Chemically Modification of Ground Tire Rubber

Supitcha Rungrodnimitchai* and Ditpon Kotatha

Department of Chemical Engineering, Faculty of Engineer, Thammasat University, Platumthanee, 12120

*Email: supitcha@enge.tu.ac.th

Abstract

The ground tire rubber with the particle size 300-700 micron was modified by treatment by Wij's reagent, followed by a reaction with Ethylenediamine (EDA) by conventional heating or under microwave irradiation. It was found that EDA modified ground tire rubber from 10 minutes of 300 W microwave reaction performed the best in Nitrate ion (NO_3^-) adsorption (2.20 mg/g adsorbent). On the other hand, the crumb rubber without modification showed ion exchange capacity only 0.24 mg/g adsorbent. All EDA modified ground tire rubber showed good agreement with Langmuir model and Freundlich model for the isotherm of NO_3^- adsorption. From Langmuir model, the maximum adsorption capacity of ETD modified ground tire rubber from 10 minutes of 300 W microwave irradiation was 1.97 mg/g, which was higher than 1.04 mg/g of ETD modified ground tire rubber from 30 minutes of conventional heating.

Keywords: Ground tire rubber, modification, adsorption, Nitrate ion, microwave

Introduction

Nowadays, as the growth of economics and industries, waste of used tire became serious problem because of the huge amount of used tire is produced each year, and it is hardly degradable in environment.

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 (Ariyadejwanich et al, 2003; Gonzalez et al, 2006), or fuel by pyrolysis (Roy et al,1999; Money & Harrison,1999). Some research groups proposed the oxidation of waste tire rubber for recycling by ozone (Cataldo et al, 2010), m-chloroperbenzoic acid, periodic acid (Sadaka et al, 2012), and nitrous oxide (Dubkov et al, 2012) that can break double bonds and other chemical bonds in waste tire rubber. There are some reports regarding the preparation of adsorbents from the chemical treatment of waste tire rubber. The group of E. M. Vizuete reported on the modification of waste tire rubber by heat treatment at 400°C and chemical treatment by immersing waste tire rubber in H_2SO_4, HNO_3 or a mixture between the two. It was found that the waste tire rubber, which was modified by heat treatment, showed higher Hg^{2+} adsorption than the chemical treatment method (Vizuete et al, 2005). Group of P. Danwanichkul reported the adsorption of Hg^{2+} in the aqueous phase using ground tire rubber. The adsorption efficiency reached 88.8% in the dynamic adsorption in a column pack (Danwanichkul et al, 2008). It was reported that adsorbents from the chemical treatment of waste tire rubber at 900°C using HCl, HNO_3 and NaOH showed adsorption ability for phenol derivatives and heavy metals (Torrado et al, 2011). Chemical and heat activated adsorbents from waste tire rubber, which can remove NO_2, was reported by M. Hofman and R. Pietrzak (Horman & Pietrzak, 2011). Group of S. Katyaem 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 (Katyaem et al, 2006).

Recently, S. Rungrodnimitchai and D. Kotatha reported the modification of ground tire rubber via bromination and aminolysis by ethylenediamine. The obtained modified rubber showed high adsorption ability toward fluoride ion. However, the reaction by pure Br_2 was very corrosive and hard to control (Rungrodnimitchai & Kotatha, 2015).

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), Fig 1 (b)). Both units contain carbon-carbon double bonds, which are useful for chemical modification.

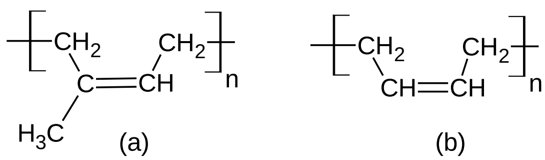


Fig. 1 (a) The chemical structure of polyisoprene unit and (b) the chemical structure of polybutadiene unit

Fig. 2 shows modification steps of carbon-carbon double bonds of ground tire rubber into the anion exchange resin. Firstly, the addition of iodine monochloride (I-Cl) of Wij's reagent to double bonds in ground tire rubber yields a halogenated ground tire rubber as shown in Fig 2. Halogenated ground tire rubber undergoes substitution reaction (or aminolysis) by ethylenediamine (EDA) and produces ethylenediamine modified ground tire rubber. The treatment of EDA modified ground tire rubber by hydrochloric acid gives a base anion exchange ground tire rubber (EDA modified ground tire rubber).

