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Review

Ground tire rubber functionalization as a promising approach for the production of sustainable adsorbents of environmental pollutants

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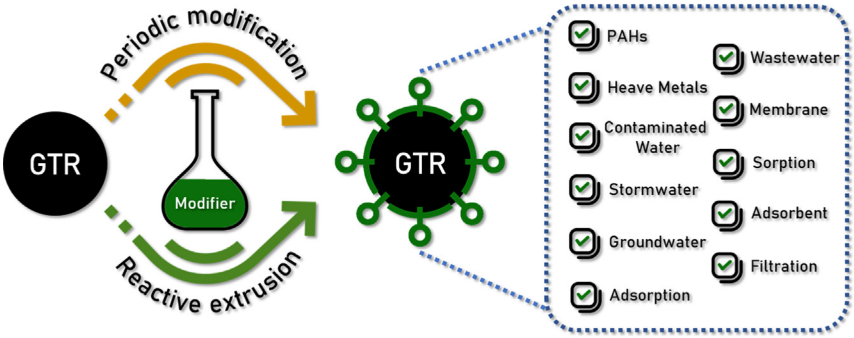
HIGHLIGHTS

- Ground tire rubber (GTR) as various pollutants adsorbent
- The role of GTR composition characteristics in rubber recycling development
- Functionalization strategies of GTR
- A review on pollutants removal using functionalized GTR covering 2011–2021
- Pros and cons of GTR functionalization via periodic methods and reactive extrusion

GRAPHICAL ABSTRACT



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ABSTRACT

Waste tires management and further utilization are currently one of the biggest concerns regarding the environment and human health protection. At present, shredding, grinding, or pulverization of waste tires are the most popular options for industrial recycling. Although many solutions for ground tire rubber (GTR) applications were checked and verified so far, their further implementation at an industrial scale is still very limited. In this brief review work, ground tire rubber functionalization strategies as a promising approach for the production of sustainable adsorbents of environmental pollutants were presented and discussed.

Our findings indicate that suitable functionalization of GTR significantly improves adsorption capacity or selectivity of prepared GTR-based adsorbents. However, it should be mentioned that most of the performed research based on multi-step and time-consuming protocols of GTR functionalization is performed usually in the presence of solvents, which results in very low efficiency and as a consequence high-cost and limited applications. Current research trends showed that reactive extrusion can be considered as efficient, solvent-free, and pro-ecological alternative for commonly investigated periodic methods of GTR functionalization. This work shows that reactive extrusion is a promising method for further development of GTR-based adsorbents dedicated to environmental pollutants.

Abbreviations: ATRP, atom transfer radical polymerization; BET, Brunauer-Emmett-Teller method; DSC, Differential Scanning Calorimetry; EDX, energy-dispersive X-ray spectroscopy; ETRMA, European Tyre & Rubber Manufacturers Association; FTIR, Fourier transform infrared spectroscopy; GC-FID, gas chromatography with flame-ionization detection; GC–MS, gas chromatography with mass spectrometry; GPC, gel permeation chromatography; GTR, ground tire rubber; GTR-*g*-MA, maleic anhydride grafted ground tire rubber; PAH, polycyclic aromatic hydrocarbon; SEM, scanning electron microscopy; TGA, thermogravimetric analysis; XRF, X-ray fluorescence; XPS, X-ray photoelectron spectroscopy.

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Contents

1. Introduction

Management and further recycling of end-of-life tires are currently a huge environmental problem and challenge for academic and industry representatives (Dabic-Miletic et al., 2021; Formela, 2021; Hu et al., 2021). This situation is due to several important factors. Firstly, tires are products with high-performance properties. To be able to meet those requirements, tires are designed by using many high-quality components, based on various rubber compounds, steel wires, and textile cords (Battista et al., 2021; Yang et al., 1993), which made the waste tires recycling very complex. However, the greatest problem when it comes to efforts to recycle waste tires effectively is the vulcanization process and related to that cross-linked structure of rubber (Barbosa et al., 2017; Joseph et al., 2016). Unlike thermoplastics which can be reprocessed without significant change in properties by simple heating/cooling, vulcanized rubber cannot be easily decross-linked or more precisely devulcanized.

According to ASTM D 6814 standard "devulcanization" is defined as a process of breaking down chemical cross-links in the cured rubber. However, it should be pointed out that 100% devulcanization without the involvement of undesired reactions (such as oxidation, main chain degradation, or even pyrolysis) is very difficult to perform and usually main chain degradation in lower or higher levels also occurs. Sutanto et al. (Sutanto et al., 2006) indicated that the selective breakage mechanism of cross-linking sulfide bonds in waste rubber by using high shear forces is possible only when the number of CC bonds is almost the same as the number of CS and SS bonds. In practice, the number of CC bonds in the rubber compound is much higher than CS and SS bonds, which results in higher probability scission of the main chain rather than selective disintegration cross-linking bonds.

As a consequence it is very difficult (or even impossible), to regain the original performance properties of tire rubber by reclaiming/devulcanization technologies, especially in the case of post-consumer tires after the whole life cycle, which is already partially degraded by environmental factors (e.g. UV, heat, ozone, etc.). Therefore, ground tire rubber (GTR) or reclaimed/devulcanized rubber are usually used in new composite materials as low-cost filler or partial substitute of fresh matrix.

At present, ground tire rubber (GTR) treatment by suitable modification and functionalization is gaining more and more attention. This is related to the possibility of applying the higher amount of modified GTR in fresh matrices or with new features of treated GTR. However, according to the best of our knowledge, this work is the first brief review of functionalization strategies of ground tire rubber (GTR) as a sustainable adsorbent of environmental pollutants. Functionalization of GTR allows for higher capacity or selectivity of prepared adsorbents. This paper highlights the issues related to the suitable characterization of GTR composition before use and possible applications of functionalized GTR in water purification.

2. Current trends in waste tire rubber recycling

According to recently published data provided by the European Tyre & Rubber Manufacturers Association (ETRMA) (European Tyre and Rubber Manufacturers' Association, 2021) shown that in 2019, almost 95% of end-of-life tires were collected and treated for material recycling and energy recovery in Europe. The statistical data indicated that for evaluated 32 countries (EU27, United Kingdom, Norway, Turkey, Switzerland, and Serbia), the most common methods for waste tires management can be categorized into: recycling (52%), energy recovery (40%), unknown/stocks (5%), and civil engineering (3%).

However, analyzing this information two particularly important facts should be noted. First, energy recovery involves the combustion of materials, and thus the potential generation of waste from the process in the form of both solid, as well as, volatile pollutions, which must be collected and also handled by suitable treatment. Moreover, this approach results in a loss of the potential of high-quality waste tire rubber that could serve as a substitute for raw matrix, thus increasing the need to draw from already limited natural sources. On the other hand, widespread recycling is fully justified and supported by a higher awareness of society.

Recycling is the most environmentally viable option, but if we look at the data provided by ETRMA, it can be observed that the granulation of the tire itself is considered to be recycling, and therefore a solution to the problem. Moreover, the part of products of waste tire shredding or granulation process, so-called "chips" are commonly used as an alternative fuel (energy recovery).

