Original Article

Selective adsorption of indium ions on polyacrylamido-2-methylpropane sulfonic acid-grafted-natural rubber

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Abstract

The adsorption characteristics for In^{3+} ions and a standard binary mix of In^{3+}/Fe^{3+} ions on polyacrylamido-2-methylpropane sulfonic acid-g-natural rubber (PAMPS-g-NR) and its vulcanized form were investigated. The adsorption capacity for In^{3+} was investigated by the batch immersion method. The following parameters were investigated in this study: pH, initial metal concentration, temperature, and regeneration. The adsorption data were fitted with the Freundlich isotherm. Thermodynamic parameters, including Gibbs free energy, enthalpy, and entropy indicate that In^{3+} adsorption onto grafted NR is a feasible, spontaneous, and exothermic process in the temperature range 303-313 K. Separation of metal ions from a binary solution based on ionic radius using vulcanized grafted NR was also investigated. The influences of method of vulcanization, solution temperature and electron dose were studied on adsorption separation efficiency for metal ion mixtures. It was found that the vulcanized rubber can act as a selective adsorbent.

Keywords: 2-acrylamido-2-methylpropane sulfonic acid (AMPS), modified natural rubber, adsorption, indium ion, vulcanized rubber

1. Introduction

Indium is currently used in a wide range of applications. The globally most significant indium consumption is in the form of indium tin oxide (ITO). ITO thin-film coatings are primarily utilized for electrical conduction in a variety of flat-panel displays, normally liquid crystal displays (LCDs). Indium consumption has reportedly increased in response to the increased demand for LCD televisions, smartphones, and tablets. Other indium uses include alloys and solders, compounds, electrical components, and semiconductors. Indium is a rare and valuable metal. Therefore, it is usually recovered from ITO waste, particularly in China, Japan and the Republic of Korea (Tolcin, 2016).

Many methods are used for indium recovery from In-containing residues. These methods can be classified into two types of treatment: hydrometallurgical or pyrometallurgical (Chou *et al.*, 2016). Previous studies have extensively reported on various methods such as solvent extraction (Chou *et al.*, 2016; Li *et al.*, 2006; Virolainen *et al.*, 2011), adsorption (Lei *et al.*, 2009), ion exchange resin (Liu *et al.*, 2006), chlorination (Osamu *et al.*, 2010; Takahashi *et al.*, 2009), and supercritical fluid extraction (Liu *et al.*, 2009). In a hydro-

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metallurgical process, leaching parameters such as acid concentration, temperature, and cementation conditions have been investigated in order to identify the best conditions for indium extraction (Li *et al.*, 2011).

Solvent extraction is commonly used to purify indium from acidic solutions (Alguacil, 1999). Several kinds of extractant have been used for indium, including carboxylic acids, phosphoric acid derivatives, chelating compounds like hydroxyoximes and azoles, and solvating extractants such as tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), and methylisobutyl ketone (MIBK) (Ruan *et al.*, 2012). Bis(2-ethylhexyl) phosphate, known as di-2-ethylhexyl phosphoric acid (D2EHPA), is the most popular extractant, because it has a high loading capacity for indium and good selectivity for indium over many other divalent and trivalent metal ions, such as $Zn(II)$, $Fe(II)$, $Cd(II)$, $Cu(II)$, $Bi(III)$, $La(III)$, $Fe(III)$, $Ga(III)$, and $As(III)$ (Fortes *et al.*, 2003; Li *et al.*, 2006; Sami *et al.*, 2011). Another organophosphorus extractant, 2-ethylhexyl 2-ethylhexyl-phosphonic acid (EHEHPA), has also been reported (Sato & Sato, 1992). Sami *et al.* (2011) studied the recovery of indium when tin is present in the solution, by using D_2EHPA or a mixture of D_2EHPA and TBP.

However, the main drawback of the solvent extraction process is the loss of extractants and solvents, which may cause environmental hazards and economic limitations. Ion exchange can be considered an alternative method. However, it also has some drawbacks, such as slow adsorption and desorption rates, poor selectivity, and a requirement for concentrated electrolytes to be used for desorption. Highly selective ion exchange resins based on chelating functional groups have been studied. However, this approach seems tedious and time-consuming (Liu *et al.*, 2006). Therefore, new methods for the separation and recovery of indium are still being developed.

The adsorption of metal ions from water by natural rubber (NR) and modified NR has attracted significant interest (Gunasekara *et al.*, 2000; Danwabichakul *et al.*, 2008; Phetphaisit *et al.*, 2016). Danwanichakul *et al.* (2008) studied the sorption of Hg^{2+} by vulcanized natural rubber chips. They proposed that sulfur groups in the crosslinks of vulcanized rubber may react with Hg^{2+} resulting in chemisorption. Phetphaisit *et al.* (2016) have used PAMPS-g-NR to remove Pb^{2+}, Cd^{2+}, and Cu^{2+} from standard solutions and from industrial waste water. The adsorption capacity correlated with the ionic radius, and the adsorption mechanism was identified as multilayer adsorption (Freundlich isotherm).