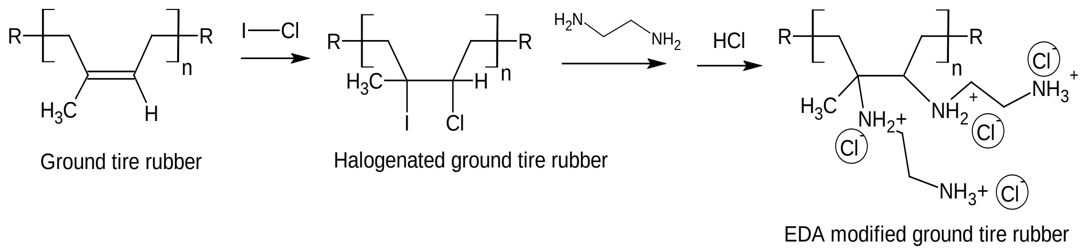


Fig. 2 Reactions for preparation of the modified ground tire rubber; halogenation of carbon-carbon double bond, aminolysis of halogenated ground tire rubber, followed by treatment by HCl to yield EDA modified ground tire rubber

EDA modified ground tire rubber is composed of insoluble site from ground tire rubber and chloride ions as ion exchangeable site in the structure.EDA modified ground tire rubber works by exchanging anions such as NO_3^- in the aqueous solutionwith chloride ion as shown in Fig. 3. Certainly, chloride ion (Cl^-) of EDA modified ground tire rubber can be exchanged with other anions, such as NO_3^-, OH^-, PO_4^{3-} etc.

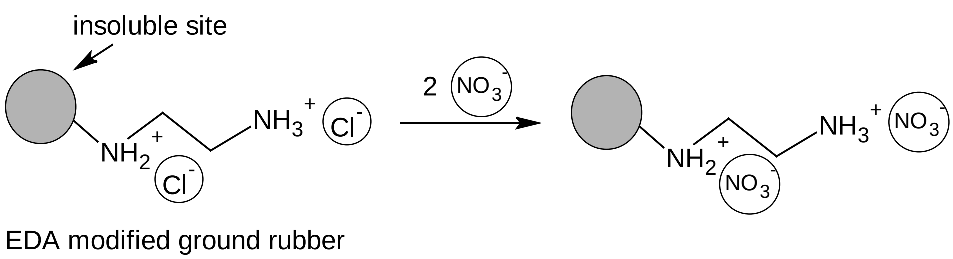


Fig. 3 Ion exchange reaction for removal of NO_3^- by EDA modified ground tire rubber

In this research, the aminolysis reaction of the halogenated ground tire rubber was performed by conventional heating or microwave heating. The ability to removeNO_3^- in aqueous solutionof the obtained modified ground tire rubber was investigated.

Research Methodology

1. Materials and Chemicals

Ground tire rubber obtained from a local recycle shop in Thailand. Ethylenediamine (98.0%), Hydrochoric acid (37%), Sodium chloride (99.5%), Toluene (99.5%), Potassium iodide (99%), Sodium thiosulfate (99.5%), Potassium nitrate (99%), Sulphanilic acid, Sulphuric acid (96%) and Wij's reagent were obtained from Carlo Erba. Brucine sulfate heptahydrate (98%) from Acros. All chemicals were reagent grade or analytical grade and used as received.

2. Preparation of EDA modified ground tire rubber

2.1 Pretreatment of the raw material of ground tire rubber

Ground tire rubber (5.0 g) was added to 150 mL of toluene. The mixture was heated up to its boiling point for 30 minutes. The obtained sample was filtered, washed, and dried at 100^{o}C for 12 hours.

