Recycling of Vulcanized Rubber Waste to Cationic Exchanger by Treating with Toluene and Oleum

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Abstract

Waste rubber wheels, are a wealth in industrialized countries and in some countries that have been able to devise scientific ways to take advantage of them. We have studied a transformation the vulcanized rubber waste (car rims) into cationic exchanger. The rubber waste is milled into small pieces except the layer containing the steel wire, then processed with sulfuric acid and toluene to insert aromatic toluene rings to the double bonds found in polybutadiene and polyisoprene, which represent about half the weight of the wheel. The next stage is the sulfonization of the aromatic rings produced with smoked sulfuric acid (oleum), thereby obtaining a cationic exchanger. Some chemical-physical properties of the prepared exchanger (acid capacity, exchange capacity, distribution coefficients, water of bloating, stability of the exchanger towards reactivation processes) were studied. The prepared exchanger is characterized by good acidic and reciprocal capacity and stability towards reactivation processes.

Keywords: Acidic capacity; Exchange capacity; Distribution coefficient of the studied cation; Rubber waste

Introduction

Environmental pollution problem has become the focus of attention of various world countries, especially, scientific research centers have found that most environmental problems dating back to the increasing population growth [1]. With an increase in the population and an increase in consumption that is inevitably associated with an increase in the amount of waste left by the population, the importance of finding ways to dispose of it using useful scientific methods increases. It is no longer acceptable to dispose of solid waste by random means, and man can no longer be against nature. Rather, he must take on the role of the caretaker and the person responsible for protecting it [2]. Rubber is one of the most manufactured waste that needs to be recycled and reused. The most important source of rubber waste is worn rubber tires, whose massive expansion in the manufacture of cars and accessories is the main reason for their accumulation [3]. Several methods were used to get rid of them. The first attempts were based on simple methods of treatment for use in fields that do not require high specifications [4]. Pyrolysis methods were used to convert rubber into fuel and to produce black carbon [5], Recently, chemical treatments of vulcanized rubber waste have been carried out in order to prepare ion exchangers [6,7]. Ion exchangers are substances that are practically not soluble in water, which have a geometric structure that is fixed by equivalent bonds, it carries a functional

group are able to replacement and can be exchanged for similarly charged ions with a [8]. Each Resin can exchange a certain amount of ions, that is, it has a certain capacity, for the separation to be complete, and the necessary amount of Resin must be chosen [9]. Successful attempts were made in the colloids and polymers laboratory at the University of Aleppo to obtain ions exchangers by treating the consumed rubber tires [10-12]. However, these attempts are still a need for development and follow-up.

Materials and Methods

Materials

A rubber tire used by the factory Apamea-Aleppo, toluene, Sulfuric acid, toluene, Hydrochloric acid, Copper sulfate, Nickle chloride, sodium hydroxide, sodium chloride.
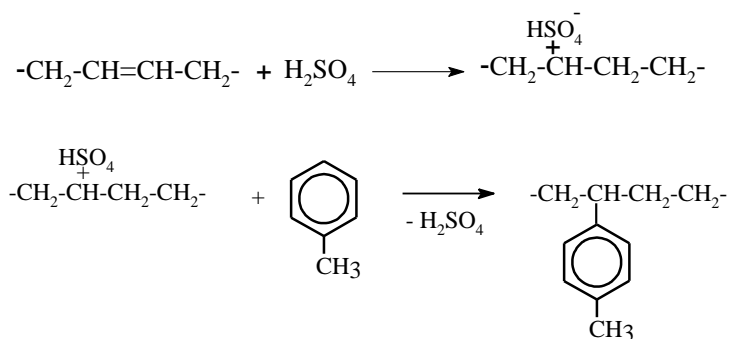
Apparatus

UV-VIS dual-beam device from PG Instruments Ltd model T90, CRISON pH device model Basic 20, Vibrating wise shake at varying speeds from Laboratory Instruments, Heat dryer Janat Instruments Syria industry, and PRECISA Sensitive Balance Model A 106 with four digits after the interval.