The aim of the present work was to use modified NR and vulcanized modified NR to adsorb the targeted metal ions from aqueous solutions. The adsorption behavior of modified NR was investigated by studying the influences of pH, initial In^{3+} concentration, adsorption isotherm, temperature, and thermodynamic parameters on adsorption. This paper also reports on the effects of vulcanization system, used with modified NR, on selective adsorption of In^{3+} and Fe^{3+} from binary standard aqueous solutions. The effects of curing technique, electron dose and adsorption temperature are also presented.

2. Experimental

2.1 Materials

The chemicals used in this work were of analytical grade and used as supplied. High ammonia natural rubber (HANR) latex (dry rubber content, DRC = 60%) was purchased from Sri Trang Company, Thailand. 2-acrylamido-2-methylpropane sulfonic acid (AMPS; 97%) was supplied from Acros Organics. Dipotassiumperoxodisulphate and sodium hydrogen carbonate were obtained from Carlo Erba Reagents. Poly(ethylene oxide fatty alcohol) (Teric 16A16) was acquired from GSP Product Company, Thailand. Indium (III) nitrate hydrate was supplied by Aldrich. Iron (III) chloride hexahydrate was supplied by Fluka.

2.2 Sample preparation

2.2.1 Modified NR

NR grafted with polyacrylamido sulfonic acid (PAMPS-g-NR) was synthesized in our laboratory as reported in a previous paper (Phetphaisit *et al.*, 2016). Briefly, the PAMPS-g-NR was prepared in one reaction step through grafting copolymerization of AMPS monomer onto the isoprene units of NR via radical polymerization. The content of PAMPS grafted on the rubber chains, in comparison with the isoprene units, was 25%. $T_{g(midpoint)}$ and temperature of degradation were -64°C and 399°C, respectively. The grafted rubber has an ion exchange capacity of approximately 0.045 mg equivalent/1 g of dry rubber.

2.2.2 Vulcanized modified NR

The crosslinked NR was prepared by two alternative methods: chemical vulcanization and electron beam irradiation

Sulfur vulcanization was used as the chemical vulcanization method. Grafted NR and all other components were mixed on a two-roll mill at 50°C. First, the PAMPS-g-NR was masticated on the two-roll mill for 5 minutes, and then stearic acid (1 phr) and ZnO (3 phr) were added and mixed for 5 minutes. After that, 2-mercaptobenzothiazole, MBT (1.5 phr) and N-tert-butyl-2-benzothiazole sulfonamide, TBBS (0.5 phr), were added and mixed thoroughly for 5 minutes. Finally, sulfur as the curing agent was added and mixed into the mixture for 5 minutes. The material was consequently tested with a moving die rheometer. After curing in a compression mold at 120°C for 90% of the cure time, the sheet was cut into square pieces of 2.5 x 3 x 0.2 cm^3 (approximately 1 g/piece)

Electron beam vulcanization was used as the second vulcanization method. Grafted NR without any chemical additives was sheeted out on a two roll mill. The sheets were cut into 2 x 2.5 x 0.3 cm^3 (about 1 g/piece) pieces. The pieces were irradiated with electron beam at doses of 300 and 400 kGy by using an electron accelerator at 20 MeV energy and 10 kW.

Water uptake from 48 h immersion in water, and gel content in dichloromethane for the vulcanized rubber are presented in Table 1.

2.3 Adsorption experiments

The adsorption studies for an In^{3+} standard solution and a mixed In^{3+}/Fe^{3+} solution using the grafted copolymers (PAMPS-g-NR) and vulcanized rubber were performed by immersing a sample (about 1 g piece) in 100 mL of the standard ion solution. In this case, all dry modified rubbers were

immersed in deionized water for 48 hours and then immersed in 0.1 M NaOH solution for 24 hours to convert $–SO_3H$ to $–SO_3^-$. The swollen rubber was placed in 100 mL of an ion solution at pH 1–5 and 30–50ºC for 2 hours. After adsorption for 2 hours, the sample was removed from the solution and Flame Atomic Absorption Spectrometer (FAAS) (Perkin Elmer, Aanalyst model 200) was used to determine the residual concentration of metal ions in solution. Three replicates of each formulation were analyzed. Metal ion concentration adsorbed per unit mass of modified rubber (mg of metal ion/g of dry rubber) was calculated as follows:

$$\text{The amount of metal ion adsorbed (mg/g)} = \frac{[(C_o - C) \text{ x V}]}{(m \text{ x } 1000)} \tag{1}$$

$$\text{The amount of metal ion adsorbed (\%)} = \frac{(C_o - C) \text{ x } 100}{C_o} \tag{2}$$

Here C_o and C are the concentrations of metal ion in the aqueous phase before and after the adsorption (mg/L), respectively; V is the volume of the aqueous phase (mL) and m is the amount of dry modified natural rubber (g).

