



## Chemically modified ground tire rubber as fluoride ions adsorbents

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### HIGHLIGHTS

- The modified ground tire rubber as fluoride ions adsorbents was successfully prepared by chemical modification.
- Microwave heating could shorten the reaction time of aminolysis.
- The modified ground tire rubber showed high ion-exchange capacity.
- In adsorption of F<sup>-</sup>, the modified ground tire rubber could perform as good as commercial resin.

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### ABSTRACT

In this study, ground tire rubber (average particle size = 280 μm) was chemically modified to produce modified ground tire rubber that can work as base anion exchange resin. The modification was performed through a reaction with bromine, followed by a reaction with ethylenediamine under conventional heating or microwave heating in order to introduce ethylenediamine into the structure of the ground tire rubber; this was followed by protonation in an acid solution. FT-IR revealed that ethylenediamine was successfully introduced into the modified ground tire rubber. The modified ground tire rubber obtained from microwave heating (2 min, 450 w) showed a 3.20 meq/g of ion exchange capacity, which corresponded to 1.60 meq/g of ethylenediamine in the form of ammonium ions. On the other hand, the modified ground tire rubber from conventional heating (150 °C, 3 h) showed a 3.60 meq/g of ion exchange capacity, which corresponded to 1.80 meq/g of ethylenediamine in the form of ammonium ions. In the adsorption kinetics of fluoride ions in aqueous solution, it was found that the modified ground tire rubber from both heating methods agreed well with the pseudo-second order kinetic model. Like commercial resin, the modified ground tire rubber could also remove fluoride, but with a higher rate constant. From the kinetic model, the maximum defluoridation capacity of the modified ground tire rubber was calculated to be 859.6 mg/Kg for the microwave heating, and 833.3 mg/Kg for the conventional heating.

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### 1. Introduction

Currently, with the growth of industries and the economy, a huge amount of waste tires are produced each year and have become a serious problem. Since waste tire is almost non-degradable, proper disposal and utilization has become challenging.

In addition to recycling tires or using them as land-fill materials, many research groups proposed several methods to convert waste tire rubber into value-added products, such as activated carbon [1–4], or fuel by pyrolysis [5,6]. Some research groups proposed the oxidation of waste tire rubber for recycling by ozone [7,8], m-chloroperbenzoic acid, periodic acid [9], and nitrous oxide [10]

that can break double bonds and other chemical bonds in waste tire rubber.

Among many chemical wastewater treatment technologies [11], the use of adsorbents for water remediation is intensively studied. For example, biosorbents, such as modified rice straw and baggage, silk sericin and chitosan displayed excellent heavy metals adsorption [12–14]. Recently, magnetic nanosorbents were reported as functional adsorbents [15]. Activated carbon is an important adsorbent for wastewater treatment. For example, various kinds of activated carbon from waste tire rubber for the removal of heavy metals and organic molecules were systematically studied by Gupta et al. [16–25]. The processing methods and adsorption behaviour of carbon materials from waste tire rubber were intensively reviewed by Saleh and Gupta [26].

There are some reports regarding the preparation of adsorbents from the chemical treatment of waste tire rubber. Vizuet et al.

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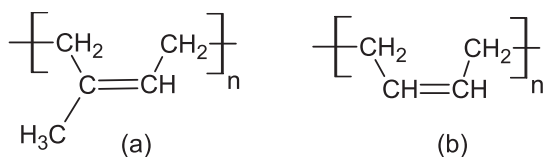


Fig. 1. (a) The chemical structure of polyisoprene unit and (b) the chemical structure of polybutadiene unit.

reported on the modification of waste tire rubber by heat treatment at 400 °C and chemical treatment by immersing waste tire rubber in H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> or a mixture between the two. It was found that the waste tire rubber, which was modified by heat treatment, showed higher Hg<sup>2+</sup> adsorption than the chemical treatment method [27]. Danwanichkul and Dechojarassri reported the adsorption of Hg<sup>2+</sup> in the aqueous phase using ground tire rubber. The adsorption efficiency reached 88.8% in the dynamic adsorption in a column pack [28]. It was reported that adsorbents from the chemical treatment of waste tire rubber at 900 °C using HCl, HNO<sub>3</sub> and NaOH showed adsorption ability for phenol derivatives and heavy metals [29]. Chemical and heat activated adsorbents from waste tire rubber, which can remove NO<sub>2</sub>, was reported by Hofman and Pietrzak [30]. Katyaem et al. proposed the removal of phenol from contaminated water using small particles of ground tire rubber. It was found that smaller particles showed better performance in the phenol adsorption [31].

