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Study on natural rubber absorption of selected actinides

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Abstract. This paper contains the research done concerning natural rubber. This included its origin, economic importance, and how the functional groups in the natural rubber reacted with selected actinides. The selected actinides discussed were Thorium, Uranium and Plutonium. The information was retrieved from different sources including information from laboratory experiments. The results obtained were gathered when conducted under different conditions. The conditions varied based on the temperatures and the pH. The functional groups exhibited different outcomes when reacted with different actinides under different conditions. The functional groups namely amine carboxyl and hydroxyl groups have different efficiency and capacity of adsorption. Besides economic importance, the environmental significance of rubber also has been discussed.

1. Natural rubber

Natural rubber which is also known as caoutchouc is an addition of polymers of an organic compound called isoprene. It was discovered by Christopher Columbus in 1495-1496 after he saw American Indians playing with balls that were made from trees juice and were bouncing. It was named caoutchouc by Charles de la Condamine, a French scientist which simply means 'weeping tree' [4]. It was first grown in London by Henry Wickham. Another attempt was done in Sri Lanka but the results were no pleasant. In Singapore which was thought as the basis of the industry in Southeast Asia another plantation was set [3]. Table 1 below shows the leading countries in the production of Natural Rubber and the amount of production in tons per year (Association of Natural Rubber Producing Countries).



Table 1. Leading countries in the production of Natural Rubber and the amount of production in tons per year (Association of Natural Rubber Producing Countries).

Country produce (tons)	Country produce (tons)	Country produce (tons)	Country produce (tons)
Thailand 4,305,069	Malaysia 826,421	Nigeria 149,052	Gabon 22,691
Indonesia 3,107,544	Philippines 444,818	Sri Lanka 130,421	Ghana 21,440
Viet Nam 946,865	Guatemala 356,392	Liberia 74,750	Cambodia 20,099
India 900,000	Coted'ivoire 289,563	Cameroon 55,605	Ecuador 18,249
China 864,806	Brazil 185,725	Mexico 51,397	

2. Economic importance

Natural rubber is one of the commodities the nation's growing the product use for export. In Thailand, it holds the fifth position of the ten export product groups. It shares 5.7% of the income the nation of Thailand gets from the exports. Rubber is used to manufacture products like tire, balls, bands, shoes which are used as commodities of trade [11]. Rubber cultivation acts as a source of employment. The rubber tree is becoming a significant source of wood as a result of improved wood technology. Rubberwood can be used to substitute timber from natural forest since it is a by-product of latex and can be grown in renewable plantations [6].

3. Composition

Rubber consists of elastic polymers or elastomers which are arranged in chainlike molecules (Table 2). The molecules can stretch and regain their original shape again. The monomer isoprene (2-methyl-1, 3-butadiene) is a joined diene hydrocarbon. In the isoprene chain, NR has C=C, a bonding which makes it difficult to be oxidized [8]. The rubber from the first opening of a mature tree consists of the solvent fraction which is insoluble. The fraction is formed through carbon-carbon bonding also called hard-gel. The 80-90 percent of the solid rubber is formed by the hard-gel. The residual solvent fraction which is soluble has low molecular weight and is formed by oxidative degradation [8].

Table 2. Composition of fresh Natural Rubber Latex.

Constituent	%, Content
Minerals	0.7-0.9
Rubber	30-40
Resins	1.5-3.0
Proteins	1.0-1.5
Water	55-60
Carbohydrates	0.8-1.0

The weight of a molecule of Latex or cis-1, 4-polyisoprene ranges from 100,000 to 1000,000 Daltons. Natural rubber contains other materials. These are resins, proteins, fatty acids some inorganic materials which salts are. Synthetic natural rubber can be obtained from the synthesis of polyisoprene (Rolere et al. 69). Shown below is the chemical structure of cis-polyisoprene and which is the major component of the natural rubber.

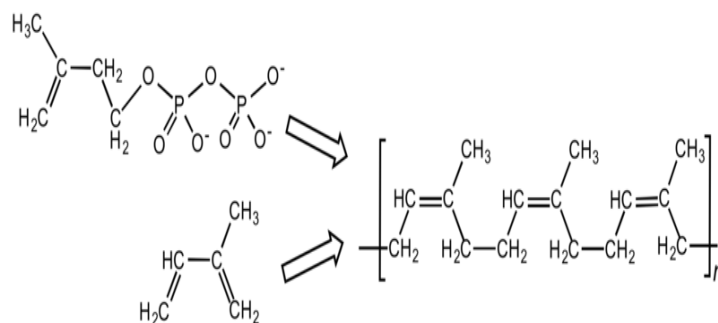


Figure 1. Natural rubber functional groups.

Natural rubber contains functional groups which include fatty acids, ester among others. Through oxirane group, an amine binds to the rubber molecule or the binding can be done by neutralizing the latex before the amine is added. The 4-amino-para-phenyl diamine (PAA) has a faster reaction than that of meta-Nitro-Aniline (mNA). The least reactive is the N-isopropyl-N'-phenyl-para-phenyl diamine (IPPD) [1]. In many polyisoprenes, the groups of the fatty acid ester are the α -terminal group structures. The long chain of fatty acid ester persists even after deproteinization and acetone extraction methods for its purification. Each one molecule of natural rubber contains two molecules of the ester with long-chain fatty acid. The glyceride and $-\text{CH}_2\text{OP}$ groups at the chain ends of the Natural rubber can be removed by saponification [1].

