Effects of natural rubber latex fraction to glycidyl methacrylate on grafting polymerization and its application as Th$^{4+}$ and UO$_2^{2+}$ ions bio adsorbent

Nurrul Assyikeen Md. Jaffary$^{1,2,a}$, Nor Hasimah Mohamed$^2$, Khoo Kok Siong$^1$, Sofian bin Ibrahim$^2$, Siti Nor Syuhada Bt Hamdan$^2$, Ungku Aida Farzana Binti Ungku Azly$^2$, Syazwani Mohd Fadzil$^1$

$^1$Nuclear Science Program, Nuclear Technology Research Center, Faculty of Science and Technology National University of Malaysia, 43600 UKM Bangi, Selangor, Malaysia
$^2$Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor, Malaysia

$^a$assyikeen@nuclearmalaysia.gov.my

Abstract. Natural rubber (NR) latex was modified by in situ gamma radiation-induced grafting copolymerization of glycidyl methacrylate (GMA). NR latex to GMA emulsion ratio of 100:0, 50:50, 40:60, 30:70 and 20:80 have been investigated at the absorbed dose of 150kGy. The grafted GMA natural rubber-based follow the subsequent chemical modification to anchor phosphate group by open up the epoxy ring. The modified NR was characterized by Fourier transform infrared. Demonstration of modified NR on Th$^{4+}$ and UO$_2^{2+}$ ions adsorption in 25ml of 10ppm standard solution gave 95% and 28% percentage removal respectively.

1. Introduction

Actinides such as thorium and uranium are radioactive materials that occur naturally in our environment and has a significant deposit in monazite [1]. These radioactive materials have upgraded to the elevated level under the chemical processing of monazite ore in order to recover rare earth elements (REEs) and hence, it is called technologically enhanced radioactive material (TENORM). Stream waters close to the rare earth processing operated near Ipoh, Malaysia plant site had revealed to have anthropogenically influenced considering the chemical mobility of radioactive elements in the environment [2]. Separation of these radioactive elements from wastewater before discharging into the stream water using conventional method such as solvent extraction and chemical precipitation are extremely difficult since the present of the radioactive materials is relatively low in concentration and have significant amounts of co-existed elements [3]. Furthermore, these methods required high capital cost, high energy or high volume of reagent, generation of toxic sludge and waste products that need further disposal. Therefore, many studies focused on the development of alternative separation methods with low capital cost and reduce the environmental burden.

Recently, a novel chitosan/clinoptilolite (CS/CPL) adsorbent has been synthesized in the beads form, and the maximum experimental adsorption capacities of 328.32mgTh$^{4+}$/g and 408.62mg UO$_2^{2+}$/g were recorded [4]. A silicon dioxide nano-balls (nano-SiO$_2$) was also prepared by Kaynar and his team with adsorption capacity of Th$^{4+}$ achieved was 188.2 mg/g [5]. An agriculture waste base
adsorbent was among the most studied by researchers for $\text{Th}^{4+}$ ion removal and recovery due to economic reason. De-oiled karanja seed cake has also been used for $\text{Th}^{4+}$ sorption, and the study showed that the bio sorbent suited with pseudo-second order kinetic model with spontaneous and endothermic in nature [6]. Other biomaterials such as rice bran, rice husk, and wheat bran have evaluated where extraction efficiencies of 95.4 and 74.6 % achieved from 4 M nitric acid of 200–4000 ppm $\text{Th}^{4+}$ for RB and WB respectively [7]. Two different groups of adsorptive materials, which are activated carbons and zeolites have been explored as $\text{Th}^{4+}$ adsorbent as well [8]. The activated carbons were prepared from solvent extracted olive pulp (SEOP) and olive stone (OS) by a two-step physical activation method with steam. The study showed that synthetic zeolites have highest removal ability for $\text{Th}^{4+}$.

Other researchers introduced groups like carboxylate on titanium dioxide-densified cellulose [9] and octyl(phenyl)-N,N-diisobutylearabamoyl-methylphosphine oxide (CMPO) ligand on merrifield chloromethylated resin with high adsorption uranium capacity [10]. The strong chelators with target metal can be shown as pKchelators/pKnatural ligands. The greater this ratio, the stronger this chelator will be. Various suitable chelators (sodium bicarbonate, citric acid, two-stage acid leaching procedure) has been used following techniques of natural attenuation, physical methods, chemical processes for uranium remediation from contaminated soil [11].