Recently, the problem of contamination of drinking water by fluoride ions (F<sup>-</sup>) was recognized. A large intake of fluoride causes dental and skeletal fluorosis. The World Health Organization specifies the tolerance limit of fluoride in drinking water at 1.5 mg/L [32,33]. A number of inorganic and organic adsorbents were proposed for the removal of fluoride from water [34]. Among them, chitosan-based adsorbents are unique since they can remove fluoride through ion exchange. Amino group (-NH<sub>2</sub>) in β-(1-4)-linked D-glucosamine units can be protonated and produce a group of ammonium salt (-NH<sub>3</sub><sup>+</sup> X<sup>-</sup>; Where X<sup>-</sup> is an anion.). A group of ammonium salt from the protonated chitosan works as a basic type of ion-exchange resin. It was reported that the protonated chitosan beads and multifunctional chitosan beads showed defluoridation capacity as much as 1664 mgF<sup>-</sup>/kg and 1800 mgF<sup>-</sup>/kg, respectively [35,36].

The objective of this research was to chemically modify ground tire rubber into basic anion-exchange resin. Ground tire rubber in this research is recycled tires from automotive and truck scrap tires. It was provided as fine rubber particles. Waste tire rubber is considered to be an important source of hydrocarbon. The structures of the Waste tire rubber contain double bonds that are derived from isoprene units of natural rubber and butadiene polymer units of synthetic rubber (Fig. 1(a) and (b)). Both units contain carbon-carbon double bonds, which are useful for chemical modification.

Fig. 2 shows modification steps of carbon-carbon double bonds of ground tire rubber into the anion exchange resin. Firstly, the addition of bromine (Br<sub>2</sub>) to double bonds in ground tire rubber (Ground tire rubber I) yields a dibromo-product (Ground tire rubber II) as shown in Fig. 2-1. Dibromo-product (Ground tire rubber II) undergoes substitution reaction (or aminolysis) by ethylenediamine and produces ethylenediamine modified ground tire rubber (Ground tire rubber III). The protonation of ethylenediamine modified ground tire rubber gives a base anion exchange ground tire rubber (Ground tire rubber IV).

Ground tire rubber IV is composed of insoluble site from ground tire rubber and chloride ions as ion exchangeable site in the structure. Ground tire rubber IV works by exchanging fluoride ions in the water with the chloride ions as shown in Fig. 3. Certainly, chloride ions (Cl<sup>-</sup>) of Ground tire rubber IV can be exchanged with other anions, such as NO<sub>3</sub><sup>-</sup>, OH<sup>-</sup>, PO<sub>4</sub><sup>3-</sup> etc.

In this research, the aminolysis reaction of modified ground tire rubber was performed by conventional heating or microwave heating. The ion exchange capacity and the ability to remove F<sup>-</sup> in aqueous solution of the obtained modified ground tire rubber were investigated.

## 2. Materials and methods

### 2.1. Materials and chemicals

Ground tire rubber obtained from a local recycle shop in Thailand was sieved into particles smaller than 500 μm. Ethylenediamine (98.0%), hydrochloric acid (37%), sodium hydroxide (97.0%), sodium chloride (99.5%), toluene (99.5%), hexane (99.5%), potassium iodide (99%), sodium thiosulfate (99.5%), and

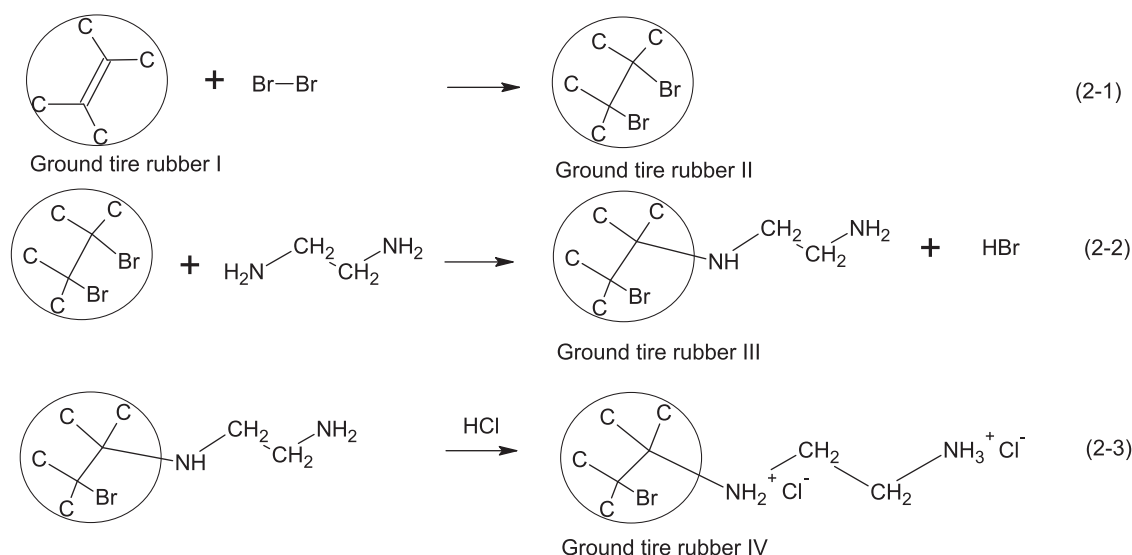


Fig. 2. Reactions for preparation of the modified ground tire rubber; (2-1) Bromination of carbon-carbon double bond, (2-2) Aminolysis of dibromide product, and (2-3) Protonation of ethylenediamine modified ground tire rubber.

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