EXTRACTION OF LITHIUM BY USING ADSORPTION PROCESS FROM LUBE OILS AND SEA WATER

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Abstract— Lithium is one of the most sought after metal in recent times due to focus in electric vehicles, renewable energy and energy storage. If the society chooses to employ only lithium ion technologies for decarbonization of transport and energy sector, the demand for lithium in the future is anticipated to significantly increase. The global lithium consumption has more than tripled from 40,000tonnes to 1, 40,000tonnes since 2000. At this growth rate we are likely to face a lithium shortage with serious economic and environmental consequences. Used Motor Oil or Waste Lube Oil can really be useless and toxic. A drop of used lube oil can contaminate thousands and thousands of gallons of water. It sticks to metals, it is slow to degrade, it is the major ingredient of oil contamination of waterways and it ends up polluting sources of drinking water. One of the contaminants in these oils are lithium. Once this gets mixed in water, it pollutes the water. A safe blood level of lithium is 0.6 and 1.2 milliequivalents per liter (mEq/L). Lithium toxicity can happen when this level reaches 1.5 mEq/L or higher. In this project the concentration of lithium in lube oils and Sea water are tested and determined. Few adsorbent materials like graphene oxide, reduced graphene oxide and its complexes were synthesized and were tested for adsorption. Characterization for a few of these was also done. The aim of this project is to develop an adsorbent material which has higher Lithium extraction efficiency so that enough lithium can be extracted to satisfy the future needs.

Keywords— Lithium, Lubricating Oils, Artificial Sea Water, Adsorption, GO, RGO

I. INTRODUCTION

Lithium is an important metal with various applications in the coming generation technologies like electric mobility, energy storage and cordless devices. The compounds of lithium are also used in ceramic industry, glass industry, pharmaceuticals, lubricating greases, aluminium production. As lithium cannot be substituted in most of its applications, the demand for lithium is increasing 8-11% annually. The main reason for the growing demand of lithium is the production of electric cars. [1]

Getting to know regarding the negative impacts on climate change and the need of reducing the carbon dioxide emissions has resulted in the electrification of vehicles.[2] Currently, only 2% of the world's electricity is used by transport sector. Electrification of road transport like small trucks and cars would solve many problems. The main option for powering the electric vehicles are lithium ion batteries, which is going to have a high demand in the coming decades.[3]

At present, global transport depends on a single fossil resource which is petrol which produces 95 percent of total energy used for transport. 62 percent of the oil consumption in the world happens in the transport sector only. The costs of oil have fluctuated drastically. On the other hand, it is known that the present trend oil dependence is environmentally, socially, economically not sustainable. [2]

The lithium salts are hygroscopic in nature which means the toxicity range in the water might increase due to its pervasive nature. Generally, when 5gms of lithium chloride dissolved in aqueous solution and if consumed, leads to fatal poisoning. Lithium salts such as lithium carbonate are used in psychiatry treatment. If the dosage exceeds 20mg/l leads to the risk of death. Though it is used in medicine for prevention of future manic and depressive episodes. Its higher intake could lead to mental disorders or permanent coma stage. From these conditions it is evident that with the very low intake of lithium salts is hazardous to human health and other environmental risks.

The negative impacts are not only intended on human health but also to the floral species. With the irregular disposal of lithium oriented batteries, engine oils and other electrical equipment into the environment could impair key soil bacterium that enhances nourishment of the plants. Lithium reduces the plant growth with numerous physiological processes interruptions and change in metabolism actions.

Because of the abundance in the reserves of lithium and its increasing demand, extraction of lithium from various sources by using different methods has attracted a great interestworldwide. It is important to extract lithium in the most effective, more environmentally sustainable, at low cost and in a scalable way. One among such methods is adsorption.

In this project, the sources concentrated were waste oils and sea water from which lithium is to be extracted. Firstly, the concentration of lithium in waste oils was tested and found out. And in sea water also it was determined and by increasing the lithium concentration in it, because of the presence of other slats, its concentration was found out. And few adsorbent materials were prepared and their efficiency was tested. Though these adsorbent materials are not a great success, more materials are to be tried and the best adsorbent materials should be found out and make the extraction process better and implement this in a larger scale to meet the demand of lithium.

II. SCOPE OF THE STUDY

The scope of the study is to extract lithium by using the method of adsorption from lubricating oils and Sea water by using different adsorbents.

- Optimizing and analyzing adsorption technique for determining the lithium concentration.
- Varying the weights of the adsorbent materials, monitoring the effectiveness of the extraction process.
- The lithium extraction in India is in the initial stage and the comparative study with different materials and methods is under progress.

III. OBJECTIVES OF THE STUDY

- To determine the concentration of lithium in the used engine oils and Sea water.
- Preparation of adsorbent materials.
- Monitoring and evaluating the adsorption efficiency.
- To study the characterization of the adsorbent materials.