By adding 1wt% mixture of saturated fatty acid, which acts as a nucleating agent and the addition of a plasticizer, that is, unsaturated fatty acid can speed the crystallization of synthetic cis-1,4-polyisoprene. The addition of hydroxyl group by the process hydroboration esterifies the Natural Rubber at the 3,4-isoprene with stearic acid. The stearyl group at the temperatures of -25°C , stimulates the crystallization of the natural rubber. When the linked fatty acids are used in the place of the stearyl group, no stimulation occurs on the crystallization. On adding methyl linoleate to the stearyl, the esterified rubber, the crystallization occurs at the highest rate at -25°C .

A drying agent such as sodium hydroxide or phosphorus pentoxide when used to remove water from the natural rubber, phospholipids and proteins at the end of the rubber chain make branching points. During the storage, the gel fraction is formed as the two functional groups of the natural rubber which are active react. The formation of a micelle structure through hydrogen bonding of polar groups found in the molecules of phospholipids brings together the phospholipids [9]. Most of the phospholipids in non-polar and polar solvents don't undergo solubilization and form the micelle structure. The hydrogen bonding does not permit the mobility of the phosphate groups which may be found in the Natural rubber.

Hydrogen peroxide and sodium nitrite are used as reagents can be used to obtain Liquid natural rubber from natural rubber latex through the degradation chemical reaction. The samples of Liquid natural rubber contain hydroxyl and carbonyl as functional groups at their ends when preparing in acidic and basic mediums. Chemically the reagents do not react in an alkaline medium and the chains of the natural rubber split through the process of oxidation. In acidic medium, the reagents react forming peroxyxynitrous acid which further decomposes to form the radicals of hydroxyl. The hydroxyl radical split the natural rubber chains to form hydroxyl groups at the ends [1]. The hydroxyl group (OH) at the end of the long chain natural rubber molecule can be esterification. The peptide bond formation is one of the most important reactions of the amine group. During these reactions, the water molecules $\alpha\text{-NH}_3^+$ group found in amino acids and COO^- which is in the second amino acid.

3.1 The functional groups remove heavy metals from solutions

The functional groups found in natural rubber have the ability to absorb some heavy metals from the liquid solution. The metals that can be absorbed include, cadmium and lead. This is done onto the

biomass of the blue-green alga *Anabaena sphaerica* from an aqueous solution which can be affected by the contact time, pH, the concentration of the metal ion and biosorbent dosage [1]. There are some peptides of amino acids which are as a result of $-\text{COOH}$ and $-\text{NH}_2$ group which combine with heavy metals like Mn^{2+} , Cu^{2+} , Co^{2+} and Ca^{2+} . The Hg^{2+} , Cd^{2+} and Pb^{2+} ions are highly toxic and can denature the proteins found in the Natural rubber especially the enzymes. The absorption of mercury and lead ions (Figure 3) can be minimized through their combination with proteins. The ions of these metals with proteins form precipitates when linked with amino groups and the carboxyl groups. The Mg^{2+} form ionic bonding between the molecules of rubber.

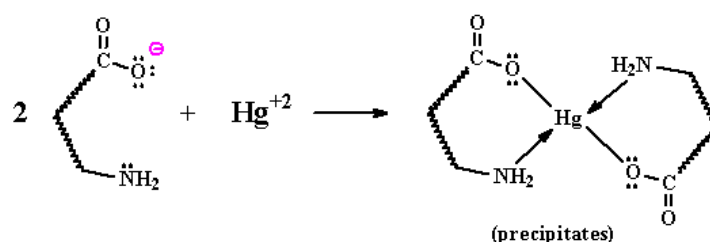


Figure 2. Absorption of mercury ions through their combination with proteins.

The chemical reaction of the amino group is determined by $\alpha\text{-NH}_2$ and $\alpha\text{-COOH}$ (carboxyl group). The Carboxyl group participates in forming an ester. The processes like decarboxylation, reduction and oxidation can be used to detect the presence of an amine group [10]. The adsorption capacity of Natural rubber increases from Pb^{2+} to Cd^{2+} and then Cu^{2+} [7]. The adsorption of the functional groups of rubber increases with the increase in the amount of PAMPS. There are optimum conditions which facilitate the adsorption process of Pb^{2+} , Cu^{2+} and Cd^{2+} by the hydroxyl, carbonyl, and amine groups. These are the temperature of $30\text{--}40^\circ\text{C}$ and pH range of 4-5. The efficiency of desorption and the capacity of adsorption do not significantly decrease [10].

The active functional groups that interact with the ions in the aqueous is affected by the amount of pathogen-associated molecular patterns (PAMPS). PAMPS also affects the swelling of rubber and the process of cavities generation in the adsorbent [10]. There is an increase in metal ions adsorption with an initial metal ion concentration increase. In the initial concentration of Pb^{2+} and Cd^{2+} of approximately 500mg of metal ion per 25mL make the exchange of the ions constant. Above 150mg of metal ion/25mL concentration of Cu^{2+} the adsorption of the copper ions remains constant [5].