It is clear that waste tire shredding, granulation, or pulverization and production of ground tire rubber (GTR) is only a step in the process that leads to the actual recycling or in future upcycling, and the provided data does not reflect an actual state of the problem. This is the reason why the scientific community, which deals with the recycling of plastics in general, focuses largely on rubber waste, looking for a solution to manage it and even to increase the degree of devulcanization, which would allow the material to be returned to the production of rubber compounds dedicated for technical applications (de Sousa et al., 2019; Quadrini et al., 2019), shoes (Barreto Luna et al., 2020; Smith et al., 1995) or tires (Hassan et al., 2021; Ma et al., 2021).

Such efforts are justified economically (no charges for waste disposal, reduction of production costs by replacing fresh material with recycled one) and environmentally (reduction of exploitation of natural resources in favor of recycled or reclaimed/devulcanized rubber). In order to highlight the above statement, Fig. 1 shows the collected data, from two commonly used databases: *Scopus*® and *Web of Science*™, which summarizes the number of papers dedicated to the topic of waste rubber and its devulcanization, which have been published between 2011 and 2021.

During searching the most frequently used keywords were used: "*ground tire rubber*"; "*waste tire rubber*"; "*crumb rubber*"; "*waste rubber*"; "*rubber devulcanization*"; "*rubber reclaiming*"; "*rubber reclamation*". The keywords were typed in phrase form while searching.

According to the presented data, the number of publications increased by 531% (according to *Web of Science*™; 2011–2021), and 365% (according to *Scopus*®; 2011–2021). Among searched phrases, the most popular is "*crumb rubber*" with 2088 items in *Web of Science*™ and 2153 for *Scopus*®. The least popular phrase is "*rubber reclaiming*" with 7 items on *Web of Science*™ and 9 items on *Scopus*®. The general difference in numbers is related to the policy of database collection between *Scopus*® and *Web of Science*™. The data indicates a growing interest in the subject, highlighting

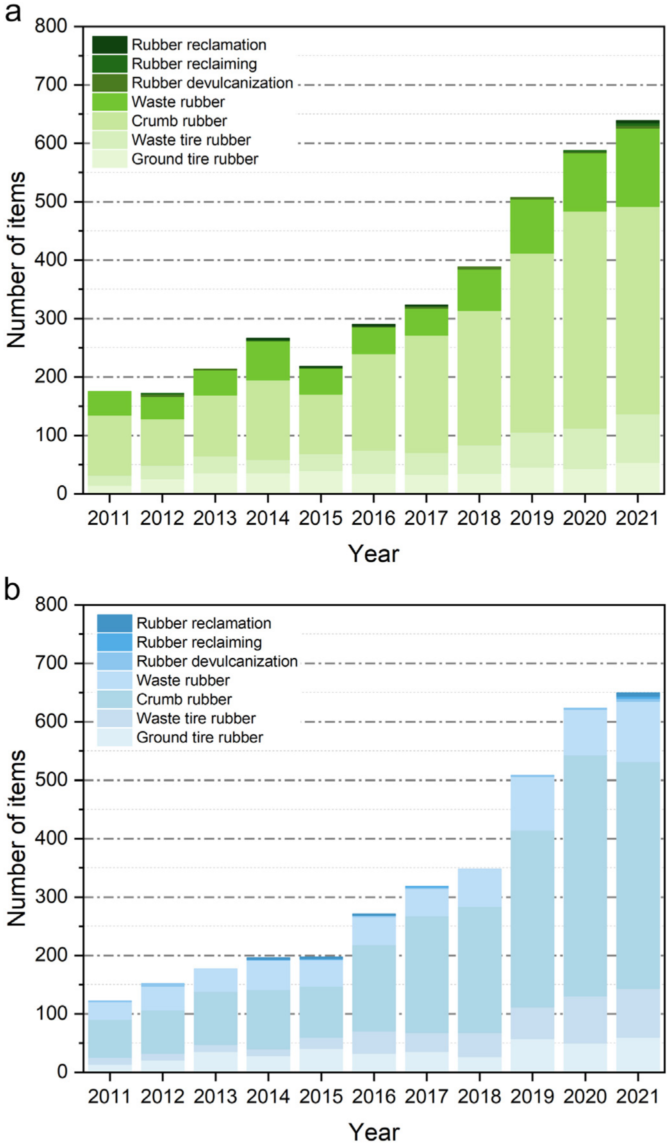

Fig. 1. The number of publications related to the topic of waste tires from 2011 to 2021 generated through: A – *Scopus®* and B – *Web of Science™* database.

the global demand for the development of efficient technologies dedicated to waste rubber recycling, in particular waste tires.

Literature data indicated that many attempts focused on waste tires recycling technologies were performed, especially during the last five years. It should be pointed out that most of them are focused on three main directions of research: grinding/pulverization (Bowles et al., 2020; Hoyer et al., 2020), reclaiming/devulcanization (Saputra et al., 2021; Zhang et al., 2021), or pyrolysis (Lewandowski et al., 2019; Wu et al., 2017) as main strategies for waste tires utilization.

Due to the cross-linked structure and complex composition of ground tire rubber (GTR), its selective and efficient devulcanization to obtain a material with the possibility of revulcanization, after which it would give similar properties to the original product, is very difficult to perform. For this reason, the work carried out most often concerns the incorporation of GTR into various matrices such as bitumens, cement, or polymers, but due to the often poor compatibility of the components, a structure with easily distinguishable phases is obtained resulting in a low-performance product. Many of the research works deal with methods of eliminating this problem by:

- reclaiming (devulcanization) – involves a transformation of cross-linked waste rubber by thermal, mechanical, and/or chemical energy, which results in disintegration of cross-linking bonds and/or degradation of the main chain. The reclaiming efficiency promotes migration of components such as unreacted cross-linking systems contained in GTR, and carbon black into the fresh matrix (Formela and Haponiuk, 2014; Song et al., 2018);
- increasing polarity of the surface – a creation of polar groups to improve interlocking between components (Colom et al., 2007; Li et al., 2022);
- using coupling agents – application of a coupling agent having an affinity for both GTR and matrix (Dong et al., 2013; Klajn et al., 2021);
- surface grafting – the possibility to obtain cross-linking bonds between phases or to create intermolecular entanglements between the matrix and the newly developed GTR surface (Fu et al., 2016; Hassan et al., 2019);
- functionalization by combined methods – based usually on a combination of devulcanization or oxidation with other modifications e.g. grafting (Cavalieri et al., 2003; Jiang et al., 2018).

Many attempts were made dedicated to devulcanization, modification, or functionalization of GTR, which were summarized in recent comprehensive review works (Hejna et al., 2020; Li et al., 2021; Phiri et al., 2021).

However, most of the papers are usually aimed at the application of a higher amount of GTR or the improvement of matrix-GTR interactions in common matrices, such as polymers, bitumens, or concrete.