Preparation of Exchanger
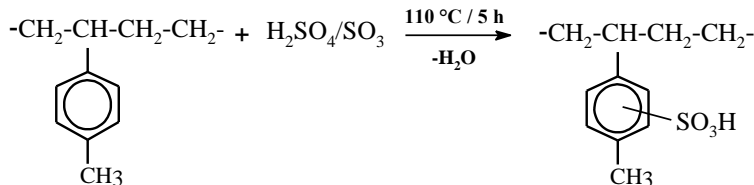
Reaction of toluene with rubber waste

Cutting the rubber frame after removing the metal wire, into pieces with dimensions of 2 mm-3 mm, prepare a mixture containing 60 ml of toluene and 62 ml of dense sulfuric acid, and submerge 120 g of rubber waste, with stirring and after full absorption of liquid add another 60 ml of toluene gradually with good stirring until full absorption and leave the reaction for the next day, the next day add 90 ml of toluene gradually with good stirring and continue stirring for 3 hours and then leave the reaction 3-7 days. The precipitate is separated and then dried on air for the next day to evaporate the toluene. Wash the product with crushed ice, then with cold distilled water until the weak acidity of the pH>3.5, filtrate and then dried on the air until the weight stability. During these processes the reaction is carried out in two phases as follows:

$$-CH_2-CH=CH-CH_2- \ + \ H_2SO_4 \ \longrightarrow \ -CH_2-\overset{\overset{\displaystyle HSO_4^-}{+}}{CH}-CH_2-CH_2-$$

$$-CH_2-\overset{\overset{\displaystyle HSO_4}{+}}{CH}-CH_2-CH_2- \ + \ \underset{CH_3}{\bigcirc} \ \xrightarrow[-H_2SO_4]{} \ -CH_2-CH-CH_2-CH_2-$$

Sulfonization of Rubber Waste which Inserted Toluene to it

Sulfonated process of the product containing the inserted toluene ring is placed in a flask containing a reversible cooler, thermometer and mixer, and slowly poured over it smoked sulfuric acid, until immersion. The reaction is stirred and the flask is slowly heated to 110°C. Keep stirring and turn on the reversible cooler, then heat up at this temperature for 5 hours. The reaction cools and separates the excess acid by washing the sulfonate product with crushed ice and then distilled cold water

until we get a low acidity filtrated solution. Finally, the product is dried on normal air until the weight is stable. The sulfonization process is expressed according to the reaction [13].

$$-CH_2\text{-}CH\text{-}CH_2\text{-}CH_2\text{-} \ + \ H_2SO_4/SO_3 \xrightarrow[-H_2O]{110\,°C\,/\,5\,h} \ -CH_2\text{-}CH\text{-}CH_2\text{-}CH_2\text{-}$$

Results and Discussion

Acid capacity

Acid capacity is defined as the number of milli-equivalents of acidic group (SO_3H) contained in one gram of prepared ion-exchanger. The acidic capacity of the prepared exchanger was determined by soaking 1 g of air-dried exchanger in a given volume (100 ml) of concentrated sodium hydroxide solution (0.1 N) for 3 days.

After soaking, the filtrate was calibrated with a normal solution of hydrochloric acid, while the acid capacity was calculated from the following relationship:

$$X_a = \frac{(N_o - N)V}{m}$$

N_o: Normal NaOH solution before soaking is estimated by mq/L

N: Normal NaOH solution after soaking is estimated by mq/L

m: Dry exchanger mass is estima ted with g

V: NaOH solution volume is estimated by ml

Xa: The acid capacity of the exchanger is estimated at mq/g

Whereas, the acid capacity was (4.7) mq/g

Qualitative Exchange and Exchange Capacity

The ability of the exchanger to extract cations from its aqueous solutions is one of the most important characteristics that determine the economic feasibility and quality of the prepared exchanges. Therefore, we studied the reciprocal properties of the prepared exchanger for copper cation and nickel cation. Then determine the specific exchange of the heat exchanger by taking 1g of the heat exchanger in the form of sodium salt and adding it to 100 ml of the studied cation solution of primary concentration (N_o) and leaving it soaked for 72 hours. To calculate the specific exchange, the relationship is used

$$X_{cation} = \frac{(N_o - N)V}{m}$$

N_o: The initial concentration of the studied cation is estimated at g-eq/L

N: The equilibrium concentration of the studied cation after the exchange is estimated at g-eq/L

m: Dry exchanger mass is estimated at g

V: The volume of cation solution in ml added to mg of the exchanger

X_{cation}: The specific exchange of the exchanger for the studied cation is estimated by mq/g

The concentration N_o is determined for copper and nickel ions in a spectral manner, where the absorbance is measured at the maximum absorption wavelength (812 nm in the case of copper ions and 389 nm in the case of nickel ions) according to the relationship:

$$N= (A/A^o) \, N_o$$

N_o: Optical absorption of the solution prior to immersion of the exchanger.

A: Optical absorption of the solution after immersion of the exchanger in it and equilibrium solutions.

