Preparation of Amphoteric Ion Exchanger by Chemical Treatment of Scrap Tires

ABDULRAHMAN MALLAH[iD]

Department of Chemistry, College of Science, Qassim University, Buraydah, Saudi Arabia

Corresponding author: E-mail: a.mallah@qu.edu.sa

An amphoteric ion exchanger containing acidic and basic groups is prepared by chemical treatment of scrap tires by reaction with Sulphuric acid then the sulphonated sample aminated by ethylenediamine at different conditions in order to choose the best product within the thermal range of 120-170 ºC. The best conditions to obtain an amphoteric ion exchanger were at 150 ºC, for a period of 12 h, and mass ratio 1:1 of sulphonated sample to ethylenediamine. The maximum acidic and basic capacities were found as 2.40 and 2.55 meq g^{-1} of the selected ion exchanger respectively, wet and dry thermal stability process of the selected exchanger were also investigated.

Keywords: Scrap tires, Amphoteric ion exchanger, Acidic capacity, Basic capacity, Thermal stability.

INTRODUCTION

Scrap tires are existed in the form of a long-living waste, and hardly decomposed under the influence of the environment factors as light, heat, atmosphere gases, and microorganisms, inflicting an irreparable damage to the nature. The resulting of pyrolysis of scrap tires produces carbon black 22 %, oil 30 %, gas 28 %, steel 10 %, and small quantity of inorganic slag or ash 5 % [1-3]. In USA only, the average annual number of scrap tires accounts for 233 million, so many researchers have tried to find a way to solve this environmental problem either using whole scrap tires as artificial reefs and break-waters, or installation of sports routes and golf sites as small particles [4,5] or after simple thermomechanical treatment in shoes soles [6,7]. Some researches tried to use scrap tire in structural engineering after grinded it and mixed with concrete to have higher strengths and lower water permeability structure [8-10] and as one of the complementary methods in tire repairing is rubber as a modification appliance in bitumen and asphalt covering. Scientific research shows that asphalt mixtures with rubberized bitumen binders are characterized by high resistance to permanent deformations. The uses of crumb tires in road construction include fill material, in asphalt, road base support and side slope stabilizers [11-14].

One of such ways is the application of crumb rubber of scrap tires of different particles in noise-suppression structures.

This is a sufficiently new method of tire management in many countries. Such utilization of scrap tires would help in solving one more ecological problem of special importance to reduce the increased noise level in the anthropogenic environment, results showed that the coarsest crumb rubber (6 mm) with wood cutting boards is most efficient in suppressing low-frequency sounds (up to 300 Hz), when noise level reduction gets changed in the range of 53 dB to 71dB [15-17]. Other scientists tried to devulcanized scrap tires to get reclaimed rubber to use it in rubber industry and revulcanize [18,19]. Scrap tires are used as derived fuel (TDF) as a substitute for a fossil fuel, which offers a higher energy value than coal or wood chips and have little or no adverse effect on air emissions [20,21]. Trying to use crumb scrap tires in water treatment of heavy metals and organic compounds was not so successful due to their small exchange capacity and little adsorption [22-24]. Chemical modification is the most recently treatment of scrap tires is in order to prepare new products by reaction with chemical reagents, to make scrap tires more hydrophilic by oxidizing or halogenating it [25,26]. The ion exchangers have been prepared by grafting scrap tires by acrylic acid [27-30], or by acryl amide, and acryl nitrile using γ-ray as physical irradiation [30]. Also, they have prepared by reacting scrap tires with sulphuric acid, resulting in two functional acidic groups -SO_3H, -OSO_3H [31, 32]. Cationic exchangers were prepared by treating scrap tires with sulphuric acid and olium [33,34], maleic anhydride [35-37],

or by grafting with acrylic acid, or polymerizing methacrylate within scrap tires [38], or by copolymerization of phenol sulfonic acid and formaldehyde [39,40]. Moreover, anionic ion exchangers have been prepared by reaction of brominated scrap tires with ethylamine, diethylamine, ethylenediamine and ethanol amine [41-43]. Mixed ion exchangers prepared by treatment of scrap tires with sulphuric acid were then treated with ammonia solution or pyridine [31,44].