It should be pointed out, that suitable treatment of GTR allows tailoring its processing or performance properties (e.g. mechanical properties, hydrophilicity, thermal stability, reactivity, etc.), which in new features of

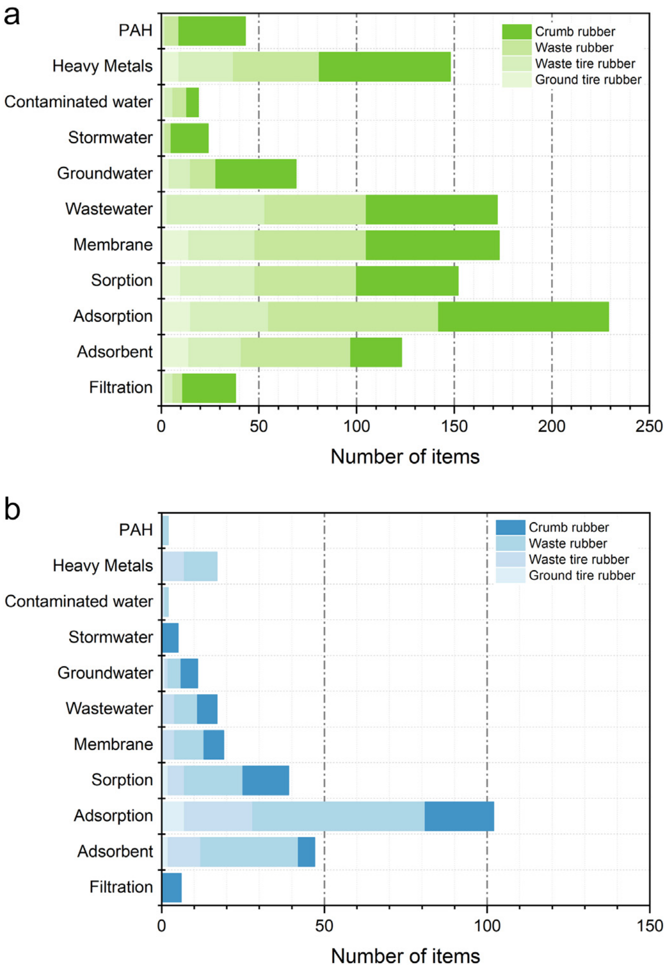

Fig. 2. The number of publications related to GTR as a sustainable adsorbent of environmental pollutants from 2011 to 2021 generated through: A – *Scopus®* and B – *Web of Science™* database.

treated GTR. This strategy fits well with the sustainable development of waste tires recycling technologies and seems to be a promising approach for GTR upcycling.

One of the interesting directions for research in this field is the application of GTR as a sustainable material for environmental applications. In this approach, GTR or functionalized GTR is used as a filter, membranes, or adsorbents dedicated usually for water treatment from pollutions, such as heavy metals (Esfandiar et al., 2022), polycyclic aromatic hydrocarbons (Esfandiar et al., 2021), spilled oil (Lapkovskis et al., 2018), or others (Alamo-Nole et al., 2012; Irfan et al., 2020; Sulyman et al., 2021).

Fig. 2, showed data, representing the number of publications in the subject, by using keywords strictly connected to the usage of GTR as an adsorbent.

The most frequently used keywords were used: "*PAH*"; "*heavy metals*"; "*contaminated water*"; "*stormwater*"; "*groundwater*"; "*wastewater*"; "*membrane*"; "*sorption*"; "*adsorption*"; "*adsorbent*" and "*filter*". All the keywords were searched as phrases. All the phrases were searched within four other phrases: "*crumb rubber*"; "*waste rubber*"; "*waste tire rubber*" and "*ground tire rubber*".

The huge difference in the number of items for *Web of Science™* and *Scopus®* (267 and 1190, respectively) results, as mentioned before, from the policy of data gathering. Moreover, the searched subjects may overlap, so the same item can be found for different phrases. Presented data indicated that using of waste rubber in the environmental applications gaining more and more attention. This trend should evolve in near future, therefore current state-of-the-art highlighted in this brief review can be inspiration for further research and development in this field.

3. GTR composition and characteristics

The application of renewable, waste, or recycled materials as adsorbents is a relatively new field of research, which continually developing (Dai et al., 2018; Dawn and Vishwakarma, 2021; Solangi et al., 2021) and it seems that this trend will be held in the future.

However, the main problem with waste-based materials application is related to lack or very limited characterization of waste materials, for which chemical composition can vary significantly. This might cause problems with the repeatability of satisfactory results in the laboratory scale and their implementation in industrial trials. Therefore, in this subchapter aspects related to GTR composition and characteristics were highlighted and discussed.

It is important to emphasize that tire is a complex composite material and according to Rodgers (Rodgers, 2020) a typical track tire consist of 14 different compounds, and six different steel wire, cords, and fabrics. Among the compounds, one can find: tread base, tread chimney, cushion, sidewall, bead region, plies, belts, overlay, shoulder wedge, inner liner, gum strips (alternatively gum strips or squeegee). Each of these elements plays a different role, and the accumulation of them resulted in a high-performance product. However, in relation to the functions performed, also differ the methods of batches preparation, and above all, their composition.

At present, the basic method of waste tires recycling is shredding and grinding (~87.5% of all forms of rubber recycling). However, to provide to enhance rubber recycling efficiency, prior to shredding, grinding or pulverization, waste rubber should be separated based on its source (chemical composition). This stage has a beneficial impact on the process repeatability and improves the quality of obtained products.

Table 1 shows a comparison of a typical composition of tires, as well as, the effect of the tires grinding method on GTR characteristics.

As can be observed, truck tires contain more natural rubber and less carbon black, compared to car tires (Fazli and Rodrigue, 2020; Pehlken and Müller, 2009).

The differences in the chemical composition of tires determine their final performance, such as wear, rolling, or skid resistance (Pehlken and Müller, 2009). Moreover, the ratio of natural rubber to synthetic rubber has a significant impact on rubber reclaiming/devulcanization efficiency. This is related to fact that natural rubber is more prone to thermal degradation than synthetic rubber (Kleps et al., 2000; Nadal Gisbert et al., 2007) and can be verified by thermogravimetric analysis. Therefore, the ground tire rubber (GTR) or ground rubber (in appearance similar to GTR) used in research should be fully characterized.

Table 1
A comparison of the typical composition of tires and the effect of the tires grinding method on GTR characteristics (based on Fazli and Rodrigue, 2020; Pehlken and Müller, 2009).

Composition	Tire (%wt.)		GTR property	Grinding technology	
	Car	Truck		Ambient	Cryogenic
Natural rubber	22	30	Specific gravity	Same	Same
Synthetic rubbers	23	15	Particle shape	Irregular	Regular
Carbon black	28	20	Surface area	Well-developed	Non-developed
Additives	14	10	Oxidation level	High	Low
Steel	13	25	Product purity	Low	High

Table 2 presents examples of methods used for GTR characterization.

At present, particle size distribution and average particle size are the commonly used and very important parameters in waste rubber processing.

For example, in binary systems, the smaller particle size of GTR results in its better dispersion in the matrix and a larger active surface area. This translates into an increase in potential interfacial interactions between GTR and used matrices (Ramarad et al., 2015).

Usually, higher GTR particle size resulted in the lower compatibility of systems modified by GTR and as a consequence deterioration of their mechanical properties (Mujal-Rosas et al., 2011). Therefore, the particle size distribution of the GTR should always be determined. If possible, the specific surface area should also be checked using the Brunauer-Emmett-Teller (BET) method. For GTR, the moisture content of the material is as important as for any other plastic. Assuming that the ongoing research on GTR is aimed at finding the optimal solution that can be used on at least a semi-industrial scale with commonly used equipment (injection or extrusion machines) or common application with a polyurethane binder, the moisture content of the material should be monitored regularly. Too high moisture leads to physical and chemical changes in the structure and the low quality of the final product.