The functional groups Carboxyl (COOH) and amine (NH_2) react with plutonium, cesium, and strontium using photoelectron spectroscopy method. The sorbent has the highest capacity of adsorption in plutonium. The cesium, strontium react with the pairs of electron of nitrogen and oxygen absorbent of Amine and carboxyl groups. The degrees of oxidation of plutonium are equal for the bisorbent [10].

There are complexes of uranium and thorium. Thorium complex is gotten when Thorium reacts with the hydroxyl group. The complex form increases the solubility and adsorption of Thorium. When the thorium reacts with the hydroxyl group in the process of adsorption, the complex form obtained is $\text{Th}(\text{OH})_4$ which is obtained above pH 5 [10].

Thorium reaction with a hydroxyl group to give Thorium hydroxide is as shown in Figure 3.

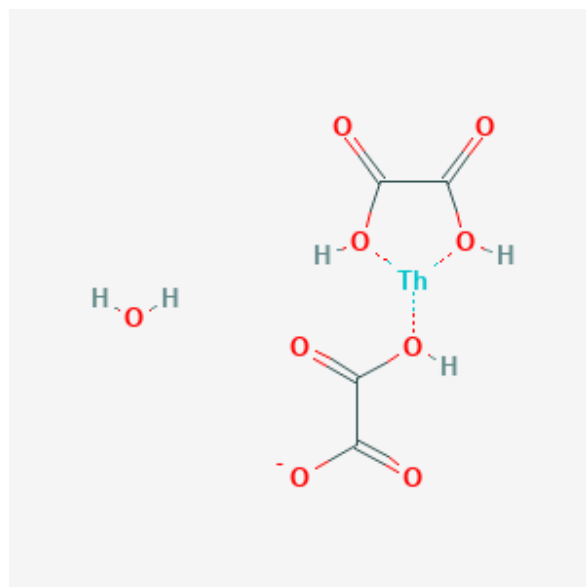


Figure 3. Thorium reaction with a hydroxyl group to give Thorium hydroxide.

As with the thorium in the reaction described above, it will occur with uranium and six of hydroxyl groups forming Uranium hydroxide in the same mechanism almost as shown in the following Figure 4.

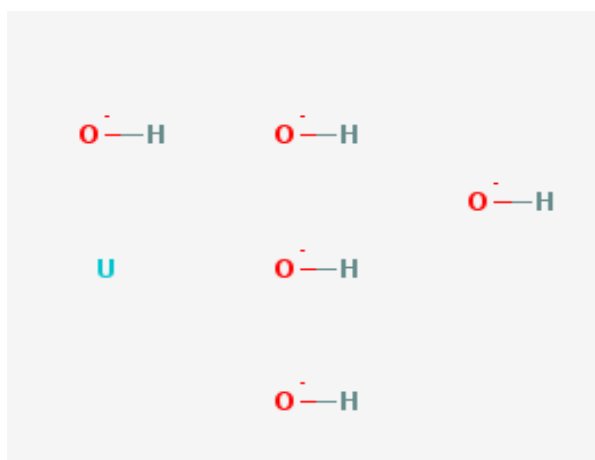


Figure 4. Hydroxyl groups forming Uranium hydroxide.

It would be very logical to assume that the plutonium would behave like the other actinides, such as uranium and thorium, and that is what happened. Plutonium reacts with the hydroxyl group following the same pattern and mechanism forming plutonium hydroxide as shown in Figure 5.

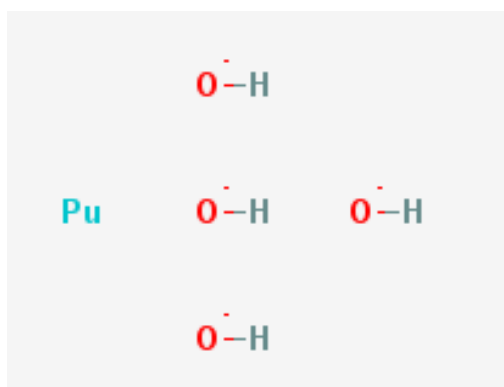


Figure 5. Plutonium reacts with the hydroxyl group, forming plutonium hydroxide.

4. Recommendations

Further research on the pH on the efficiency and adsorption capacity of the heavy metals by the functional groups associated with natural rubber. More research on how these functional groups react with other metal apart from cadmium, copper, and lead and how the reaction behaves under different conditions. Also, more research on the adsorption of other metals in the actinide group can be done.

5. Conclusion

The Natural which is a renewable product has a very great economic importance to the countries' economy and has an environmental advantage over the synthetic products. Natural rubber molecule has functional groups linked at its terminals and they take part in reaction with heavy metals, that is, hydroxyl, amine and carbonyl groups. The groups react with the metal ions in water solution or an aqueous solution in optimum conditions which gives nearly constant results if no external interference is applied.

6. References

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