EXPERIMENTAL

Scrap tires were mechanically grinded to small particles at a size of 2-3 mm, conc. sulphuric acid, ethylenediamine, sodium hydroxide, hydrochloric acid, silver nitrate, sodium nitrate (Merck), closed stainless steel reactor volume 100 mL, and memmert oven 220 ºC, were used in this research.

Preparation of an amphoteric ion exchanger

Sulphonation of scrap tires: Grinded scrap tires were reacted with sulphuric acid at 180 ºC, for 12 h and 1:5 mass ratio of scrap tires to sulphuric acid, respectively. The product was then hydrolyzed by treatment with hot NaOH solution of 1 N to get Na^+-form of cationic ion exchanger containing sulfonic groups, this sample washed with distilled water to get a washed solution pH 9-10. In order to prepare the H^+ form of the product, we treated Na^+-form by hot 1N HCl solution, then washed with distilled water to get a washed solution pH 3.5-4 (**Scheme-I**). The maximum number of sulphuric groups was 4.20 meq g^{-1}, swelling water of H^+-form was 1.50-2.75 g H_2O g^{-1}, and for Na^+-form was 7.25-9.50 g H_2O g^{-1}.
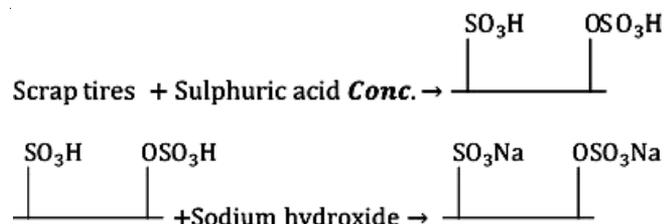
Scheme-I: H^+-form and Na^+-form of sulphate and sulphonate groups

Amination of sulphated samples: Amination of H^+-form and Na^+-form of samples using ethylenediamine at the same conditions, period, temperature, and mass ratio were done. As a result, we observed there is no effect of the acidic groups form on the number of amine groups bonded to products. Therefore, Na^+-form was chosen (ease to deal with). We have studied the effect of three factors on the amination reaction, the first was increasing the temperature within the thermal range of 120 to 170 ºC, the second factor was the period of amination reaction from 3 to 24 h, and the last one was mass ratio of amine to Na^+-form samples 1:1, 1:2, 1:3 of Na^+-form samples to amine (**Scheme-II**). An amphoteric ion exchanger (SE ion exchanger) with amine and acidic groups was produced.
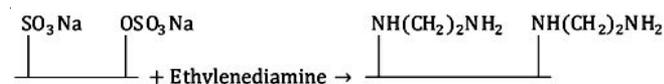
Scheme-II: Amination reaction of Na^+-form of sulphate and sulphonate groups

Properties of products

Water swelling: Water swelling can be calculated using the following equation:

$$W = \frac{m^* - m}{m} gH_2O \; g^{-1} \tag{1}$$

where: W is water swelling, m^* and m are masses of wet and dried ion exchanger at 105 ºC for 4 h, respectively.

The water swelling of three forms of all products were studied, the first form was treated with 1 N HCl (SEA), the second treated with 1 N NaOH (SEB), and the final form treated with 3 N NaCl (SES).

The salted form of products SES (Na^+-form of acidic groups, and Cl-form of basic groups) were also prepared as follows: a particular mass of SEB was soaked in water, then gradually added HCl solution until neutralization (pH ≈ 7) acheived, then separate the ion exchanger by filtration, followed by soaking it in NaCl 3 N solution for one day, then finally washed it with distilled water.

Acidic and basic capacities: A weighed mass of amphoteric ion exchanger in 1 N HCl solution was soaked for 24 h with constant stirring and then washed it with distilled water until pH ≈ 3.5 of the ion exchanged achieved, and then dried at 70 ºC for one day. A weighed amount of dried exchanger SEA (m g) is placed in glass column and added a 100 mL of $NaNO_3$ 3 N solution for each gram of exchanger, and then collected the washed solution.