Table 1.   Water uptake and gel content for grafted NR and vul-canized grafted NR

Property	PAMPS-g-NR	PAMPS-g-NR crosslinked		
		Sulfur vulcanization	Electron beam vulcanization	
			300 kGy	400 kGy
Water uptake (%)	116.3	43.7	31.1	28.9
Gel content (%)	soluble	90.3	76.7	78.8

2.4 Re-use of the modified natural rubber

Metal ions loaded into the grafted NR samples were desorbed by immersing them in 4 M HNO_3 solution (50 mL) at room temperature for 24 hours. The final metal concentration in the aqueous solution was determined by FAAS. Three replicates of each condition were tested. The desorption efficiency was calculated as follows:

$$\text{Desorption efficiency} = \frac{\text{Amount of metal ions desorbed into the aqueous solution x } 100}{\text{Amount of metal ions adsorbed onto the grafted NR}} \tag{3}$$

3. Results and Discussion

3.1 Adsorption of In^{3+}on PAMPS-g-NR

3.1.1 Effect of pH

The pH of the aqueous solution may play an important role in the adsorption ability of a metal ion on the adsorbent. To study this effect, the adsorption of PAMPS-g-NR was studied in the pH region between 1.0 and 5.0 and the results are presented in Figure 1. The PAMPS copolymer in the isoprene structure is primarily responsible for the specific binding of the In^{3+} ions on the sulfonate groups of PAMPS. The amount of In^{3+}adsorbed increased from 0.27 to 0.88 mg/g

of rubber with increasing pH.   The adsorption efficiency increased by about 60% when the pH changed from 1.0 to 5.0. This may be due to the fact that at low pH, the higher concentration of H^+ may compete with metal ions for adsorption on the grafted rubber.   Moreover, the protons may stabilize the negative charge of the sulfonate groups in the PAMPS copolymer, therefore In^{3+} adsorption becomes unfavorable. On the other hand, at high pH, the competition between protons and indium ions becomes less significant, and electrostatic attraction between the negatively charged sulfonate group and positively charged indium ion takes place. This improves the adsorption of indium at high pH values (Calagui *et al.*, 2014; Kwak *et al.*, 2012; Yetimoglu *et al.*, 2007).
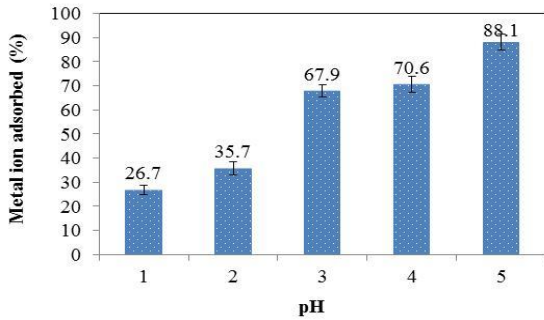
Figure 1.   Effect of pH on adsorption exchange capacity of In^{3+} with grafted NR [C_o = 10 ppm; 40°C]

3.1.2 Effects of initial metal ion concentration and adsorption isotherm

Figure 2 shows the effects of various initial concentrations of In^{3+} on the adsorption capacity of modified natural rubber under fixed pH and temperature. It can be seen that the increase in the initial indium concentration from 10 to 250 ppm increased the equilibrium adsorption capacity from 0.88 to 14.57 mg/g. At a low concentration, the ratio of available binding sites to In^{3+} is high, and all In^{3+} can be bound to the active sites of modified NR. On the other hand, at high concentrations, the percentage of adsorption is lower. This may be caused by the competition between external transport mechanisms of the highly concentrated metal ions from solution through the boundary layer onto the adsorbent, and the adsorption of metal ions on the interior surfaces of pores and voids in the modified NR (Prakash *et al.*, 2011).

The adsorption isotherm was studied to understand the relationship between the quantity of metal adsorbed and the remaining concentration of metal ions in solution at equilibrium at a constant temperature. The equilibrium data of In^{3+} sorption onto modified NR at 313 K were studied using Langmuir and Freundlich isotherm models (Yuan *et al.*, 2010; Data *et al.*, 2012; Kwak *et al.*, 2012).