Many existing GTR management methods are based on partial reclaiming of the material to achieve the ability to revulcanize the material. Therefore, it is also necessary to determine, interrelated, the degree of devulcanization, chemical composition, molecular weight, viscosity, and glass transition temperature. As the reclaiming process progresses, changes occur in the physical as well as the chemical structure of the waste rubber (Asaro et al., 2018), resulting in a size decrease of the gel particles in favor of the sol fraction, thereby increasing the degree of reclaiming. Furthermore, the molecular weight of the sol fraction is being reduced, and there is a shift in the glass transition temperature of the material due to changes in structure. Therefore, as the process progresses, the GTR changes

Table 2
Examples of methods useful for GTR characteristics.

GTR property	Method	Standard
Particle size distribution and average particle size	Sieve analysis	ASTM D5644
	Optical method	–
Surface area	BET method	–
Hydrophilicity/hydrophobicity	Contact angle test	–
Moisture content	Moisture analyzer	ASTM D6980
Devulcanization degree	Equilibrium swelling	ASTM D 6814
Chemical composition	TGA (TGA-FTIR, TGA-GC–MS)	ASTM D6370
	XRF/SEM-EDX	–
	FTIR	–
	XPS	–
	Elemental analysis	–
Molecular weight	GPC	–
Viscosity	Mooney viscosity	ASTM D1646
Glass transition temperature	DSC	–
Volatile organic compounds emission	GC–MS, GC-FID	–

Table 3
Comparison of functionalization strategies of GTR-based materials dedicated for environment applications.

Application of treated GTR	GTR functionalization protocol	References
Lead ions adsorbent	GTR particles size smaller than 0.125 mm. The composition of GTR is unknown. *Pretreatment:* Acetone extraction in order to remove impurities, curing residues, processing additives, etc. *Step I: Immobilization of ATRP initiator onto GTR surface.* GTR (1.0 g) was gently stirred with tetrahydrofuran and trimethylamine in the ice batch (nitrogen atmosphere). 2-bromoisobutyryl bromide was then added into the solution, which was refluxed in an oil bath under stirring for about 8 h. Prepared brominated GTR was filtered, washed, and then dried in a vacuum oven at 60 °C for 12 h. *Step II. Polymerization of maleic anhydride* via *ATRP method.* Brominated GTR (0.5 g) was added and stirred to the mixture of *N*,*N*-dimethylformamide, maleic anhydride, and catalysts (bipyridyl and CuBr) in the nitrogen atmosphere. Polymerization of maleic anhydride onto GTR surface was performed at 110 °C for about 40 h.	Liu et al., 2010
Lead ions adsorbent	*Pretreatment:* GTR (8.0 g) was added to a mixture of distilled water, toluene, pentene, H_2SO_4, or KOH. The mixture was heated up to its boiling point for 30 min. Subsequently, the obtained product was filtered, washed, and dried at 80 °C for 12 h. *Step I: Bromination* of GTR. GTR, Br_2, and CCl_4 were mixed at 30 °C for 4 h. Next, brominated GTR was filtered, washed, and dried in a vacuum at 80 °C for 12 h. *Step II: Reaction with lysine.* Brominated GTR (5.0 g) was mixed with lysine and $NaHCO_3$ solution at 100 °C for 6 h. The prepared product was washed and dried at 80 °C for 12 h.	Wang et al., 2017
Fluoride ions adsorbents	GTR particles size smaller than 0.5 mm. The composition of GTR is unknown. *Pretreatment:* GTR (5.0 g) was added to distilled water, HCl, NaOH, and toluene or hexane. The mixture was heated up to its boiling point for 30 min. Subsequently, the obtained product - GTR I was filtered, washed, and dried at 80 °C for 12 h. *Step I: Bromination* of GTR. Bromine solution (Br_2 and hexane) and GTR I were mixed and stirred for 2 or 3 h at room temperature. Subsequently, the obtained product - brominated GTR was washed with distilled water and dried at 80 °C for 12 h. *Step II: Aminolysis* of brominated GTR by conventional or microwave heating. Ethylenediamine and GTR were mixed and heated: i) under reflux in an oil bath at 150 °C for 2 or 3 h (conventional heating) or ii) under reflux by microwave irradiation at 300 W (2, 4, and 6 min), 450 W (2, 4 and 6 min), and 600 W (2, 4 and 6 min). Subsequently, the prepared product – aminolysed GTR was washed with distilled water and dried at 80 °C for 12 h. *Step III: Protonation* of aminolysed GTR by immersion in HCl solution for 12 h, then the product was washed with deionized water and dried at 80 °C for 12 h.	Rungrodnimitchai and Kotatha, 2015
Nitrate adsorbents	GTR particles size 0.1–0.5 mm. The composition of GTR is unknown. *Pretreatment:* GTR (5.0 g) was added to toluene. The mixture was heated up to its boiling point for 30 min. Subsequently, the obtained product was filtered, washed, and dried at 100 °C for 12 h. *Step I: Halogenation* of GTR. GTR and Wijs' reagent were mixed at 25 °C for 2 h. Subsequently, the obtained product was washed with ethanol and dried at 100 °C for 12 h. *Step II: Aminolysis* of the halogenated GTR. Polyamine (ethylenediamine, diethylenetriamine, and pentaethylenehexamine) and halogenated GTR were heated under reflux by microwave irradiation (300 or 450 W) for 10 min. After cooling down to room temperature, the obtained product was washed with distilled water and dried at 100 °C for 12 h. *Step III: Protonation* of aminolysed GTR by immersion in HCl solution for 12 h, then the product was washed with distilled water and dried at 100 °C for 12 h.	Rungrodnimitchai and Kotatha, 2019
Arsenite and arsenate removal from wastewater	GTR with an average particle size of 0.295 mm. The composition of GTR is unknown. GTR (0.5 g) was mixed with (3-acrylamidopropyl)trimethylammonium chloride, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and *N*,*N*′-methylenebisacrylamide. Then, the mixture was sonicated for 15 min followed by purging with nitrogen for 1 h. In the next step, ammonium persulfate solution was added, and the mixture was stirred continuously at 100 rpm for 1 h to complete the modification. Functionalized GTR was then separated by filtration, washed several times with deionized water, and dried for 24 h in an oven at 50 or 100 °C before further use.	Imyim et al., 2016
Removal of organic dyes and antibiotics (methylene blue, methyl orange, and tetracycline) from water	No information about particle size or composition of GTR. GTR was treated by boiling H_2SO_4 for 3 h. Subsequently, sulfonated GTR was cooled to room temperature, filtered by vacuum filtration, and washed with deionized water. The obtained product was dried in a vacuum oven at 65 °C for 12 h. The efficiency of GTR treatment was 94% (4.7 g).	Islam et al., 2018
Removal of anti-inflammatory drugs ibuprofen, diclofenac, and naproxen from aqueous solutions	GTR with an average particle size of 0.3 mm. The composition of GTR is unknown. In the first step, GTR was pulverized in order to increase its surface area. Subsequently, GTR was mixed with the variable content of chitosan solution (chitosan powder in acetic acid) for 1 h. The content of chitosan in treated GTR was in the range: 0–50%wt. After that, the GTR/chitosan mixture was dried at 100 °C in the oven for 24 h.	Phasuphan et al., 2019
Removal of boron from water	GTR particles in the range of: 0.125–1 mm. The composition of GTR is unknown. GTR (10.0 g) was treated with the acids: H_2SO_4, HNO_3, or a mixture of acids in the ratios 1:3; 3:1, and 1:1 were used. Subsequently, the treatment was carried out at room temperature by immersion of the GTR in the acid solution for 24 h. Subsequently, the obtained product was dried, neutralized by NaOH, and washed with distilled water until the neutral pH.	Babiker et al., 2019

its physical properties to the point where Mooney viscosity studies are possible.