Natural rubber (NR) is one of the leading commodity in Malaysia and interesting material for chemical modification for actinides removal. Natural rubber possesses a double bond on its polymeric backbone prone to various chemical modifications. Recently, NR latex has successfully functionalized with sulfonic through grafting polymerization for heavy metal removal application [12]. Therefore, in this study we will demonstrate a modification of NR latex by radiation-induced graft polymerization as actinides bio adsorbent. This study will focus on the effect of GMA concentration on the degree of grafting and their effect on adsorption of $\text{Th}^{4+}$ and $\text{UO}_2^{2+}$ from acidic solution.

These adsorbents with chelate effect can be introduced by grafting polymerization for heavy metal removal [13][14]. Study on grafting glycidyl methacrylate (GMA) through electron beam irradiation technique on water hyacinth fibers (Eichhornia crassipes) [15] and banana trunk based fibrous [16] has successfully done for wastewater treatment application.

2. Materials and methods

2.1. Materials

High ammonia natural rubber, HANR latex (60% DSC) used in the present work supplied by Titilatex Sdn Bhd, Malaysia. Glycidyl methacrylate monomer (purity 97%) and Tween 20 (polyethylene glycol sorbitan monolaurate) supplied by SIGMA. Phosphoric acid (85%) was supplied by R&M. $\text{UO}_2^{2+}$ and $\text{Th}^{4+}$ standard solution in 2% nitric acid were supplied by Perkin Elmer. The dose rate of gamma loop in SINAGAMA facilities was determined to be 2.14 kGy/hr by Fricke dosimetry before grafting experiments.

2.2. Radiation-induced graft polymerization

Grafting polymerization was carried by adding NR latex to monomer emulsion containing 5% GMA, 0.5% Tween 20 and 94.5% deionized water at a weight ratio of 100:0, 50:50, 40:60, 30:70 and 20:80 (%wt:%wt) in 60ml screw-capped plastic bottles. All samples were purged with nitrogen gas for 20 minutes before irradiated with gamma ray at a dose of 150 kGy. The GMA grafted natural rubber (GMA-g-NR) were washed using acetone and distilled water in order to remove glycidyl methacrylate homopolymer (PGMA). The residue was dried in drying oven at 50°C for several days until a constant weight was reached. The following Eq. Error! Reference source not found. measured the degree of grafting for grafted NR:
\[ \% \text{Grafting} = \frac{Treated - Untreated}{Untreated} \times 100\% , \]  

where, treated and untreated are the weights of the dry natural rubber (g) after and before grafting, respectively.

2.3. Chemical modification
GMA-g-NR were placed into phosphoric acid solution in the presence of solvent at 80ºC for 3 hours. Finally, the functionalized NR refer as Ph-g-NR was washed with distilled water and dried in an oven overnight.

2.4. FT-IR analysis
FTIR spectra were recorded on a Bruker Platinum ATR TENSOR II. NR, GMA-g-NR and Ph-g-NR were sliced and directly characterized using ATR cell. FTIR spectra were recorded in the range from 500 to 4000 cm\(^{-1}\), with a resolution of 4 cm\(^{-1}\) and averaged over 50 scans.

2.5. Water sorption test
Water uptake was determined by immersing 0.5 gram of Ph-g-NR in excess of deionized water at room temperature [12]. Samples weight were recorded at time 0, 4, 12 and 36 hours. The water uptake was calculated as follows Eq. 2:

\[ \text{Water uptake} (\%) = \frac{(m_t - m_o)}{m_o} \]  

where \( m_o \) and \( m_t \) are the mass of the modified rubber at initial and time \( t \), respectively.

2.6. ICPMS analysis for adsorption efficiency
The sorption efficiencies of Ph-g-NR toward representative actinide ions were carried out using 10 ppm concentration of Th\(^{4+}\) and UO\(^{2+}\) ions in 25 ml 0.1 M HNO\(_3\) acid medium. 0.5g of modified NR were used and the sorption was done using Wisd shaker bath at 25°C and shaking were set at 200 RPMs for 4hrs. The concentration of the solutions was measured by using a Perkin-Elmer Nexion 350x model Inductively Coupled Plasma Mass Spectrometry (ICPMS).