In order to determine acidic capacity, 20 mL of washed solution was titrated with NaOH solution, using pH-metric titration. The number of acidic groups was calculated by the following equation:

$$C_A = \frac{N_H \cdot V}{m} meq \; g^{-1} \tag{2}$$

where C_A is acidic capacity in meq g^{-1}, V is the volume of $NaNO_3$ solution (100 mL), m is the mass of SEA ion exchanger (g) dried at 70 ºC, N_H eq L^{-1} is the equilibrium concentration of liberated H^+ ions which is calculated using the following equation:

$$N_H = \frac{N \cdot V_2}{V_1} eq \; L^{-1} \tag{3}$$

where N_H eq L^{-1} is the equilibrium concentration of liberated H^+ ions, N eq L^{-1} is the concentration of NaOH solution, V_1 mL is the volume of sample, V_2 mL is the volume of NaOH solution needed to equivalent V_1.

To determine basic capacity, washed solution (V mL) was titrated with $AgNO_3$ solution, by Mohr method, and the number of amino groups was calculated by the following equation:

$$C_B = \frac{N_{Cl} \cdot V}{m} meq \; g^{-1} \tag{4}$$

where C_B is acidic capacity (meq g^{-1}); V is the volume of $NaNO_3$ solution, m is the mass of SEA ion exchanger (g) dried at 70 ºC, N_{Cl} eq L^{-1} is the equilibrium concentration of liberated chloride ions which is calculated using the following equation:

$$N_{Cl} = \frac{N \cdot V''}{V'} eq \; L^{-1} \tag{5}$$

where N_{Cl} eq L^{-1} is the equilibrium concentration of liberated chloride ions, N eq L^{-1} is the concentration of $AgNO_3$ solution, V′ is the volume of sample (mL), V″ is the volume of $AgNO_3$ solution (mL).

Determination of maximum acidic and basic capacities of best product: The product with conditions of 18 h period 170 °C temperature and 1:2 mass ratio, as best amphoteric ion exchanger SEP was chosen because it contains maximum equal number of acidic and basic groups in 1 g. The maximum acidic and basic capacities were determined by studying the change concentration and volume of sodium nitrate solution at three different concentrations (1 N, 2 N and 3 N).

Wet thermal stability: The chemical stability of functional groups of SEP against wet heating was studied. We boiled a mass of best product in form of SEPA (best product treated with HCl) in 1N of NaOH solution for 4 h, and then washed with distilled water until nearly pH ≈ 10. The same sample was then treated with 1 N HCl solution for 4 h at boiling point of solution, washed until weak acidity of solution is obtained at pH ≈ 3.5. The resulted sample was dried at 70 °C for one day. The acidic and basic capacities were determined each time as described above by using 3 N $NaNO_3$ solution. This process was repeated ten times.

Dried thermal stability: The chemical stability of functional groups of best product in form of SEPA against temperature in thermal range of 60-150 °C was studied. For this, a dried mass of SEPA at particular temperature and for specific period from 4 h until a period of three days was considered. The acidic and basic capacities were determined each time as described above by using 3 N $NaNO_3$ solution. This process was also repeated ten times.

RESULTS AND DISCUSSION

Water swelling of products: The water swelling of all products (SEA, SEB and SES) are shown in Table-1. It is noticed that the increase in the mass ratio doesn′t affect the quantity of water swelling for all products. Also, raising the temperature and increasing the period of amination reaction has a little effect on water swelling of products. This is due to the reaction of scrap tires with sulphuric acid, breaking down most cross-linking bridge and the polymers chains carrying sulphate and sulphonate groups which are hydrophilic functional groups. It is observed that water swelling of form SEB or SES having more water than SEA, due to Na^+-form of acidic groups which is more dissociated and more soluble in water than H^+-form. In general, basic and Cl-form of amine groups are less water swelling when compared with acidic groups. Therefore, bonded amine groups to product has negligible effect on the water swelling of products.