The last method is to determine the volatile organic compounds released into the atmosphere. When GTR is heated, typical compounds such as cyclooctane; decane; limonene; undecane; dodecane; tridecane; tetradecane (natural rubber degradation products) benzene; toluene; ethylbenzene; xylene; styrene; benzaldehyde; α-methylstyrene (styrene-butadiene degradation products) are released into the atmosphere (Saeb et al., 2022). Some of them can be used as "markers" for main chain degradation or devulcanization efficiency evaluation.

The suitable quality control of waste rubber and waste rubber-based products is a very important task for the further development of recycling technologies. Especially that recently published results (Skoczyńska et al., 2021), indicate that the level of heterocyclic aromatic compounds emitted from commercially available recycled rubber mats exceeds the European Union limits.

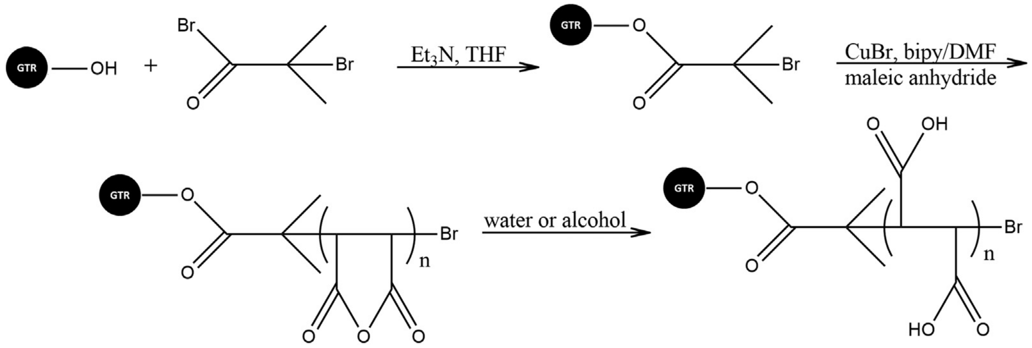

Fig. 3. Scheme with the mechanism of maleic anhydride polymerization into GTR surface (redesigned based on Liu et al., 2010).

Table 4
The effect of GTR-*g*-MA polymerization time on MA grafting efficiency and lead adsorption capacity (data adopted from Liu et al., 2010).

Parameter	GTR-*g*-MA polymerization time (h)			
	10	20	30	40
Grafting degree (%)	32.5	48.6	61.3	69.4
Lead adsorption capacity (mg/g)	48.1	60.7	71.2	76.8

4. Functionalization strategies of GTR-based adsorbents

Commercially available GTR in form of granulate or powder can be successfully used as sustainable material dedicated for environmental applications. However, it seems that further development of GTR-based materials dedicated for this purpose should consider GTR functionalization, which is a relatively new field of research. Therefore, so far, the number of publications on this topic is rather limited. The summary with the comparison of functionalization strategies for GTR-based materials dedicated to environmental applications is presented in Table 3.

According to our findings, one of the first attempts related to the application of functionalized GTR for water purification was made in 2010 by Liu et al. (Liu et al., 2010), who used maleic anhydride grafted GTR (GTR-*g*-MA) for lead ions adsorption. The mechanism of maleic anhydride polymerization onto the GTR surface is presented in Fig. 3.

In the first step, GTR (1.0 g) was brominated for about 8 h, during which the solution was refluxed in an oil bath under stirring. Prepared brominated GTR was washed and dried at 60 °C in a vacuum oven for 12 h. Subsequently, ATRP polymerization of maleic anhydride (MA) into brominated GTR (0.5 g) was performed in the presence of *N*,*N*-dimethylformamide as a solvent, and bipyridyl/CuBr as catalysts. The polymerization process was held at 110 °C for about 40 h. Obtained GTR-*g*-MA was then washed and dried in a vacuum oven at 65 °C for 12 h. To sum up the whole procedure, the total time necessary for the synthesis of 0.5 g GTR-*g*-MA was approximately 72 h, including 48 h of syntheses and 24 h of drying. The authors confirmed that a higher degree of MA grafting onto GTR was possible with a longer polymerization time. Grafting efficiency had a significant impact on lead ions adsorption capacity. As presented in Table 4 for grafting degree 32.5% lead adsorption capacity was 48.1 mg/g, while for 69.4% the capacity was 76.8 mg/g.

Wang et al. (Wang et al., 2017) chemically treated GTR through the reaction with bromine, followed by a lysine reaction to develop the carboxylic and amino groups on the GTR surface. Obtained modified GTR was applied as lead ions adsorbent. The preparation and surface complexation of lysine modified GTR is presented in Fig. 4.

The authors used a pretreatment two-step protocol in which preparation of 5 g lysine modified GTR takes approximately 46.5 h, including 10.5 h of synthesis and 36 h of drying at 80 °C. The prepared adsorbent showed an excellent removal efficiency of 92% with an adsorbent dosage of 1.0 g/L, which was related to functional groups present onto the GTR surface as well as the higher porosity of treated GTR.

Rungrodnimitchai and Kotatha functionalized GTR by ethylenediamine in order to remove fluoride ions from water (Rungrodnimitchai and Kotatha, 2015). The authors proposed a multi-step treatment protocol, including: pretreatment via heating in solvents, bromination, aminolysis, and protonation. The results showed that modified ground tire rubber could be used as a good adsorbent for defluoridation (0.84–0.86 mg/g) with efficiency similar to the commercial resin (0.95 mg/g). However, it should be highlighted that the total time necessary to perform all procedures mentioned in the GTR treatment protocol for modification of 5 g GTR was approximately 64.5–66.5 h, including 16.5–18.5 h of mixing with various chemical agents (2.5–3.5 h mixing at elevated temperature – 150 °C) and 48 h of drying at 80 °C. The authors studied the idea of using

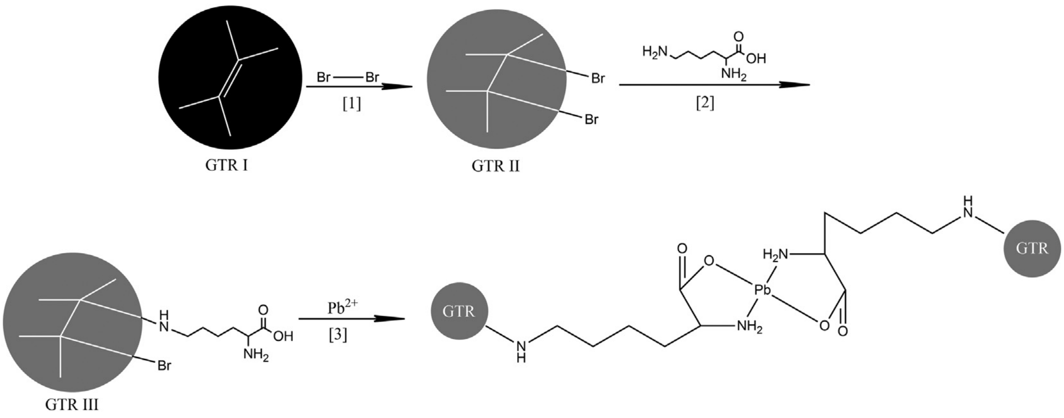

Fig. 4. Preparation and surface complexation of lysine modified GTR: 1) Bromination of GTR; 2) Lysine reaction with brominated GTR; 3) surface complexation of lysine modified GTR (redesigned from Wang et al., 2017).

microwave heating for reducing the time necessary for GTR modification. The results showed that short-time microwave treatment (2–6 min) has similar reaction efficiency to long-term conventional heating (2 – 3h). Moreover, microwave irradiation can be successfully applied also for the drying of GTR.