3. Results and discussion

3.1. Grafting degree (GD)
Effect GMA concentration on the grafting yield is shown in Figure 1. The grafting degree for formulation with NR latex to GMA emulsion ratio of 100:0, 50:50, 40:60, 30:70 and 20:80 has been measured to be 0, 5, 10, 20 and 40 \% respectively. It can be noted that grafting degree increases with increased of GMA content. The increased of monomer concentration provides enough contact area between monomer and thermally activated radicals of NR latex particles which will benefit to the grafting polymerization. [16, 17]. It is showed that the graph still increasing dramatically with the increase in GMA concentration. The study at higher GMA monomer concentration shall be conducted and discuss in the future study.
3.2. FTIR analysis on grafted natural rubber, GMA-g-NR

FTIR spectra in Figure 2 shows that the grafting polymerization of GMA onto NR was confirmed by the presence of absorption band at 1728cm$^{-1}$ assigned to C-O stretching of the ester group from GMA and symmetrical stretching of the epoxy ring near 1251cm$^{-1}$. The band at 993cm$^{-1}$ and 908cm$^{-1}$ was attributed to asymmetrical epoxy ring. The successful of GMA grafting on NR based is clearly seen on the formulation NR latex to GMA ratio (%,%) of 20:80 and 30:70 by the existence of 993cm$^{-1}$ and 908cm$^{-1}$ bands. Based on the FTIR spectra, clearly showed that increasing of GMA concentration had increases the grafting degree of modified NR, thus giving the higher integrated area at 993cm$^{-1}$ and 908cm$^{-1}$.

Figure 1. Grafting degree at different ratios between latex to GMA.
3.3. FTIR analysis on modified natural rubber, Ph-g-NR

FTIR spectra in Figure 3 shows the effect of phosphate modification on grafted GMA-g-NR at various fraction. The contraction of epoxy ring to anchor phosphate group was established by appearance of wide band in the region 900–1080 cm\(^{-1}\) which was assigned to P–OH stretching vibration. The wideband around 3100-3600 cm\(^{-1}\) attributed to -OH band that verifies the hydrophilic properties of Ph-g-NR. GMA-g-NR has transformed into Ph-g-NR showed by reducing of the C-O stretching at 1728 cm\(^{-1}\).

The successful of Ph anchored on the opening epoxide can be observed on NR latex to GMA ratio (%,%) of 20:80 and 30:70 where these formulations are chosen for water sorption test and actinides removal application.
Figure 3. FTIR analysis on dry phosphate modified NR at various fraction of NR latex to GMA.

3.4. Water sorption test
Water uptake study conducted using sample formulation NR latex to GMA ratio (%,%) of 20:80 and 30:70 with 20% and 40% grafting degree respectively in Figure 4 showed that the water uptake of the modified rubber is increasing with higher grafting degree.

The GMA-g-NR modification using phosphoric acid leads to the hydrolysis of the epoxide. Figure 3 show that the phosphate group functionalized on the epoxide has increased according to the grafting degree while the phosphate group come with -OH group functionality that will increase hydrophilic properties.
3.5. ICPMS analysis for adsorption efficiency
In order to demonstrate the effect of grafted GMA onto NR, actinide adsorption test performed on Ph-g-NR. Figure 5 shows the Th⁴⁺ and UO₂²⁺ removal using modified NR at 20% and 40% grafting degree. The high percentage removal of thorium was observed using 40% GD compared to the 20% GD. This is due to the higher density of phosphate functional group anchored that will form the ligand binding with Th⁴⁺. Acidic phosphates are known to have an affinity toward actinide ions [18].

**Figure 4.** Effect of grafting degree on water uptake.
It is also observed that the adsorbent tends to remove Th$^{4+}$ ion compared to UO$_2^{2+}$ ion. When the chelate has modified with adding the R-OH groups, it contributes to the addition of the neutral oxygen donors and gives rise to a rule of ligand design [19, 20]. Addition of groups containing neutral oxygen donor leads to an increase in selectivity of the ligand due to the higher magnitude of charge/radius (nm) ratio for large metal ions of Th$^{4+}$ ($4/0.100=40$) over smaller metal ions of UO$_2^{2+}$ ($2/0.2807$)$^{[20]}$. The results suggested that the neutral oxygen donors in Ph-g-NR prefer undergoing complexation with Th$^{4+}$ than UO$_2^{2+}$.

4. Conclusion
Grafting polymerization of GMA onto NR in the latex form by gamma irradiation as actinides bio adsorbents were successfully developed. Grafting degree has been showed increases with increasing of monomer. FTIR analysis has confirmed the success of grafting by the presence ester group and an epoxy ring of GMA in the grafted NR. The fraction of NR latex to GMA gave effect on the grafting degree and does affect the removal efficiency of actinide ion. It was found that the modified NR has a higher tendency for Th$^{4+}$ removal compared to UO$_2^{2+}$ ion.

5. References
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