Acidic and basic capacities of products: The acidic and basic capacities of all products are given in Table-2, respectively. From Table-2, it is noticed a decrease in acidic capacity for all the products when increasing the period of amination reaction at all temperatures and by raising temperature, which is attributed due to an increase in substitution of acidic groups by amino groups. An increase of basic capacities caused by increasing the number of amino groups bonded to exchanger structure is also observed which is caused by increasing the duration and the raising temperature of amination reaction (Table-2). It is also noticed that an increase in the mass ratio of amine has slightly affect in decreasing acidic groups and increasing amine groups for all products.

From Table-2, the best product SEP was selected at conditions of 150 °C, 12 h period and 1:1 mass ratio with 2.00 and 2.10 meq g^{-1} of acidic and basic capacities, respectively. The maximum capacities were determined by varying the concentration of $NaNO_3$ solutions.

From Table-3, an increase in acidic and basic capacities of SEP is observed by increasing the concentration of $NaNO_3$ solution, which resulted an increase of releasing hydrogen and

		TABLE-1 — WATER SWELLING CAPACITY OF DIFFERENT AMPHOTERIC ION EXCHANGERS

		Time (h)							
Temp. (°C)	Ratio	3	6	9	12	15	18	21	24
g H_2O g^{-1} of SEA
120	(1:1), (1:2), (1:3)	1.80	1.80	1.85	1.85	1.85	1.90	1.95	1.95
130	(1:1), (1:2), (1:3)	1.80	1.85	1.85	1.90	1.90	1.95	2.10	2.10
140	(1:1), (1:2), (1:3)	1.85	1.90	1.90	1.95	2.10	2.10	2.15	2.15
150	(1:1), (1:2), (1:3)	2.05	2.10	2.10	2.20	2.20	2.30	2.30	2.35
160	(1:1), (1:2), (1:3)	2.15	2.25	2.30	2.35	2.45	2.45	2.50	2.60
170	(1:1), (1:2), (1:3)	2.25	2.40	2.55	2.65	2.70	2.80	2.90	2.90
g H_2O g^{-1} of SEB
120	(1:1), (1:2), (1:3)	7.30	7.30	7.45	7.50	7.55	7.55	7.55	7.65
130	(1:1), (1:2), (1:3)	7.50	7.55	7.65	7.65	7.75	7.75	7.85	7.85
140	(1:1), (1:2), (1:3)	7.60	7.75	7.85	7.85	7.95	7.95	8.10	8.10
150	(1:1), (1:2), (1:3)	7.75	7.85	7.90	7.95	8.10	8.15	8.15	8.35
160	(1:1), (1:2), (1:3)	7.90	7.90	8.10	8.20	8.25	8.30	8.30	8.45
170	(1:1), (1:2), (1:3)	8.15	8.20	8.30	8.30	8.35	8.55	8.65	8.65
g H_2O g^{-1} of SES
120	(1:1), (1:2), (1:3)	7.35	7.35	7.45	7.55	7.55	7.55	7.60	7.65
130	(1:1), (1:2), (1:3)	7.50	7.60	7.65	7.75	7.75	7.75	7.85	7.85
140	(1:1), (1:2), (1:3)	7.65	7.70	7.85	7.85	7.95	7.95	8.10	8.15
150	(1:1), (1:2), (1:3)	7.85	7.85	7.90	7.95	8.10	8.20	8.25	8.35
160	(1:1), (1:2), (1:3)	7.95	7.95	8.20	8.20	8.25	8.30	8.35	8.55
170	(1:1), (1:2), (1:3)	8.20	8.20	8.30	8.35	8.45	8.55	8.65	8.76