2.2 Modification of ground tire rubber

After pre-treatment by toluene, ground tire rubber was modified by the steps shown in Fig. 2.

2.2.1 Halogenation of ground tire rubber

Ground tire rubber (4.0 g) was added to 25 ml of Wij's solution, which is a solution of iodinemonochloride in acetic acid (1 M) in a 120-mL glass bottle. The mixture was stirred for 2 hours at 25^{o}C. The obtained the halogenated ground tire rubber. It was washed by ethanol and dried at 100 ^{o}C for 12 hours.

2.2.2 Aminolysis of the halogenated ground tire rubber by conventional heating method

Ethylenediamine (50 ml) was added to 5.0 g of the halogenated ground tire rubber. Then it was heated under reflux in oil bath at 120 ^{o}C for 10 and 30 minutes. After cooling down to room temperature, the obtained product was washed with distilled water and dried at 100°C for 12 hours.

2.2.3 Aminolysis of the halogenated ground tire rubber by microwave heating

Ethylenediamine (50 ml) was added to 5.0 g of the halogenated ground tire rubber. Then it was heated under reflux by microwave irradiation (Elextrolux EMM 2005) at 180, 300 and 450 W, respectively, for 10minutes. After cooling down to room temperature, the obtained product was washed with distilled water and dried at 100°C for 12 hours.

2.2.4 Treatment by HCl solution

5 g of the product from 2.1.2.3 was immersed in 500 ml of 0.2 M HCl solution for 12 hours, then it was washed by de-ionized water and dried at 100°C for 12 hours.

3. Study of samples

3.1 Thermal gravimetric analysis (TGA)

Thermal gravimetric analyser (Mettler Toledo model TGA/SDTA 851^{e}) was used to find the component of ground tire rubber (raw material). The sample was run at a heating rate of 20°C/min in the range of 30-850°C, under N_2 and O_2 atmosphere of 20 psi.

3.2 Evaluation of iodine value

The iodine value determination was applied from ASTM D 5902-96 (2001), (Standard Test Method for Rubber-Determination of Residual Unsaturation in Hydrogenated Nitrile Rubber (HNBR) by Iodine Value), for determination double bond content of the samples. 1.0 g of samples was placed into a 125-mL Erlenmeyer flask. Then 25 ml of Wij's solution was added. The mixture was stirred at 23± 1°C for 2 hours. After that 10 ml of 10%wt of potassium iodide (KI) was added. The mixture was titrated with 0.1 N of $Na_2S_2O_3$ standard solution until yellow color disappeared. Then 1 ml of starch indicator solution was added and the mixture was titrated until the deep blue color disappeared. The iodine value was calculated from the equation as follows:

$$A = \frac{N \text{ x } (V_0 - V_1) \text{ x } 12.69}{m}$$

Where A is the iodine value (g of iodine/ 100 g of sample), N is normality of $Na_2S_2O_3$ (N), V_0 is the volume of $Na_2S_2O_3$ used for titration of the blank (ml), V_1 is the volume of $Na_2S_2O_3$ used for titration of the sample (ml), 12.69 is atomic mass of iodine x100 /1000, and m is weight of the sample (g).

3.3 Fourier transform infrared spectrometry (FT-IR) analysis

FT-IR analysis was performed by Spectrum Spotlight FT-IR Imaging System (Elmer model Spectrum Spotlight 300) to identify functional groups of the obtained samples by pyrolysis technique. The samples were added into a test tube and heated with alcohol burner until it became liquid. Then the liquid samples were placed on a KBr plate. All FT-IR spectra were scanned with a resolution of 1 cm^{-1} in the range of 4000–600 cm^{-1}.

3.4 Morphology analysis

The morphology of the samples was analysed by scanning electron microscopy (SEM) (Hitachi model S-3400N) at 20 kV with 1000 magnification.