The exchange was determined by adding 1g of prepared exchanger taken in sodium salt form to solutions with the following volumes estimated by ml and the following concentrations estimated by eq/l and we obtained the following results, **(TABLES 1 and 2)** and **(FIG. 1 and 2)**

TABLE 1. **Change of the specific exchange for Copper cation with the change of volume and concentration of the solution.**

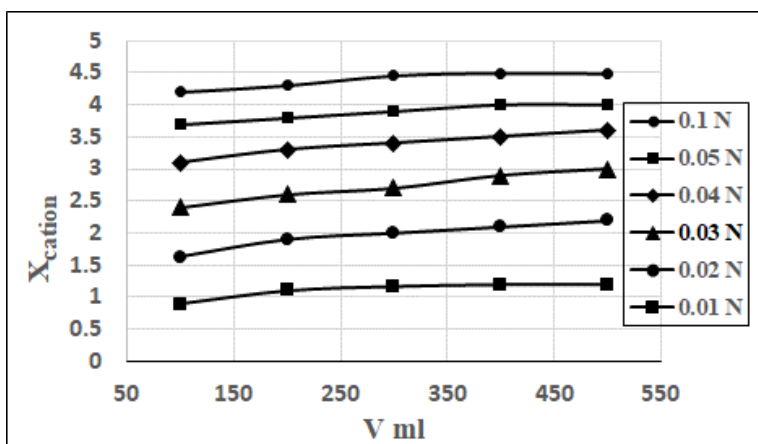| Volume / Concentration	500	400	300	200	100
0.1 N	4.48	4.49	4.45	4.3	4.2
0.05 N	4	4	3.9	3.8	3.7
0.04 N	3.6	3.5	3.4	3.3	3.1
0.03 N	3	2.9	2.7	2.6	2.4
0.02 N	2.2	2.1	2	1.9	1.62
0.01 N	1.2	1.2	1.17	1.1	0.89

FIG. 1. **Change of specific exchange for Nickle ion with constant of solution concentration and volume change.**

We note from the foregoing that the qualitative exchange increases with the increase in the volume of the cation solution and the increase in its initial concentration, Increasing the volume of the solution and increasing its concentration leads to an increase in the amount of cations and thus its competitiveness with sodium cation to bind to the exchanger structure.

Distribution Coefficient

The cation-exchanger solution consists of two phases, the first phase is the structure of the exchanger containing active groups capable of replacing the studied cations, and the second phase is the studied cation solution. When a mass of the saline form of the studied exchanger is soaked in a solution containing cations, cations begin to replace sodium cation and this process continues until balance is achieved. The number of substituted cation equivalents is equivalent to the number of depleted cation equivalents. There is a balanced distribution of the studied cation between the exchanger phase and the cation solution phase. The cation distribution coefficients between the exchanger and the solution are calculated according to the following relationship.

$$\alpha_{cation} = \frac{X_{cation}}{N_{cation}}$$

α_{cation}: The distribution coefficient of the studied cation is estimated in ml/g

X_{cation}: The specific exchange of the cation studied in the solution is estimated by mq/g

N_{cation}: The equilibrium concentration of the studied cation in g-eq/L

TABLE 2. **The results of calculating the distribution coefficients for Copper cation are estimated in ml/g.**

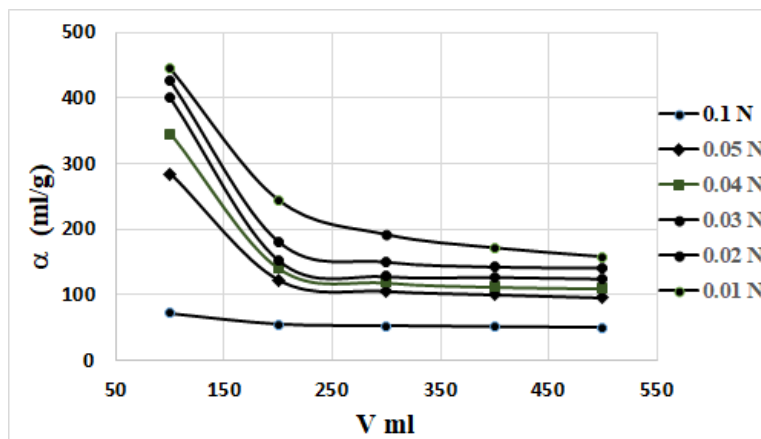| Volume / Concentration	500	400	300	200	100
0.1 N	49	51	52	55	72
0.05 N	95	100	105	123	285
0.04 N	110	112	119	140	344
0.03 N	125	127	129	153	400
0.02 N	141	142	150	181	426
0.01 N	158	171	192	244	445

FIG. 2. **Study changing of the distribution coefficient of Nickle cation as a function of the concentration of the solution at a constant volume.**

Note that the distribution coefficient decreases by increasing the volume of the solution when the concentration is constant; Increasing the volume of the solution increases the equilibrium concentration of cation in the solution and increases the qualitative exchange. However, the intensity of the increase in the qualitative exchange with the increase in the volume of the solution decreases and then stops, In any case, the increase in the volume of the solution leads to a significant increase in the denominator of the relationship (X/N) compared with the increase in the extension of the relationship, also, the distribution coefficient is also observed to increase by decreasing the initial concentration of cation, which is due to the very low for cation equilibrium concentration.