TABLE-2
ACIDIC AND BASIC CAPACITIES OF AMPHOTERIC ION EXCHANGERS IN AMINATION CONDITIONS

Temp. (°C)	Ratio	Acidic capacity (C_A, meq g^{-1})								Basic capacity (C_B, meq g^{-1})							
		Time (h)								Time (h)							
		3	6	9	12	15	18	21	24	3	6	9	12	15	18	21	24
120	1:1	4.20	4.00	4.00	4.00	3.90	3.70	3.35	3.15	0.00	0.00	0.10	0.25	0.40	0.65	0.85	1.00
	1:2	4.20	3.85	3.75	3.55	3.25	3.00	2.90	2.80	0.00	0.20	0.35	0.55	0.75	1.00	1.20	1.30
	1:3	4.00	3.85	3.55	3.35	3.00	2.90	2.80	2.65	0.00	0.20	0.40	0.55	0.80	1.05	1.30	1.45
130	1:1	3.90	3.60	3.30	3.05	2.75	2.50	2.20	2.10	0.35	0.55	0.75	1.00	1.30	1.60	1.85	2.10
	1:2	3.70	3.50	3.30	3.00	2.75	2.45	2.15	1.80	0.60	0.85	1.05	1.30	1.45	1.85	2.10	2.35
	1:3	3.60	3.40	3.20	2.85	2.60	2.30	2.00	1.70	0.65	0.95	1.15	1.40	1.60	1.95	2.25	2.75
140	1:1	3.55	3.30	3.10	2.70	2.50	2.25	2.10	1.70	0.65	0.95	1.15	1.45	1.70	2.10	2.35	2.90
	1:2	3.30	2.85	2.70	2.50	2.25	2.00	1.75	1.40	0.85	1.15	1.45	1.70	2.10	2.45	2.75	3.05
	1:3	3.10	2.70	2.50	2.25	2.00	1.85	1.50	1.20	0.90	1.25	1.55	1.95	2.40	2.75	2.90	3.20
150	1:1	3.10	2.75	2.45	2.00	1.65	1.25	1.05	0.65	1.00	1.40	1.80	2.10	2.45	2.75	2.95	3.35
	1:2	2.80	2.45	2.05	1.65	1.30	1.00	0.75	0.40	1.25	1.65	2.05	2.50	2.80	3.05	3.35	3.50
	1:3	2.70	2.15	1.55	1.25	0.95	0.65	0.30	0.15	1.35	1.65	2.05	2.65	2.95	3.15	3.45	3.70
160	1:1	2.70	2.15	1.70	1.40	1.05	0.75	0.50	0.15	1.00	1.45	1.50	1.90	2.70	2.95	3.15	3.35
	1:2	2.55	2.00	1.70	1.35	1.00	0.55	0.30	0.00	1.35	1.65	2.00	2.40	2.70	3.05	3.35	3.70
	1:3	2.45	1.80	1.40	0.85	0.70	0.20	0.00	0.00	1.55	1.75	2.10	2.55	2.75	3.10	3.40	3.80
170	1:1	2.10	1.65	1.30	0.85	0.60	0.35	0.15	0.00	1.40	1.75	2.10	2.55	2.75	3.10	3.45	3.80
	1:2	1.65	1.35	1.00	0.75	0.35	0.15	0.00	0.00	1.60	2.35	2.45	2.80	3.15	3.45	3.80	4.00
	1:3	1.30	0.95	0.60	0.30	0.15	0.00	0.00	0.00	1.85	2.55	2.70	3.00	3.35	3.75	4.00	4.00

TABLE-3
ACIDIC AND BASIC CAPACITIES OF AMPHOTERIC ION EXCHANGERS AT
DIFFERENT VOLUME AND CONCENTRATIONS OF SODIUM NITRATE

Conc. (eq/L)	Basic capacity (C_B, meq g^{-1})						Acidic capacity (C_A, meq g^{-1})					
	0.1 L	0.2 L	0.3 L	0.4 L	0.5 L	1.0 L	0.1 L	0.2 L	0.3 L	0.4 L	0.5 L	1.0 L
1 N	2.10	2.10	2.20	2.30	2.40	2.55	2.00	2.00	2.10	2.20	2.30	2.40
2 N	2.10	2.20	2.30	2.40	2.55	2.55	2.00	2.10	2.20	2.30	2.40	2.40
3 N	2.10	2.30	2.40	2.55	2.55	2.55	2.00	2.30	2.40	2.40	2.40	2.40

chloride ions into solution because of the increased number of bonded sodium and nitrate ions to acidic and amine groups in the exchanger structure, but this increase in capacities is limited by the number of acidic and amine groups in the exchanger. The maximum capacities reached to 2.40 and 2.55 meq g^{-1} of acidic and basic capacities, respectively, and the bulk density was found to be 0.80-0.90 g cm^{-3} for SEPS.