3.5 Adsorption test and Isotherm study

Experiments were carried out at ambient temperature (25^{o}C). KNO_3^- solution (20 ppm of NO_3^-) and each adsorbent (0.5 g/50 ml) were added into the flasks. The mixture was stirred at 25^{o}C for 24 hours. Then the concentration of NO_3^- before and after adsorption was measured by UV-vis spectrophotometer (Hitachi model U-2900 spectrophotometer 200V) with Brucine method. The same procedure was employed to isotherm study with difference initial concentration of NO_3^- (20, 30, 40 and 50 ppm NO_3^-).

Results and Discussions

1. Raw material

By thermal gravimetric analysis, it was found that ground tire rubber is composed of about 28.7% of combustible substance such as carbon black, 68.4% of organic molecules which considered to be rubber and synthetic rubber content, 2.9% of ash such as ZnO, and other inorganic substances.

2. Iodine value

The iodine values of various kinds of ground tire rubber are listed in Table 1. It was found that ground tire rubber with particle size of 300-700 μm showed a much larger iodine value (41.2) than ground tire rubber with particle size of 2000 μm (5.2). Ground tire rubber was not soluble in Wij's reagent, then it is considered that the smaller particle of ground tire rubber with large amount of carbon-carbon on the larger surface area had more possibility to react with I-Cl rather than the large ground tire rubber. The data revealed that cleaning ground tire rubber by toluene did not change much of iodine value. As a consequence, ground tire rubber with particle size of 300-700 μm after cleaning by toluene was used as raw material in this work.

Table 1. Iodine value of ground tire rubber with different particle sizes before and after cleaning by toluene

Sample	**Size**	**Iodine value (g of Iodine/100 g of sample)**
Ground tire rubber	300 - 700 μm	41.2
Ground tire rubber treated with	300 - 700 μm	40.8
Ground tire rubber	2,000 μm	5.2
Ground tire rubber treated with	2,000 μm	5

3. Reaction conditions

Heating methods, reaction time and reaction temperature for the aminolysis of halogenated ground tire rubber are shown in Table 2. The temperature in conventional heating method was fixed at 120°C. On the other hand, the temperature for microwave heating after reaction about 90-100°C for 180W, 110°C for 300W and 130°C for 450W.

Table 2. Heating methods, conditions for the aminolysis of halogenated ground tire rubber

No.	Heating method	Conditions	Reaction time (minutes)	Temp (°C)	Sample name
1	Ground tire rubber			-	GTR
2	Conventional	Oil bath	10	120	GTR-Oil bath 10min
3		Oil bath	30	120	GTR-Oil bath 30min
4	Microwave heating	180W	10	110	GTR-MW180W 10min
5		300W	10	110	GTR-MW300W 10min
6		450W	10	130	GTR-MW450W 10min