The Langmuir isotherm describes saturated monolayer adsorption with physical interaction on the adsorbent surface, and can be represented by the following equation.

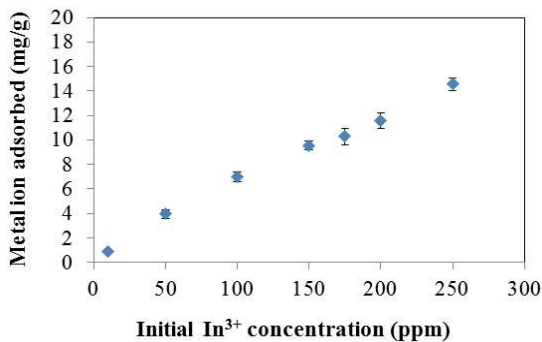$$\frac{C_e}{q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \tag{4}$$

Here C_e is the equilibrium concentration of metal ions (mg/L), q_e is the adsorbed amount at equilibrium (mg/g), the constant Q_m is the maximal metal ion monolayer coverage capacity (mg/ g) and b is related to the surface energy of sorption (L/mg). The plot of C_e/q_e against C_e should be linear with intercept and slope equaling 1/ $Q_m b$ and 1/ Q_m, respectively.

The Freundlich isotherm is normally used to describe multilayer adsorption on heterogeneous surfaces of adsorbents. It is describes both chemical and physical adsorption and is represented by the following equations.

$$q_e = K_F C_e^{1/n} \tag{5}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

Here K_F is an approximate indicator of the adsorption capacity (mg/g) and n is the heterogeneity factor of the favorability of adsorption. Plot of log q_e against log C_e should be linear with intercept and slope equal to log K_F and 1/ n, respectively. Figure 3 and Table 2 show the parameters obtained from fitting the experimental data for adsorption of In^{3+} onto the grafted NR with Langmuir and Freundlich isotherms. The concentration range and volume were 10–250 ppm and 100 mL, respectively. The results show that the Freundlich equation fit the experimental data better than the Langmuir equation, with R^2 value of 0. 994. The slope of Freundlich isotherm for In^{3+} is less than 1. A value of n between 1 and 10 represents heterogeneous adsorption on the adsorbent and implies a strong interactions between the adsorbent and metal ions (Rocha *et al.*, 2009) . Therefore, the adsorption of In^{3+} from aqueous solution was of multilayer type on the modified NR, through both chemical and physical adsorption.
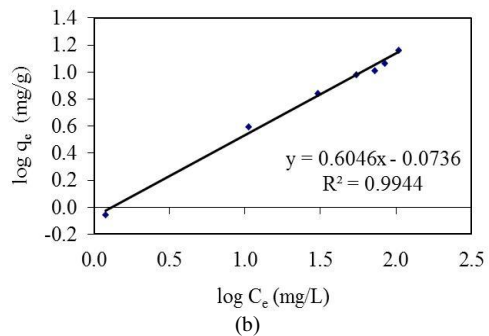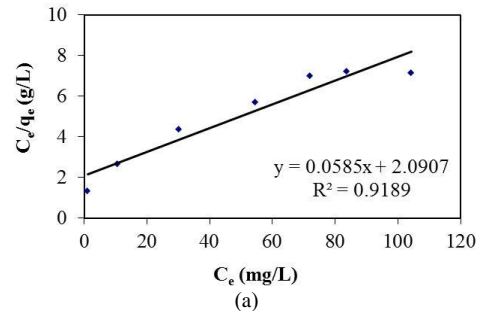

Figure 2.   Effect of initial metal ion concentration on adsorption capacity of In^{3+}onto PAMPS-g-NR [pH = 5; T = 40°C]

(a)

(b)

Figure 3.   Adsorption isotherms for adsorption of In^{3+} ions onto PAMPS-g-NR; (a) Langmuir and (b) Freundlich models

Table 2.   Langmuir and Freundlich isotherm parameters for In^{3+} adsorption

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	Q_m(mg g^{-1})	b (L g^{-1})	R^2	K_F (mg g^{-1})	n	R^2
PAMPS-g-NR	17.09	0.028	0.9189	0.84	1.65	0.9944

3.1.3 Effects of temperature

The influence of temperature on the indium adsorption efficiency of grafted NR was studied by varying the temperature between 30 and 50°C. The adsorption efficiency of the modified NR increased with temperature in the range 30–40°C (Figure 4). An increase in temperature may facilitate the transfer of metal ions from aqueous solution into the porous rubber adsorbent, as the external and intraparticle transport mechanisms are comparatively rapid. However, further elevated temperatures (50°C) may also induce desorption of the heavy metals that are adsorbed by multilayer adsorption, as described by the Freundlich isotherm model (Phetphaisit *et al.*, 2016).