Thermal stability: SEP exchanger has a good stability against heating in acidic and basic solutions (Table-4), also SEP exchanger has good stability against dried heating (Table-5).

TABLE-4
ACIDIC AND BASIC CAPACITIES OF SEP AGAINST NUMBER OF WET HEATING PROCESSES

No.	1	2	3	4	5	6	7	8	9	10
	Basic capacity (C_B, meq g^{-1})									
meq/g	2.55	2.50	2.40	2.40	2.30	2.30	2.20	2.20	2.00	2.00
	Acidic capacity (C_A, meq g^{-1})									
meq/g	2.40	2.40	2.40	2.30	2.30	2.20	2.20	2.20	2.20	2.20

TABLE-5
ACIDIC AND BASIC CAPACITIES OF SEP AGAINST TIME AND TEMPERATURE

Temp. (°C)	Basic capacity (C_B, meq g^{-1})								Acidic capacity (C_A, meq g^{-1})							
	Time (h)								Time (h)							
	4	8	12	16	20	24	48	72	4	8	12	16	20	24	48	72
60	2.55	2.30	2.20	2.10	2.10	2.10	2.00	2.00	2.40	2.30	2.30	2.20	2.20	2.20	2.10	2.10
70	2.55	2.20	2.20	2.10	2.00	2.00	1.90	1.90	2.40	2.30	2.30	2.20	2.20	2.10	2.05	2.05
80	2.55	2.20	2.10	2.00	1.90	1.90	1.90	1.90	2.40	2.30	2.20	2.10	2.10	2.05	2.05	1.80
90	2.25	2.05	2.05	2.05	2.05	2.05	1.90	1.80	2.40	2.20	2.10	2.05	2.05	1.80	1.80	1.80
100	2.05	2.05	2.00	2.00	1.90	1.90	1.80	1.70	2.40	2.20	2.05	2.05	2.05	1.80	1.80	1.70
110	1.90	1.90	1.80	1.70	1.70	1.60	1.50	1.50	2.40	2.10	2.05	1.80	1.80	1.80	1.80	1.70
120	1.90	1.70	1.60	1.50	1.50	1.40	1.20	1.10	2.15	1.80	1.80	1.70	1.70	1.60	1.40	1.40
130	1.80	1.60	1.50	1.40	1.20	1.10	1.00	0.90	2.05	1.70	1.70	1.60	1.60	1.40	1.40	1.20
140	1.80	1.60	1.40	1.20	1.00	0.90	0.80	0.60	1.80	1.70	1.50	1.30	1.20	1.10	1.00	0.80
150	1.40	1.20	0.90	0.80	0.60	0.50	0.30	0.30	1.70	1.50	1.30	1.10	1.00	0.80	0.70	0.70

The reason is attributed due to the number of amino groups does not change below 80 ºC, whereas acidic capacity was stable until 110 ºC. The increasing the temperature beyond 110 ºC, the acidic groups were exposed to desulphonation at temperature, whereas the amino group exposed to deamination above 80 ºC.