4. Characterization

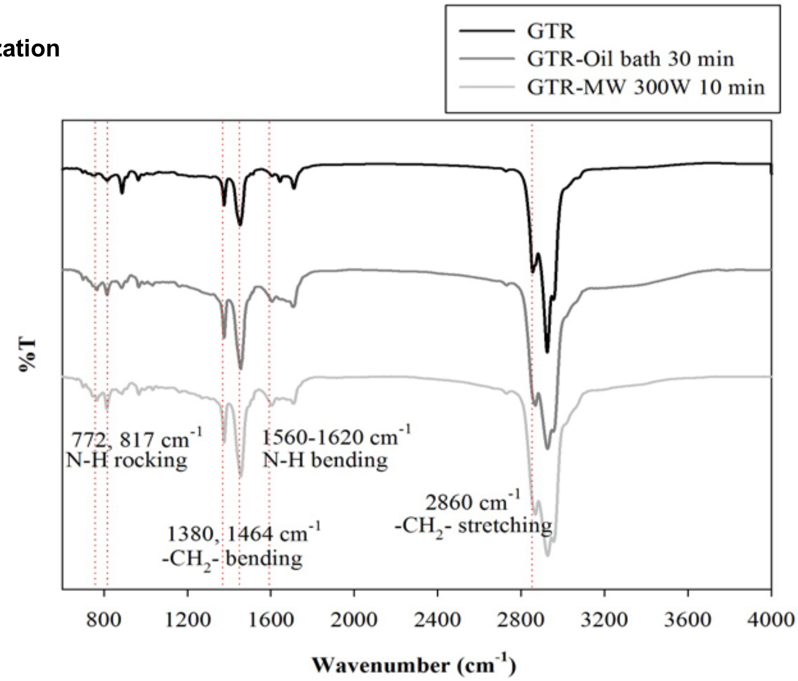


Fig. 4 FT-IR spectra of ground tire rubber (GTR) and EDA modified ground rubber (GTR-Oil bath 30 min and GTR-MW 300W 10 min).

The FT-IR spectra of ground tire rubber (GTR) and EDA modified ground rubber (GTR-Oil bath 30 min and GTR-MW 300W 10 min) are shown in Fig.4. The FTIR spectra of the EDA modified ground rubber similar to GTR, except that the EDA modified ground rubber showed an increase of absorption peak at 772, 817 cm^{-1} corresponded to the rocking vibration of N-H, and peak about 1560-1620 cm^{-1} corresponded to the bending vibration of N-H of secondary ammonium salt. The result suggests the presence of $C–NH_3^+$ and $C–NH_2^+$-groups from EDA in the EDA modified ground rubber (GTR-Oil bath 30 min and GTR-MW 300W 10 min) increased after aminolysis reaction. Moreover, the absorption peak also showed increasing at 1380, 1464 cm^{-1} as induced by bending vibration of $-CH_2$-of EDA, and peak about 2860 cm^{-1} due to the stretching vibration from-CH_2-of EDA

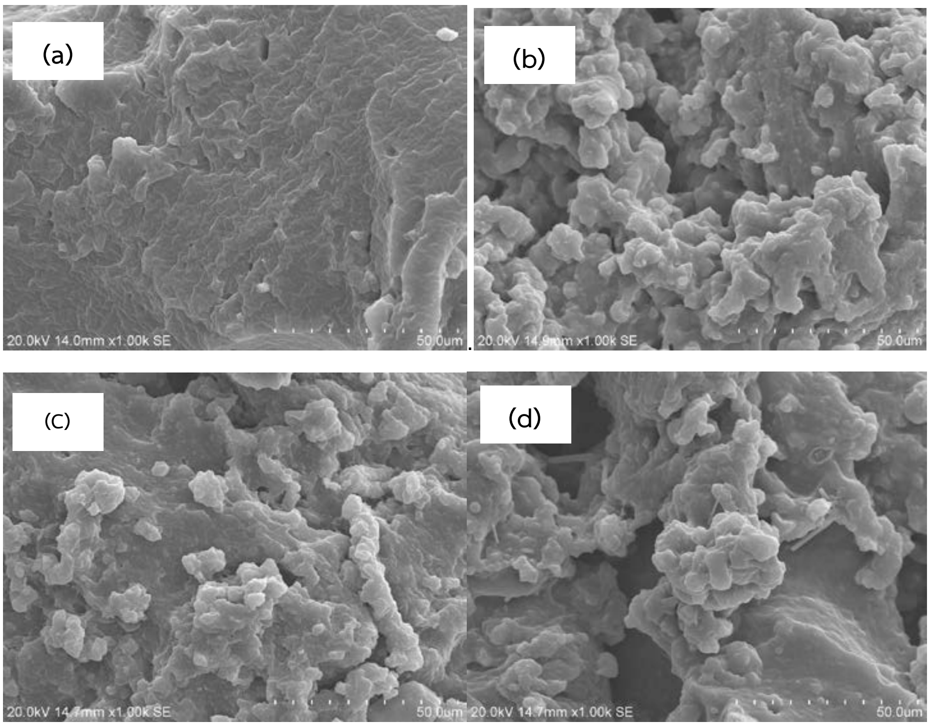


Fig. 5 SEM images of (a) ground tire rubber (GTR), (b) halogenated ground tire rubber, (c) EDA modified ground tire rubber by conventional heating (GTR-Oil bath 30 min) and (d) EDA modified ground tire rubber by microwave heating (GTR- MW 300W 10 min).