Thermodynamic parameters such as the Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were considered for the adsorption process. These were estimated using the following equations

$$K^o = \frac{C_{solid}}{C_{liquid}} \qquad (7)$$

$$\Delta G^o = -RTlnK^o \qquad (8)$$

$$lnK^o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (9)$$

Here lnK^o is the equilibrium constant, C_{solid} is the equilibrium metal concentration in the adsorbent (mg/L), C_{liquid} is the equilibrium metal concentration in solution (mg/L), T of the temperature (K), and R is the gas constant.
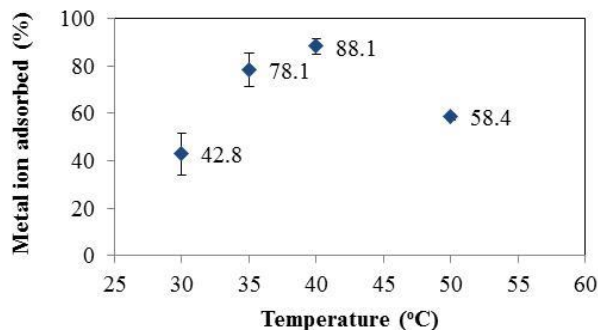

Figure 4.   Effect of temperature on the adsorption capacity of In^{3+} onto PAMPS-g-NR [C_o = 10 ppm; initial pH = 5]

The plot of lnK^o versus 1/T is shown in Figure 5. ΔH^o and ΔS^o were obtained from the slope and intercept of the linear fit to lnK^o versus 1/T. The thermodynamic parameters for the adsorption of indium ions calculated from equations (7)–(9) are presented in Table 3. The negative values of Gibbs free energy at the different temperatures indicate that the process is spontaneous. Furthermore, the decrease of ΔG^o with temperature shows that the adsorption process is more favorable at higher temperatures. Moreover, in general values of ΔG^o from -20 to 0 kJ/mol indicate physisorption, whereas for chemisorption the values lie in the range -80 to -400 kJ/mol (Özcan & Özcan, 2005). The estimates are in the range from -356 to -362 kJ/mol, indicating that adsorption was spontaneous and the adsorption of In^{3+} on sulfonate groups of grafted NR took place via chemisorption. The negative enthalpy change, ΔH^o, shows that the adsorption of In^{3+} onto modified NR is exothermic and that the process is stable energetically. A highly negative value of ΔH^o (-181.30 kJ/mol) supports the notion that the adsorption is chemisorption involving strong forces of attraction and strong bonding on adsorbent surface of the metal ions. The positive ΔS^o indicates that the adsorption process is stable and that the degrees of freedom are increased by adsorption (Calagui *et al.*, 2014; Karapinar & Donat, 2009; Kwak *et al.*, 2012; Li *et al.*, 2012).
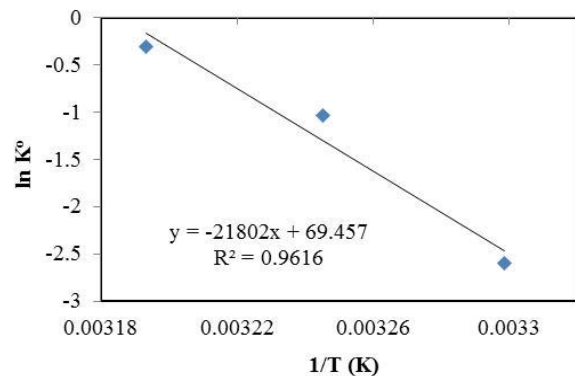

Figure 5.   Linear fit of 1/T versus In K^o for the adsorption of In^{3+} onto PAMPS-g-NR

Table 3.   Thermodynamic parameters for the adsorption of In^{3+} onto modified NR

Temperature (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol)
303	-356.32		
308	-359.21	-181.30	0.58
313	-362.10		

3.1.4 Regeneration of the PAMPS-g-NR

The reusability of the grafted NR was studied, as with multilayer adsorption it might be possible to regenerate the adsorbent. Five adsorption/desorption studies were performed for In^{3+} using optimal 4 M HNO_3 (50 mL) concentration based on our previous work (Phetphaisit *et al.*, 2016). The amount of indium adsorbed by PAMPS-g-NR was determined using 100 mL of 50 ppm In^{3+} solution at 40°C and pH 3 or pH 5, for 2 hours. Table 4 shows that the adsorption and desorption ability of the grafted NR depends on pH of the metal solution. The capacity of the first adsorption at pH 5 was higher than that at pH 3, with values 78% and 50%, respectively. The desorption efficiency using 4 M HNO_3 after the first adsorption was higher than 90% at both pH levels. The adsorption/desorption efficiency decreased with reuse cycles. Especially at pH 5 the desorption ability at the fourth cycle had decreased by more than 30%. The incomplete release of In^{3+} may be caused by the strong interactions of In^{3+} with sulfonate in PAMPS and by pore blockage, which tend to retain ions in the sample.