The same authors (Rungrodnimitchai and Kotatha, 2019) used GTR modified by Wijs' reagent (solution of I-Cl in acetic acid), polyamines, and microwave irradiation heating for the preparation of reusable adsorbents dedicated for nitrate. GTR modification (5.0 g) was performed according to the multi-step protocol which in total takes around 50.6 h, including pre-treatment (0.5 h in boiling toluene), halogenation (2 h of modification at 25 °C and 12 h of drying at 100 °C), aminolysis (microwave treatment for 10 min and 12 h of drying at 100 °C) and protonation (12 h of treatment at room temperature and 12 h of drying at 100 °C). During GTR modification, the authors used three polyamines, such as ethylenediamine, diethylenetriamine, and pentaethylenehexamine. The chemical structures of resulted modified GTR are presented in Fig. 5.

The results showed that nitrogen numbers of polyamines increased the maximal adsorption capacity of nitrate from 0.06 mg/g determined for untreated GTR to: 2.16 mg/g for ethylenediamine modified GTR (microwaves irradiation with energy 300 W), 3.08 mg/g for diethylenetriamine modified GTR (microwaves irradiation with energy 450 W), and 3.61 mg/g for pentaethylenehexamine modified GTR (microwaves irradiation with energy 300 W).

Imyim et al. (Imyim et al., 2016) functionalized GTR by a cationic polymer - poly(3-acrylamidopropyl)trimethylammonium chloride. The total time necessary for modification of 0.5 g GTR was approximately 2.25 h of mixing and polymerization at room temperature, washing several times, and 24 h drying at 50 or 100 °C. The prepared modified GTR was used for adsorption of arsenite As(III) and arsenate As(V) from an aqueous solution. It was observed that cationic polymer modified GTR is more effective for As(V) and the level of adsorption increased proportionally to increasing polymer concentration and contact time. An arsenic adsorption efficiency for prepared cationic polymer modified GTR was 0.33–0.46 mg/g. The authors demonstrated that obtained sorbent can be successfully reused by desorption of As(III) and As(V) by HCl, with the highest efficiency at concentration 0.1 mol/L.

Islam et al. (Islam et al., 2018) treated GTR by boiling H_2SO_4 to produce sulfonated GTR, according to the scheme presented in Fig. 6.

According to the protocol described by the authors, modification of 5 g GTR takes approximately 3 h of stirring with H_2SO_4, washing, and then drying in a vacuum at 65 °C for 12 h. Prepared sulfonated GTR was used as a high-capacity reusable adsorbent dedicated to the removal of organic dyes and antibiotics such as methylene blue, methyl orange, and tetracycline from water with maximum adsorption: 833 mg/g, 588 mg/g, and 303 mg/g, respectively.

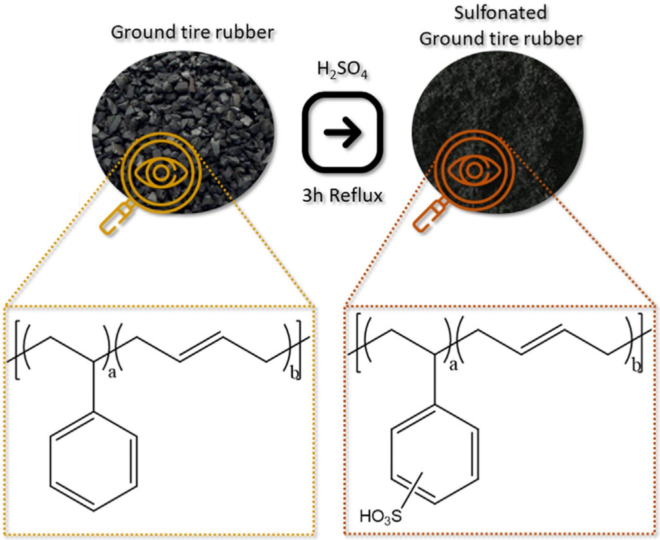

Fig. 6. Preparation of sulfonated GTR (adopted from Islam et al., 2018).

Phasuphan et al. (Phasuphan et al., 2019) demonstrated that chitosan-modified GTR can be considered as an efficient and low-cost adsorbent for the removal of anti-inflammatory drugs from water. Prior to modification authors pulverized GTR in order to increase its surface area. The modification was performed by simple mixing of GTR with chitosan solution (chitosan powder in acetic acid) for 1 h at ambient temperature and subsequently drying at 100 °C for 24 h. The chitosan content in chitosan-modified GTR was in the range of: 0–50%wt. The scheme of chitosan-modified GTR preparation is presented in Fig. 7.

The results showed that the removal capacity of ibuprofen, diclofenac, and naproxen from the water was: 17.7, 70.0, and 2.3 mg/g, respectively. This indicates that chitosan-modified GTR is the most effective in the case of diclofenac.

Babiker et al. (Babiker et al., 2019) performed a modification of GTR via pulverization (nano-GTR) or chemical treatment by using HNO_3, H_2SO_4, and their mixtures (in the ratio: 1:3; 1:1 and 3:1). The obtained products were used as boron adsorbents. The highest adsorption capacities determined for GTR, nano-GTR, and chemically modified GTR were 16.7 mg/g, 12.7 mg/g, and 13.8 mg/g, respectively. As could be expected, the boron adsorption capacity decreased with the increasing size of GTR particles. The authors showed that the adsorption capacity of GTR for boron is highest as compared to other adsorbents reported in the literature.

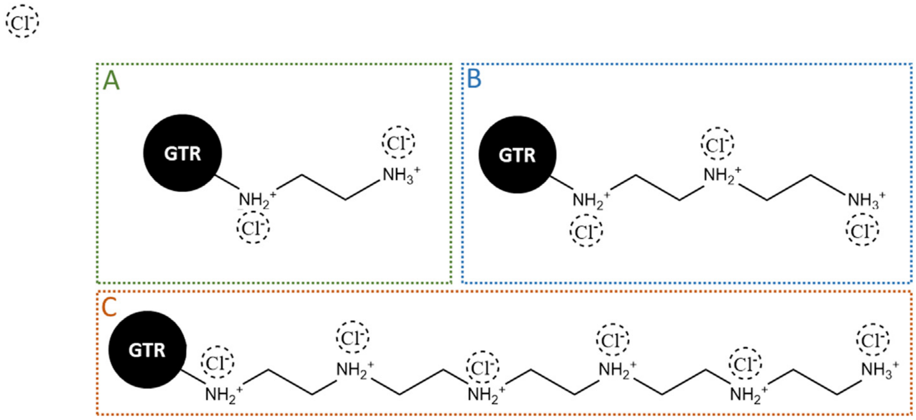

Fig. 5. The structure of (a) ethylenediamine modified GTR, (b) diethylenetriamine modified GTR, and (c) pentaethylenehexamine modified GTR (redesigned based on Rungrodnimitchai and Kotatha, 2019).

