiourea incorporation. These results presented on Table 4 were convergent to the results obtained for the incorporation of urea. Hence, the efficiency of this process was higher when the R9 resin has employed as starting material. (This result should be due to the higher amount of chloride groups presented in this resin.)
Finally, the incorporation of guanidine group was conducted the same way. At first, the hydrochloride guanidine was solubilized on 1,2-dimethoxyethane to obtain the free guanidine (RG1). The R8 chlorinated resin was treated with a solution of free guanidine. This reaction employed a reagent ratio (guanidina/SO_2Cl) = 2 at 85ºC and reaction time of 24 h. The modified resin after purification was analyzed by FTIR (Figure 9) which presented the main characteristic absorptions of guanidine group broad band at ~ 3300 cm^{-1} ν (NH_2 and NH), 1660 cm^{-1}, ν (C=N), 1450-1400 cm^{-1}, ν (C-N)] [17, 25].

Table 4: Elemental analysis results of modified resins containing thiourea groups

Resin	Chlorinated resin	C (%)	H (%)	N (%)	S (%)	Modification (%)
RT1	R8	50.18	4.87	8.86	22.51	62
RT2	R8	46.60	4.91	8.73	19.50	62
RT3	R9	48.69	5.23	9.44	21.53	68

[a]Modification (%) = [N(%) x 100 x 32/ (14 x 2)] / 17.13[b]
[b]S(%) of commercial resin

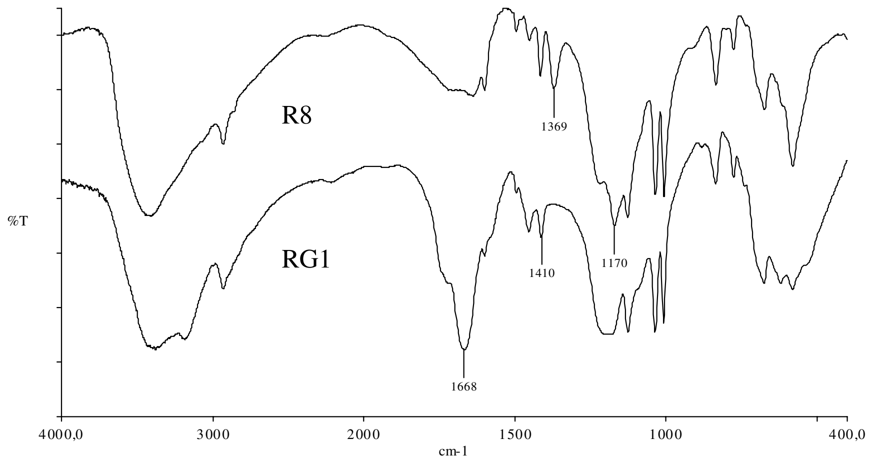

Figure 9: FTIR spectra of resins: R8 chlorinated and RG1 modified with guanidine

The new reaction was conducted with R9 chlorinated resin and guanidine using 1,2-dimetoxyethane as solvent. The reaction parameter involved a reaction time of 24 h and a temperature of 85ºC (RG2). The FTIR spectrum of RG2 has shown the characteristic bands of guanidine groups. This result suggested that chemical modification at resin has been obtained. The yields of reaction were analyzed by elemental analysis (Table 5). These results showed that the best chloride group amount (R9 resin) should have led to a higher incorporation of guanidine group in the RG2 resin (the same way in the reactions involving urea and thiourea).

Table 5: Elemental analysis results of modified resins with guanidine

Resin	Chlorinated resin	C (%)	H (%)	N (%)	S (%)	Modification (%)[a]
RG1	R8	44.15	5.71	14.60	13.13	85
RG2	R9	44.19	5.85	15.62	12.77	93

[a]Modification (%) = [N(%) x 100 / (14 x 3)] / S(%) / 32

Conclusions

This article reported a new methodology to preparation new sulfonylamides derivatives employing network commercial sulfonic resin. It was possible to achieve a good extension of chemical modification of sulfonic groups present on the Lewatit VPOC1812® resin using the mechanical stirring. The experimental procedures have produced sulfonylurea, sulfonylthiourea and sulfonylguanidine derivatives in 55, 68 and 93% yields, respectively. The guanidine reaction has presented higher efficiency maybe due to its higher nucleofilicity compared to urea and thiourea. In addition, this procedure was adequate to maintain the beads spherical morphology. The formation of sulfonylurea, sulfonylthiourea and sulfonylguanidine derivatives during the second step of synthesis was dependent on the amount of sulfonyl chloride groups introduced during the first step.

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