3.2 Adsorption of In^{3+}/Fe^{3+} by vulcanized modified NR

As discussed above, PAMPS-g-NR showed a high capacity to adsorb In^{3+}. The adsorption isotherm was well fit by the Freundlich isotherm. This means that not only did ion exchange take place on the sulfonate groups, but In^{3+} was also captured in the free volume between the rubber chains. In this section, we describe the reduction of interior space in grafted rubber by two alternative vulcanization methods: chemical and electron beam irradiation vulcanization. Furthermore, the vulcanized rubbers were used to study the competitive adsorption of ions from a binary solution of species with the same ionic valence number but different ionic radii. The experiment was carried out with In^{3+} and Fe^{3+} at concentrations of 10 ppm and 50 ppm, respectively. The adsorption experiment used a volume of 100 mL at pH 2 and 40°C for 2 hours. The pH was limited to values less than or equal to 2 because of precipitation of Fe^{3+} at higher pH.

It was observed that the original grafted NR can adsorb both In^{3+} and Fe^{3+}. The In^{3+} with ionic radius 0.094 nm, which is higher than that of Fe^{3+} (0.069 nm), was more efficiently adsorbed. After vulcanization by the alternative crosslinking methods the materials exhibited selective adsorption based on the ionic radius. The diffusion of the larger In^{3+} into the internal structure of the vulcanized rubber was comparatively limited. The vulcanized rubber prepared by chemical modification contains polysulfidic linkages, while the material prepared with electron beam contains C-C linkages. The looser crosslinking by the polysulfidic linkages resulted in complete adsorption of both types of metal ions. On the other hand, the C-C linkages gave tighter packing, which in turns gave diminished and more selective ion adsorption (Figure 6).

In the case of sulfur vulcanization, it can be seen that more than 4% of In^{3+} can transfer from the bulk solution into the porous vulcanized rubber. A decrease in the adsorption temperature may impede the transfer of metal ions from aqueous solution into the adsorbent. As a consequence, selectivity of the ions using sulfur vulcanized rubber increased with a decrease in the adsorption temperature (Table 5).

Table 4. Amount of In^{3+} after repeated adsorption-desorption cycles at various pH levels of In^{3+} standard solution [C_o = 50 ppm; temp 40°C]

| Cycle no.	pH 3			pH5		
	Adsorption (mg/g)	Desorption		Adsorption (mg/g)	Desorption	
		(mg/g)	%		(mg/g)	%
1 (fresh g40)	2.50 ± 0.35	2.34 ± 0.30	93.36 ± 1.21	3.92 ± 1.17	3.53 ± 0.53	90.04 ± 1.36
2 (1st recycle)	2.37 ± 0.60	2.16 ± 0.26	90.96 ± 1.09	3.73 ± 0.89	3.15 ± 0.80	84.62 ± 2.16
3 (2nd recycle)	2.12 ± 0.86	1.85 ± 0.25	87.02 ± 1.17	3.57 ± 1.19	2.78 ± 0.75	77.84 ± 2.11
4 (3rd recycle)	1.97 ± 0.74	1.65 ± 0.13	83.32 ± 1.18	3.45 ± 1.22	2.37 ± 0.56	68.77 ± 1.63
5 (4th recycle)	1.77 ± 0.50	1.43 ± 0.21	80.66 ± 1.16	3.21 ± 1.93	1.86 ± 0.81	57.82 ± 2.53
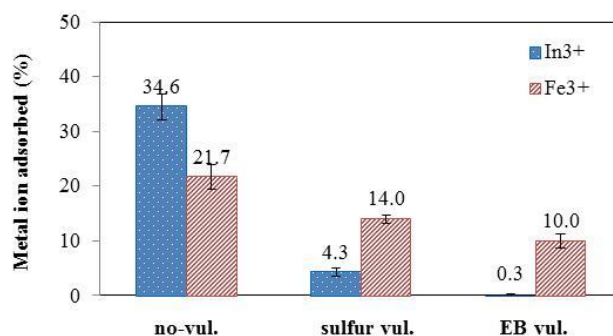
Figure 6. Effect of vulcanization on adsorption capacity of In^{3+}/Fe^{3+} onto PAMPS-g-NR [pH = 2; T = 40°C]

In the case of irradiation vulcanization, decreasing the electron beam dose increased the free volume between polymer molecules, leading to more water swelling (Frounchi *et al.*, 2006). However, although the adsorption capacity for Fe^{3+} increased with decreased electron beam dose, the ion separation at 300 kGy is worse than at 400 kGy.