Water of Bloating

The amount water of bloating was determined by taking 1 g of air dried exchanger and soaking it with distilled water until the bloating stopped (72 hours) and weighing, then dried at 105˚C until the weight was stabilized using the following relationship

$$W = \frac{m^* - m}{m}$$

The weight of the sample after soaking with distilled water is estimated in grams

m: Weight of sample after drying at 105°C until weight stability

W: Amount water of bloating

The water of bloating was 0.52 for acid and 0.59 for salt form

Stability of the Exchanger towards Activation Processes

The process of activating the exchanger is aimed for its repeated use, and we test this process to ensure the physical stability of the prepared exchanger structure, the effect of activation processes on its interchangeability for the studied cation (copper). The process of activating the exchanger prepared and consumed in the process of exchanging mineral electrolytes is soaked in sodium chloride solution 3 N and left for the next day, stirring from time to time, finally, separate the liquid and adding a second batch of it and repeat the process until the demise of copper electrolytes, then wash it from the residues of sodium chloride and then dried with air.

TABLE 3. **Results of the study of the stability of the exchanger towards activations.**

Number of activations	0	1	2	3	4	5	6	7	8	9	10
Exchange capacity	4.20	4.20	4.20	4.20	4.16	4.16	4.16	4.14	4.14	4.14	4.14

Note from **TABLE 3** that the exchanger prepared maintains from practically constant exchange capacity toward reactivations.

Conclusion

➢ Cation exchanger was prepared by inserting Aromatic toluene rings to the rubber waste and then sulfonated with smoked sulfuric acid, where the acidic capacity was (4.7) mq/g

➢ The prepared exchanger had a good ability to exchange cations (copper-nickel) from its aqueous solutions.

➢ The prepared exchanger was found to maintain practically constant exchange capacity for reactivation processes

REFERENCES

1. Falazi BA, Alromian FA, Mallah AB. Preparation of bifunctional ion exchanger contains carboxyl and amine groups based on vulcanized scrap rubber and determination of its capacity and thermal stability. J Nat Sci Math. 2009;3(2):69-78.

2. Svec OT, Veizer RO. Note on structural strength of asphalt rubber concrete developed through the stone mastic asphalt concept. Can J Civ Eng. 1996;23(1):295-301.

3. Mohajerani AA, Burnett LU. Recycling waste rubber tires in construction materials and associated environmental considerations: A review. Resour Conserv Recycl. 2020;155:4-20.

4. Rehan AH, Klundert AV. Rubber recycling. 20th WEDC conference. Colombo, Sri Lanka, 1994.

5. Roy CH, Darmstadt HA. Carbon blacks recovered from rubber waste by vacuum pyrolysis: comparison with commercial grades. Plastics. 1998;27(7):341-45.

6. Collins KJ, Jensen AC. Environmental impact assessment of a scrap tyre artificial reef ICES J Mar Sci. 2002;59:S243-49.

7. Roy CR, Chaala A, Darmstadt HA. The vacuum pyrolysis of used tires. End-uses for the oil and carbon black products. J Anal Appl Pyrol. 1999;51:201-21.

8. Mallah AB . Preparation of amphoteric ion exchanger by chemical treatment of scrap tires. Asian J Chem. 2019;31(6):1378-82.

9. Osayi JI, Iyuke SU, Ogbeide SE. Biocrude production through pyrolysis of used tyres. J Catal. 2014, Article ID 386371.

10. Su HA, Yang JI. Properties of concrete prepared with waste tyre rubber particles of uniform and varying sizes. J Clean Prod. 2015;91:288-96.

11. Presti DL. Recycled tyre rubber modified bitumens for road asphalt mixtures: a literature review. Constr Build Mater. 2013;49:863-81.

12. Fadhli ML, Alhumoud JA. Properties of concrete containing scrap-tire rubber. Int J Eng Res Appl. 2017;7(3):36-42.

13. Burla SW. M.Sc dissertation. University of the Witwatersrand, Johannesburg. 2017.