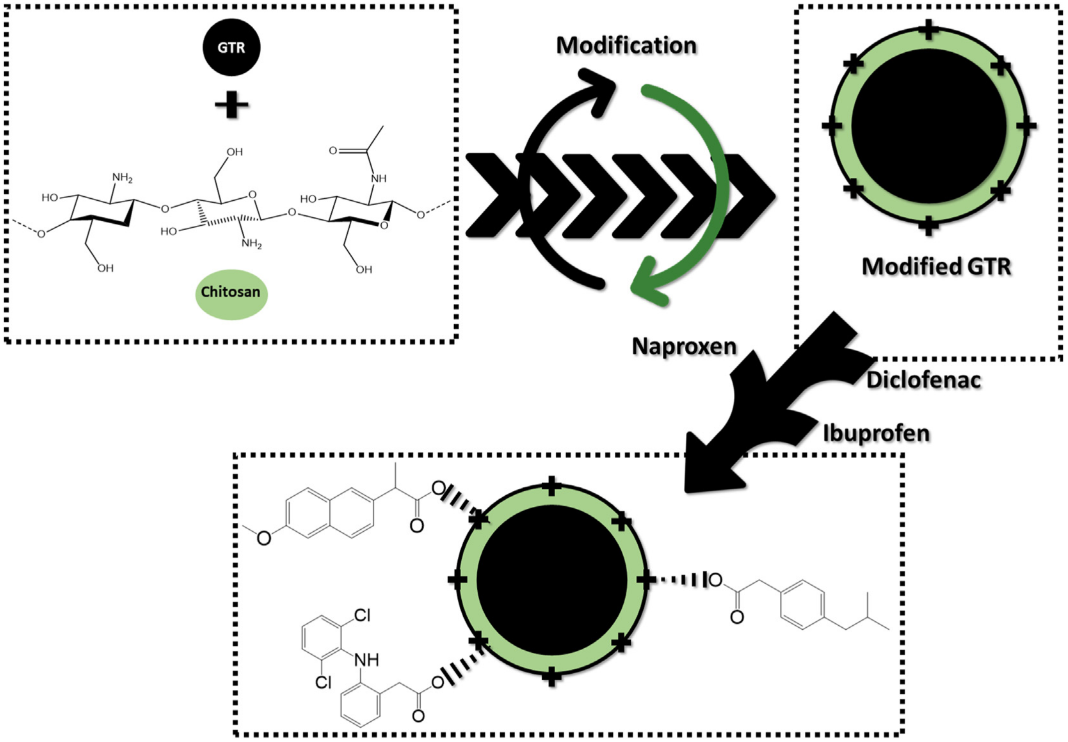

Fig. 7. Scheme of chitosan-modified GTR preparation (redesigned based on Phasuphan et al., 2019).

Nano-GTR particles were prepared by high-speed milling performed at liquid nitrogen. Unfortunately, the authors did not provide detailed information about the used equipment or milling conditions (e.g. time, amount of GTR, etc.). Nano-GTR particles size was investigated by SEM analysis. During chemical treatment, GTR was immersed at room temperature in the inorganic acids (or their mixtures) for 24 h. Subsequently, the obtained product was air-dried for 5 min and washed until neutral pH was achieved. Surface characteristics and elemental composition of GTR, nano-GTR, and chemically treated GTR are summarized in Table 5.

It was found that grinding and acid treatment of GTR have a significant impact on the specific surface area, elemental composition (GTR surface oxidation – higher O content and devulcanization – lower S content), and volume of meso- and micro-pores. However, there is no simple correlation between these parameters.

Recently, Araujo-Morera et al. (Araujo-Morera et al., 2021) investigated the effect of mechano-chemically modified GTR as sustainable filler in styrene-butadiene rubber composites. Similar to Babiker et al. (Babiker et al., 2019), the authors performed a modification of GTR by cryo-grinding and chemical treatment by different oxidizing agents (H_2SO_4, HNO_3, and H_2O_2). Treatment of 10 g GTR with inorganic acids was performed at 100 °C for 3 h, while in the case of H_2O_2 room temperature was used. Prepared treated-GTR fillers were washed until neutral pH and dried at 70 °C for 24 h. The stability of water-GTR suspension as a function of GTR treatment conditions is presented in Fig. 8.

As can be observed, GTR treated by H_2SO_4, HNO_3, and their mixture resulted in the stable suspension of GTR in water, which confirms higher hydrophilicity of GTR particles related to suitable oxidation level.

5. Future development of GTR functionalization

Multi-step and time-consuming protocols resulted in the high cost of GTR modification methods performed at a laboratory scale, which limits the industrial implementation of GTR treatment technologies. Some of the problems, related to the long heating or drying time of functionalized GTR could be resolved by the application of microwave irradiation, especially since microwave-induced devulcanization and pyrolysis are nowadays considered as promising approaches in rubber recycling (Formela et al., 2019).

It should be pointed out, that many of the technical problems could be eliminated by performing GTR functionalization via reactive extrusion, which involves carrying out a designed chemical reaction with high efficiency and in a flexible manner. Reactive extrusion effectiveness is strongly

Table 5
Pore size, surface area, and elemental analysis of GTR-based adsorbents prepared via grinding and chemical treatment by inorganic acids (data adopted from Babiker et al., 2019).

Adsorbent and treatment method	Surface characteristics		Elemental composition (%wt.)					
	Mesopores volume (cm^3/g)	Micropores volume (cm^3/g)	Specific surface area (m^2/g)	C	O	Si	S	Zn
Untreated GTR	0.0311 ± 0.0009	0.0255 ± 0.0011	67.7 ± 0.3	88.2	4.8	0.3	3.1	3.0
Nano-GTR	0.0019 ± 0.0010	0.0764 ± 0.0014	123.5 ± 0.3	85.1	10.5	0.3	1.6	1.6
GTR treated by HNO_3	0.0388 ± 0.0008	0.0245 ± 0.0009	95.1 ± 0.4	78.5	19.1	1.0	–	–
GTR treated by H_2SO_4	0.0399 ± 0.0009	0.0222 ± 0.0010	99.3 ± 0.4	90.8	6.6	–	1.4	0.8
GTR treated by HNO_3:H_2SO_4 1:3	0.0451 ± 0.0012	0.0201 ± 0.0011	110.9 ± 0.4	83.2	14.7	–	1.0	–
GTR treated by HNO_3:H_2SO_4 1:1	0.0381 ± 0.0010	0.0239 ± 0.0011	101.2 ± 0.4	75.6	18.2	0.1	0.1	–
GTR treated by HNO_3:H_2SO_4 3:1	0.0378 ± 0.0009	0.0219 ± 0.0008	89.5 ± 0.4	73.5	19.3	0.1	1.9	–

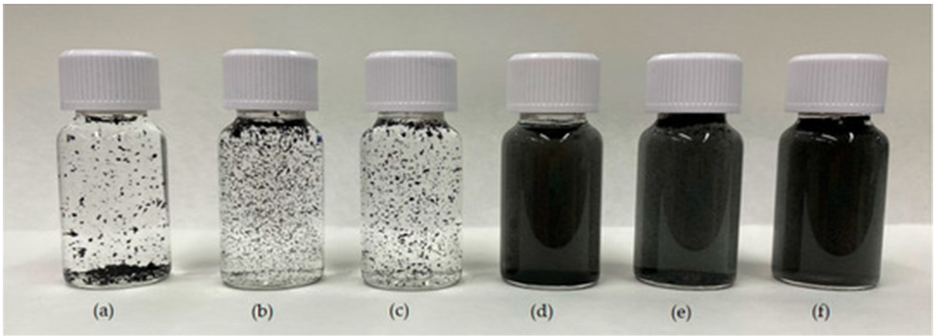

Fig. 8. Stability of water-GTR suspension as a function of GTR treatment conditions: (a) untreated GTR; (b) cryo-grinded GTR; (c) GTR treated by H_2O_2; (d) GTR treated by H_2SO_4; (e) GTR treated by HNO_3; and (f) GTR treated with H_2SO_4:HNO_3 3:1 (Araujo-Morera et al., 2021).

related to the correlation between various processing conditions (e.g. shear forces, temperature, screw configurations, etc.) and the course of chemical reactions inside the extruder barrel (Formela et al., 2018).