Table 5.   Metal ion adsorbed fraction (%) by variously vulcanized PAMPS-g-NR

Metal ion	Metal ion adsorbed (%)			
	Sulfur system		Electron beam system	
	30°C	40°C	300 kGy, 40°C	400 kGy, 40°C
In^{3+}	1.83 ± 0.81	4.31 ± 0.67	8.92 ± 0.92	0.32 ± 0.09
Fe^{3+}	15.76 ± 0.44	14.01 ± 0.71	13.05 ± 0.54	10.02 ± 1.25

4. Conclusions

In this study, the adsorption of In^{3+} on grafted NR and selective adsorption, based on ionic radius, of In^{3+}/Fe^{3+} on vulcanized grafted NR have been investigated. The best adsorption conditions for adsorption of In^{3+} were at 10 ppm initial metal ion concentration and 40°C, with pH 5, giving adsorption capacity of almost 88%. The PAMPS-g-NR could be regenerated using 4M HNO_3 with desorption efficiency better than 90% in the first cycle. The adsorption mechanism of In^{3+} by modified NR was a match with the Freundlich adsorption isotherm. Furthermore, the Gibbs free energy for In^{3+} adsorption increased with adsorption temperature (35–40°C). The enthalpy and entropy changes on grafted NR adsorbing In^{3+} were -181.30 kJ/mol and 0.58 kJ/mol, respectively. It is possible that In^{3+} could react with modified NR, and this specific reaction may constitute chemisorption.

We also investigated the effect of free volume between the rubber chains, which can be affected by vulcanization. Selectivity based on ionic radius was achieved using vulcanization. The decrease of interior space by vulcanization resulted in diminished water uptake by the vulcanized rubber and reduced diffusion of the larger sized In^{3+} into the rubber adsorbent, resulting in decreased adsorption capacity for In^{3+}. At 40°C and pH 2, ion separation by the irradiation vulcanized rubber was better than that of the chemically cured one. This is especially true for the material prepared at high radiation dose (400 KGy). Reduction of the adsorption temperature (30°C) increased the separation efficiency at the same level of sulfur curing.

Acknowledgements

References

Alguacil, F. J. (1999). Solvent extraction of indium by LIX 973N. *Hydrometallurgy, 51*, 97–102.

Calagui, M. C., Senoro, D. B., Kan, C., Salvacion, J. W. L., Futalan, C. M., & Wan, M. (2014). Adsorption of indium(III) ions from aqueous solution using chitosan-coated bentonite beads. *Journal of Hazardous Materials, 277*, 120–126.

Chou, W. H., Shen Y. H., Yang, S. J., Hsiao, T. C., & Huang, L. F. (2016). Recovery of Indium from the Etching Solution of Indium Tin Oxide by Solvent Extraction. *Environmental Progress & Sustainable Energy, 35*, 758-763.

Danwabichakul, P., Dechojarasrri, D., Meesumrit, S., & Swangwareesakul, S. (2008). Influence of sulfur-crosslinking in vulcanized rubber chips on mercury (II) removal from contaminated water. *Journal of Hazardous Materials, 154*, 1-8.

Data, A. O., Olalekan, A. P., Olatunya, A. M., & Dada, O. (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn^{2+} Unto Phosphoric Acid Modified Rice Husk. *Journal of Applied Chemistry, 3*, 38–45.

Fortes, M. C. B., Martins, A. H., & Benedetto, J. S. (2003). Indium recovery from acidic aqueous solutions by solvent extraction with D2EHPA: A statistical approach to the experimental design. *Brazilian Journal of Chemical Engineering, 20*, 121–128.

Frounchi, M., Dadbin, S., & Panahinia, F. (2006). Comparison between electron-beam and crosslinking of silicon rubber. *Nuclear Instruments and Methods in Physics Research section B, 243*, 354-358.

Gunasekara, A. S., Donovan, J. A., & Xing, B. (2000). Ground discarded tires remove naphthalene, toluene, and mercury from water. *Chemosphere, 41*, 1155-1160.

Karapinar, N., & Donat, R. (2009). Adsorption behavior of Cu^{2+} and Cd^{2+} onto natural bentonite. *Desalination, 249*, 123–129.

Kwak, N. S., Baek, Y., & Hwang, T. S. (2012). The synthesis of poly(vinylphosphonic acid-co-methacrylic acid) microbeads by suspension polymerization and the characterization of their indium adsorption properties. *Journal of Hazardous Materials, 203–204*, 213 –220.