Conclusion

It is concluded that SEP exchanger has good acidic and basic capacities, as well as good thermal stability below 110 ºC. Thus, amphoteric ion exchanger has good water swelling and can be used to improve of properties of soil.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. C. Roy, A. Chaala and H. Darmstadt, *J. Anal. Appl. Pyrolysis*, **51**, 201 (1999);
https://doi.org/10.1016/S0165-2370(99)00017-0.
2. J.I. Osayi, S. Iyuke and S.E. Ogbeide, *J. Catalysts*, **2014**, Article ID 386371 (2014);
https://doi.org/10.1155/2014/386371.
3. S. Karthikeyan, C. Sathiskumar and S. R. Moorthy, *J. Scient. Ind. Res.*, **71**, 309 (2012).
4. K.J. Collins, A.C. Jensen, J.J. Mallinson, V. Roenelle and I.P. Smith, *ICES J. Marine Sci.*, **59**, S243 (2002);
https://doi.org/10.1006/jmsc.2002.1297.
5. K.J. Collins, A.C. Jensen and S. Albert, *Chem. Ecol.*, **10**, 205 (1995);
https://doi.org/10.1080/02757549508037679.
6. S. Rapo-Brunet, Shoe Sole Comprising a Rubber Composition Based on Nitrile-butadiene Rubber, an Oil and a Resin, US Patent 20140336311A1 (2014).
7. V.M. Makarov and V.F. Drozdovski, Reprocessing of Tires and Rubber Wastes Recycling from the Rubber Products Industry, Ellis Harwood: Chichester, p. 209, (1991).
8. H. Su, J. Yang, T.-C. Ling, G. Ghataora and S. Dirar, *J. Clean. Prod.*, **91**, 288 (2015);
https://doi.org/10.1016/j.jclepro.2014.12.022.
9. M. Al-Fadhli, *Int. J. Eng. Res. Appl.*, **7**, 36 (2017).
10. E. Ganjian, M. Khorami and A.A. Maghsoudi, *Constr. Build. Mater.*, **23**, 1828 (2009);
https://doi.org/10.1016/j.conbuildmat.2008.09.020.
11. Y. Huang, R.N. Bird and O. Heidrich, *Resour. Conserv. Recycl.*, **52**, 58 (2007);
https://doi.org/10.1016/j.resconrec.2007.02.002.
12. N.S. Mashaan, A.H. Ali, M.R. Karim and M. Abdelaziz, The Scient. World J., **2014**, Article ID 214612 (2014);
https://doi.org/10.1155/2014/214612.
13. D.L. Presti, *Constr. Build. Mater.*, **49**, 863 (2013);
https://doi.org/10.1016/j.conbuildmat.2013.09.007.
14. P. Radziszewski, *J. Civil Eng. Manag.*, **13**, 307 (2007);
https://doi.org/10.3846/13923730.2007.9636451.
15. D. Borelli, C. Schenone and P. Ilaria, *J. Acoust. Soc. Am.*, **133**, 3554 (2013);
https://doi.org/10.1121/1.4806460.
16. V. Vaisis and T. Janusevièius, *J. Environ. Eng. Landsc. Manag.*, **17**, 181 (2009);
https://doi.org/10.3846/1648-6897.2009.17.181-188.
17. A. Venslovas and R.L. Idzelis, Scrap-Tire Crumb Rubber Application in Noise-suppression Structures Recovered of the Building Materials, Experimental Investigation, 8th International Conference on Environmental Engineering, ICEE 2011, Vilnius Gediminas Technical University, Vilnius, Lithuania, pp. 446-451, May 19-20 (2011).