Fig. 5 showed the SEM images of ground tire rubber (GTR), halogenated ground tire rubber, EDA modified ground tire rubber by conventional heating (GTR-Oil bath 30 min) and EDA modified ground tire rubber by microwave heating (GTR-MW 300W 10 min). It can be seen that ground tire rubber has relatively smooth surface. The surface became rougher after reacting with I-Cl. This change was possibly explained by the change of chemical structure in ground tire rubber after halogenation. The surface of GTR-Oil bath 30 min and GTR-MW 300W 10 min showed similar rough surface. It seemed that the modification of ground tire rubber introduced a functional group to the surface and also increased the surface area of the rubber particles.

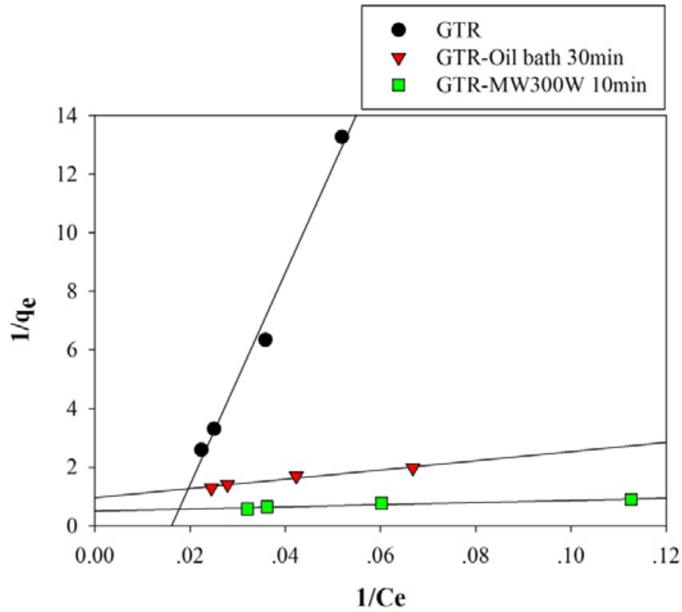
5. Adsorption test

Adsorption test for NO_3^- (20 ppm) were carried out at ambient temperature (25^{o}C) for each adsorbent (0.5 g/50 ml). GTR (raw material) adsorbed only 0.24 mg/g of adsorbed NO_3^- ,while the GTR-Oil bath 30 min and GTR-MW300W 10 min showed 1.75 mg/g and 2.01 mg/g of adsorbed NO_3^-, which was about 8-9 times of that of GTR.

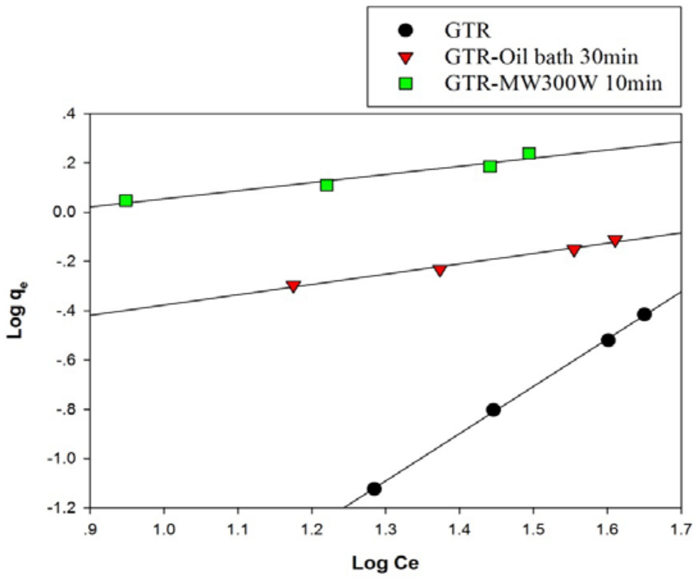
Table 3. Adsorption amount of NO_3^- by ground tire rubber and EDA modified ground tire rubber.