The comparison of advantages and disadvantages of GTR functionalization via batch methods and reactive extrusion is presented in Table 6.

As can be seen, the main advantage of batch methods, when functionalizing the GTR, is the availability of equipment and its low price. This translates into the possibility of using these devices in laboratories. The periodic methods of GTR functionalization are usually very time and energy-consuming, which results in their low efficiency and very limited possibility for further upscaling. On the other hand, as presented in Table 6 these problems are very limited when reactive extrusion is applied. The main disadvantages of reactive extrusion are related to the application of expensive apparatus, adjustment and stabilization of a material feeding system, and degassing/treatment of volatile degradation products or by-products.

Fig. 9 shows data representing the number of publications published between 2011 and 2021, in the subject including terms: "*modification*"; "*functionalization*" and "*reactive extrusion*" in combination with the usage of terms related to rubber recycling: "*waste rubber*"; "*crumb rubber*"; "*waste tire rubber*" and "*ground tire rubber*".

During searching two databases were used: *Scopus*® and *Web of Science*™. This summary clearly presents that number of published about reactive extrusion of waste rubber is still very limited in comparison to other treatment methods performed by batch/periodic and multi-step protocols.

6. Conclusions

The development of adsorbents based on renewable, waste, or recycled materials is gaining more and more attention. This trend is also observed for ground tire rubber (GTR) more often applied as a low-cost and environmentally-friendly adsorbent of diverse environmental pollutants, e.g. polycyclic aromatic hydrocarbons, spilled oils, heavy metals, etc.

As demonstrated in this paper, suitable treatment and functionalization of GTR allow improving or tailoring of adsorption efficiency and capacity and also modification of adsorption kinetics or thermodynamics. The main limitation for further development in this field is related to usually complex procedures and multiple steps protocols during periodic/batch methods of GTR functionalization. This resulted in the long treatment time of GTR and very low efficiency of this process (e.g. in some cases the total time for functionalization of a few grams GTR was approximately more than 50 h). Moreover, the most of investigated methods of GTR functionalization used an excessive amount of solvents, which should be recovered or removed by multiple washing (wastewater treatment) and drying (energy consumption).

Current research trends in different fields (e.g. natural filler/fibres modifications) indicated that reactive extrusion can be considered as a very efficient, solvent-free, low-cost, and environmentally-friendly alternative for commonly investigated modification methods of GTR via periodic methods.

This brief review confirms that suitable GTR functionalization (especially via reactive extrusion) is a very promising approach for the production of sustainable adsorbents of environmental pollutants.

CRediT authorship contribution statement

Łukasz Zedler: Writing-Reviewing and Editing.
Shifeng Wang: Writing-Reviewing and Editing.
Krzysztof Formela: Conceptualization, Writing-Reviewing and Editing.

Table 6
Pros and cons of GTR functionalization via batch methods and reactive extrusion.

Batch methods		Reactive extrusion	
Pros	Cons	Pros	Cons
Easy to perform at laboratory scale	Usually multi-step method	High efficiency	The necessity of expensive apparatus applications
Inexpensive and commonly available apparatus	Time and energy consuming	Modification without or with a limited amount of solvents	Technical problems related to continues feeding of an extruder with difficult materials (e.g. powders, liquids)
	Usually exceeded amount of solvents	Short time and low-cost method	Problems with volatile degradation products or by-products emission and degassing and suitable treatment during extrusion
	Necessity for product purification	Easier for upscaling	
	Usually low efficiency	Efficient mixing of difficult materials with variable rheological properties	
	Difficult for upscaling	Possibility for quick evaluation of process stability and repeatability (direct measurement of: melt-temperature, pressure, torque, or specific mechanical energy during extrusion)	
	Technical problems with efficient mixing of high-viscous systems	Possibility for development of extrusion line (e.g. new extrusion die, co-extrusion, foaming, etc.)	

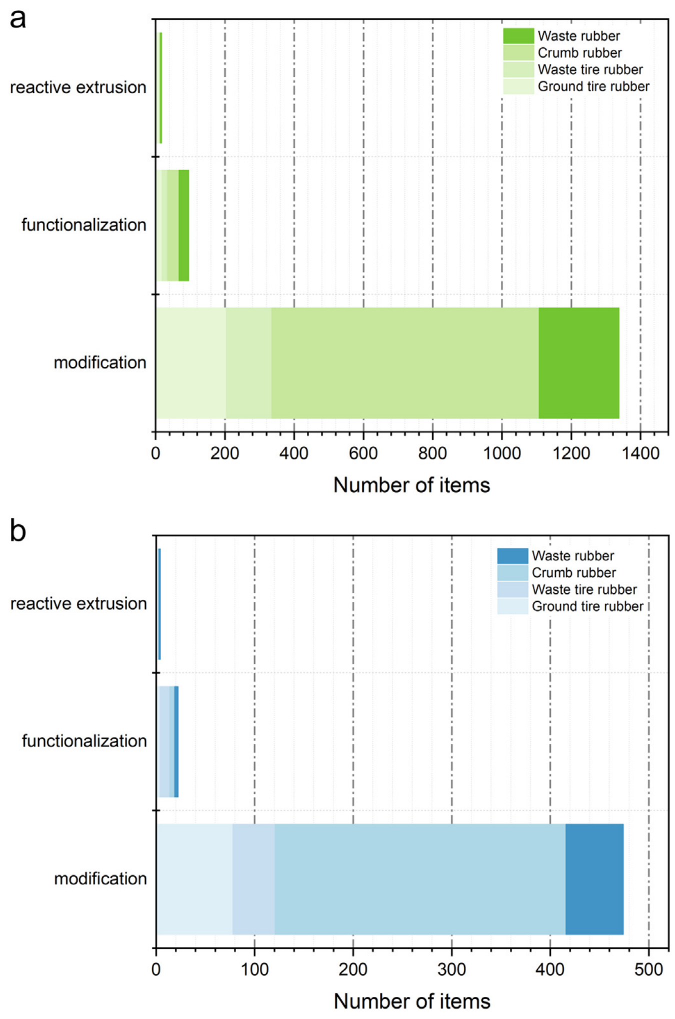

Fig. 9. The number of publications related to the modification, functionalization, and reactive extrusion of waste rubbers from 2011 to 2021 generated through: A – *Scopus*® and B – *Web of Science*™ database.

All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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