Lei, Z., Wang, Y., Guo, X., Zhu, Y., & Zhao, Z. (2009). Separation and preconcentration of trace indium(III) from environmental samples with nanometer-size titanium dioxide. *Hydrometallurgy, 95*, 9295.

Li, H., Liu, J., Gao, X., Liu, C., Guo, L., Zhang, S., . . . Liu, C. (2012). Adsorption behavior of indium(III) on modified solvent impregnated resins (MSIRs) containing sec-octylphenoxy acetic acid. *Hydrometallurgy, 121-124*, 60-67.

Li, S., Tang, M., He, J., Yang, S., Tang, C., & Chen, Y. (2006). Extraction of indium from indium–zinc concentrates. *Transactions of Nonferrous Metals Society of China, 16*, 1448–1454.

Li, Y., Liu, Z., Li, Q., & Li, Z. (2011). Recovery of indium from used indium-tin oxide (ITO) targets. *Hydrometallurgy, 105*, 207–212.

Liu, J. S., Chen, H., Chen, X. Y., Guo, Z. L., Hu, Y. C., Liu, C. P., & Sun, Y. Z. (2006). Extraction and separation of In(III), Ga(III) and Zn(II) from sulfate solution using extraction resin. *Hydrometallurgy, 82*, 137–143.

Liu, H. M., Wu, C. C., Lin, Y. H., & Chiang, C. K. (2009). Recovery of indium from etching wastewater using supercritical carbon dioxide extraction. *Journal of Hazardous Materials, 172*, 744–748.

Osamu, T., Takashi, S., Ryoji, I., & Masahiro, H. (2010). Pyrometallurgical recovery of indium from dental metal recycling sludge by chlorination treatment with ammonium chloride. *Materials Transactions, 51*, 1136–1140.

Özcan, A., & Özcan A. S. (2005). Adsorption of acid red 57 from aqueous solutions onto surfactant-modified sepiolite. *Journal of Hazardous Materials, 125*, 252 –259.

Phetphaisit, C. W., Yuanyang, S., & Chuachuad-Chiyasith, W. (2016). Polyacrylamido-2-methyl-1-propane sulfonic acid-grafted-natural rubber as bio-adsorbent for heavy metal removal from aqueous standard solution and industrial wastewater. *Journal of Hazardous Materials, 301*, 163-171.

Prakash, N., Acharylu, R., Sudha, P. N., & Renganathan, N. G. (2011). Kinetics of copper and nickel removal from industrial wastewater using chitosan impregnated polyurethane foam. *Journal of Chemical Research, 1*(4), 1–11.

Rocha, C. G., Zaia, D. A. M., Ventura da Silva Alfaya, R., & Alberto da Silva Alfaya, A. (2009). Use of rice straw as biosorbent for removal of Cu(II), Zn(II), Cd(II) and Hg(II) ions in industrial effluents. *Journal of Hazardous Materials, 166*, 383–388.

Ruan, J., Guo, Y., & Qiao, Q. (2012). Recovery of indium from scrap TFT-LCDs by solvent extraction. *Procedia Environmental Sciences, 16*, 545–551.

Sami, V., Don I., & Erkki, P. (2011). Recovery of indium from indium tin oxide by solvent extraction. *Hydrometallurgy, 107*, 56–61.

Sato, T., & Sato, K. (1992). Liquid–liquid extraction of indium (III) from aqueous acid solutions by acid organophosphorus compounds. *Hydrometallurgy, 30*, 367–383.

Takahashi, K., Sasaki, K., Dodbiba, G., Sadaki, J., Nobuaki, S., & Fujita, T. (2009). Recovering indium from the liquid crystal display of discarded cellular phones by means of chloride-Induced vaporization at relatively low temperature. *Metallurgical and Materials Transactions A, 40*, 891–900.

Tolcin, A. C. (2016, September 1). Indium. U.S. geological survey, minerals commodity summaries, January 2016. Retrieved from http://minerals.usgs.gov/mine rals/pubs/commodity/indium/mcs-2016-indiu.pdf

Virolainen, S., Ibana, D., & Paatero, E. (2011). Recovery of indium from indium tin oxide by solvent extraction. *Hydrometallurgy, 107*, 56–61.

Yetimoglu, E. K., Kahraman, M. V., Ercan, O., Akdemir, Z. S., & Apohan, N. K. (2007). N-vinylpyrrolidone /acrylic acid/2-acrylamido-2-methylpropane sulfonic acid based hydrogels: Synthesis, characterization and their application in the removal of heavy metals. *Reactive and Functional Polymers, 67*, 451–460.

Yuan, Y., Liu, J., Zhou, B., Yao, S., Li, H., & Xu, W. (2010). Synthesis of coated solvent impregnated resin for the adsorption of indium (III). *Hydrometallurgy, 101*, 148-155.