18. N. Kawabata, Y. Nishigaki and S. Yamashita, *Nippon Gomu Kyokaishi*, **52**, 764 (1979);
https://doi.org/10.2324/gomu.52.12_764.
19. A. Gursel, E. Akca and N. Sen, *Period. Eng. Nat. Sci.*, **6**, 154 (2018)
20. G. Richards and I.E. Agranovski, *J. Air Waste Manag. Assoc.*, **65**, 186 (2015);
https://doi.org/10.1080/10962247.2014.984084.
21. H.F. Mark, N.M. Bikales, C.G. Overberger and G. Menges, Encyclopedia of Polymer Science and Engineering, Wiley: New York, vol. 14 pp. 787-804 (1988).
22. S. Canepari, P. Castellano, M.L. Astolfi, S. Materazzi, R. Ferrante, D. Fiorini and R. Curini, *Environ. Sci. Pollut. Res. Int.*, **25**, 1448 (2018).
https://doi.org/10.1007/s11356-017-0377-4.
23. A. Lucchesi and G. Maschio, *Conserv. Recycl.*, **6**, 85 (1983);
https://doi.org/10.1016/0361-3658(83)90033-4.
24. J. Gomes, H. Mota, J. Bordado, M. Cadete, G. Sarmento, A. Ribeiro, M. Baiao, J. Fernandes, V. Pampulim, M. Custódio and I. Veloso, *J. Air Waste Manag. Assoc.*, **60**, 741 (2010);
https://doi.org/10.3155/1047-3289.60.6.741.
25. B. Falazi, M.R. Bazzet and A.M. Sobahi, Chlorination of Vulcanized Waste Rubber, The 36th Science Week, University of Aleppo, Aleppo, Syria (1996).
26. B. Falazi, M.R. Bazzet and A.M. Sobahi, Halogenation of the Vulcanized Waste Rubber Residues, The Second Syrian Egyptian Conference of Chemical Engineering, Al-Baath University: Homs, Syria, May 20-22 (1997).
27. B. Falazi and S. Keda, *Res. J. Aleppo Univ. Basic Sci. Series*, **58**, 449 (2008).
28. B. Falazi and S. Keda, Physio-Chemical Study of Ion-Exchanger Prepared by Grafting the Hydrophilic Scrap Tires by Acrylic Acid, *Res. J. Aleppo Univ. Basic Sci. Series*, **58**, 163 (2008).
29. S. Keda, Ph.D. Thesis, Preparation of Cation Exchangers by Grafting Scrap Tires and Physio-Chemical Study on the Products, aculty of Science, Aleppo University, Aleppo, Syria (2009).
30. E. Abdel-Bary, A. Dessouki, E.M. El-Nesr and M.M. Hassan, *Polym. Plast. Technol.*, **36**, 241 (1997);
https://doi.org/10.1080/03602559708000617.
31. E.M. Abdel-Bary, A.M. Dessouki, E.M. El-Nesr and M.M. Hassan, Third Arab International Conference on Polymer Science and Technology, vol. 1, p. 255, September 4-7 (1998).
32. E.M. Abdel-Bary, B. Falazi and A.A. Yehia, Application of Sulphated Waste Rubber Powder as Ion Exchanger, Third Arab International Conference on Polymer Science and Technology, vol. 2, p. 636, Mansoura University, Mansoura, Egypt, September 4-7 (1995).
33. B. Falazi and A. Sobahi, *Res. J. Aleppo Univ. Basic Sci. Series*, **40**, 251 (1999).
34. A. Sobahi, Ph.D. Thesis, Chemical Treatment of Vulcanized Waste Rubber, and Studying Physicochemical Properties of Products, Faculty of Science, Aleppo University, Aleppo, Syria (1999).
35. B. Falazi, M. Amine and S. Keda, *Res. J. Aleppo Univ. Basic Sci. Series*, **37**, 209 (2002).
36. A. Sulaiman, M.Sc. Thesis, Preparation of Ion Exchangers by Poly-condensation of Aniline and Formaldehyde in the Matrix of the Product of Reaction between Scrap Tires and Maleic Anhydride, Faculty of Science, Aleppo University, Aleppo, Syria (2010).
37. S. Keda, M.Sc. Thesis, Preparation of Ion-exchange Resins from Scrap Tires and Physicochemical Study of Products, Faculty of Science, Aleppo University, Aleppo, Syria (2003).
38. B. Falazi and F. Koro, *Res. J. Aleppo Univ. Basic Sci. Series*, **47**, 281 (2005).
39. B. Falazi, *Res. J. Aleppo Univ. Basic Sci. Series*, **57**, 16 (2007).
40. B. Falazi, *Res. J. Aleppo Univ. Basic Sci. Series*, **57**, 19 (2007).
41. B. Falazi, N. Kutiesh and A. Mallah, *Res. J. Aleppo Univ. Basic Sci. Series*, **38**, 231 (2003).
42. B. Falazi, N. Kutiesh and A. Mallah, *Res. J. Aleppo Univ. Basic Sci. Series*, **40**, 251 (2003).
43. A. Mallah, M.Sc. Thesis, Chemical Modification of Scrap Tires and Physicochemical Study of the Products, Faculty of Science, Aleppo University, Aleppo, Syria (2004).
44. B. Falazi and A. Sobahi, *J. Basic Sci.*, **17**, 95 (2001).