Sample name	**Adsorption capacity (mg/g of adsorbents)**
GTR	0.24
GTR-Oil bath 10min	1.73
GTR-Oil bath 30min	1.75
GTR-MW180W 10min	1.83
GTR-MW300W 10min	**2.01**
GTR-MW450W 10min	1.94

In the adsorption isotherm, the adsorption ability of GTR was compared with those of GTR-Oil bath 30 min and GTR-MW300W 10 min. However, all adsorbents showed a good agreement with Langmuir model and Freundlich model for adsorption isotherm of NO_3^- as shown in Fig. 6 and 7.



(A)



(B)

Fig. 6 Linearized Langmuir (A) and **Fig. 7** Linearized Freundlich (B) adsorption isotherm for NO_3^- adsorption by ground tire rubber (GTR) and EDA modified ground rubber (GTR-Oil bath 30 min and GTR-MW 300W 10 min).

Table 4. Absorption isotherm and parameter for NO_3^- adsorption by ground tire rubber (GTR) and EDA modified ground rubber (GTR-Oil bath 30 min and GTR-MW 300W 10 min).

Sample name	**Langmuir Isotherm**			**Freundlich Isotherm**		
	K_L (L/mg)	**q_{max}(mg/g)**	**R^2**	**K_F**	**n**	**R^2**
GTR	-0.02	-0.17	0.988	2.6×10^{-4}	0.52	1.000
GTR-Oil bath 30min	0.06	1.04	0.964	1.6×10^{-1}	2.39	0.985
GTR-MW300W 10min	0.14	1.97	0.91	5.3×10^{-1}	3.03	0.949

Table 4 showed the results for parameters of the two models and their regression coefficients (R^2) at different concentrations. Adsorption isotherm of both modified ground rubber showed a good agreement with Langmuir model and Freundlich model. From the Langmuir model, the maximum adsorption capacity (q_{max}) of the GTR-MW300W 10 min was 1.97 mg/g, which was higher than 1.04 mg/g of GTR-Oil bath 30 min. The higher K_L value for MW300W 10 min also implied the higher affinity to NO_3^- than that of GTR-Oil bath 30 min. Moreover, K_F from Freundlich model also showed a similar trend of adsorption capacity (K_L) from Langmuir model (1.6×10^{-1} for GTR-MW300W 10 min and $5.3 \times 10^{-1}$for GTR-Oil bath 30min).

The results showed that the modification of ground tire rubber did increase adsorption ability toward NO_3^- because they have functional group for anion adsorption ($–NH_3^+$ and $–NH_2^+–$) after aminolysis reaction. The maximum adsorption capacity from Langmuir (K_L) and Freundlich isotherm (K_F) indicated that the EDA modified ground tire rubber by microwave heating has almost 2 times of adsorption ability of that of GTR-Oil bath 30 min.

Conclusion

Ground tire rubber was successfully modified by the reaction with Wij's reagent followed by the reaction with ethylenediamine. FT-IR indicated that ethylenediamine was successfully introduced into the structure of ground tire rubber. SEM images revealed the rougher surface after the modification.

On adsorption test, EDA modified ground tire rubber (GTR-MW300W 10min) could adsorb almost 9 times of NO_3^- amount of ground tire rubber because they have functional group for anion adsorption ($–NH_3^+$ and $–NH_2^+–$) after aminolysis reaction. The adsorption isotherm of EDA modified ground tire rubber agreed with both Langmuir model and Freundlich model. However, the EDA modified ground tire rubber from microwave heating (GTR-MW300W 10 min) showed higher adsorption ability than EDA modified ground tire rubber from conventional heating (GTR-Oil bath 30 min).

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