IV. MATERIALS AND METHODS

Sample preparation:

Solvent 1- Distilled water

A weighing bottle was taken and was put on the weighing pan. Three Oil samples were weighed separately for 1.23g and were put in three different bottles and 25ml of distilled water was added in each bottle. These three bottles were put in the water bath for a contact time of 1 hour at room temperature of 30°C. After 1 hour, three bottles are removed from the water bath. As the density of water is greater than the density of oil, the oil floats on the water. The floating oil was removed from each bottle and to the remaining water; 25ml of distilled water was added in each bottle and was put in water bath for 1 hour at room temperature. Again after one hour, the three bottles were taken out and the oily portions were removed and to it 25ml of water was added and put in water bath for the same time and at the same temperature as before. The process of removing the oil portion and adding 25ml of water into each bottle at keeping in the water bath was repeated two more times. That is, a total of four cycles was done.

Solvent 2- Warm Water

The same procedure that is mentioned above was repeated. But the only difference is that in the place of distilled water, warm water whose temperature is 40°C was used as solvent. And the contact time in the water bath is 1hr and the temperature of it was set to 40 °C.

The same procedure is done for fresh engine oil of cars and bikes.

These samples are analysed for lithium concentration and also the concentration of other elements using icp-oes (Inductively coupled plasma optical emission spectroscopy). Before analysing the samples, these samples are to be filtered using nylon micro syringe filters of size 0.2 microns.

Synthetic Sea water preparation

The concentration of lithium in sea water is 0.178ppm. There are also many salts present in the sea water which might have an effect on the concentration of lithium. To check this, 1 litre of synthetic sea water was prepared and the effect of these salts on the lithium concentration was studied.

The main constituents of sea water are Cl^-, Na^+, $SO4^{2-}$, Mg^{+2}, Ca^{+2}, K^+, $HCO3^-$, Br^-, Sr^{2+}, B^{3+}, F^- Lyman and Fleming formula which was derived in 1940 is the most common recipe used for the preparation of artificial sea water. The mass of every compound per kilogram of the solution for artificial sea water with salinity of 35% was calculated. There are two important factors that are to be considered for the preparation of this water. They are: The composition of the reagents must be known and they have to be weighable and addition of these salts is to be done in order to avoid precipitation of insoluble compounds.

Table 1 Formula for 1kg of 35.00% salinity artificial sea water

Gravimetric Salts	
Salt	**G/Kg of solution**
NaCl	23.926
Na2SO4	4.008
KCl	0.677
NaHCO3	0.196
KBr	0.098
H3BO3	0.026
NaF	0.003
Volumetric Salts	
Salt	**G/Kg of solution**
MgCl2.H2O	10.831
CaCl2.2H2O	1.518
SrCl2.6H2O	0.023

The salts NaCl, Na_2SO_4, KCl, KBr, NaF were dried for about 1hour in the oven and then weighed. These salts were weighed in anhydrous form. And the remaining salts which include $NaHCO_3$ and H_3BO_3 were weighed without drying. This is because of the uncertainty in the composition of these salts in the dried forms. There is a chance of precipitation of the salts like $CaCO_3$, $CaSO_4$, $SrCO_3$ and $SrSO_4$ while mixing the contents of artificial sea water. To prevent this, the total artificial sea water is divided into two portions taken in two different containers. In one container, two-third of total amount of water was taken and the gravimetric salts were added to it and were mixed thoroughly. The remaining one-third of the water was taken in another container and into it $MgCl_2$, $CaCl_2$ and $SrCl_2$ were added and mixed. And finally the two solutions were thoroughly mixed while stirring continuously.

Fig 1 *Artificial Sea water preparation*

Preparation of adsorbent materials

The method selected for the extraction of lithium is adsorption. **Adsorption** is the most prominent method for the extraction of lithium from sea water or brines. Most commonly used adsorbent for lithium extraction are manganese oxide, titanium hydroxide, amorphous aluminium oxide, etc. It is important to identify that the lithium has to be in contact with the adsorbents for a long period of time. The adsorbents are available mostly in the powder from which would require energy intensive process for the recovery of lithium. Some adsorbents are very expensive. Various adsorbents have been used for the selective recovery of lithium from sea water and brine lakes. The recovery from sea water would be of less purity because of it being contaminated by Na^+ions.

The lithium adsorption of different materials is studied. The materials are as follows:

- Bentonite Clay
- Reduced graphene oxide
- Graphene oxide
- Graphene oxide –aluminium oxyhydroxide
- Reduced Grapheneoxide –aluminium oxyhydroxide

V. RESULTS AND DISCUSSIONS

The concentration of Lithium in engine oils

The metals in the lubricating oils come from a large number of sources like contamination, wear and additives. Wear metals are a result of friction and corrosion of the components of engine such as bearings, pistons etc during operation. These include additive elements like Ca,Zn and P and the wear metals such as Ag, Al, Ba, Cd, Cr, Cu, Fe, Mg, Mo, Na, Ni, Pb, Sn. Additive metals are macro and the wear metals are trace(Yuna Kim et al 2013). Used Motor Oil or Waste Lube Oil can really be useless and toxic. A drop of used lube oil can contaminate thousands and thousands of gallons of water. The useful metals can be recovered from these oils.

The physical and chemical composition of the used oil differs from virgin oil because of the changes that occur during their use. From the results below it can be observed that in both virgin and used oils the concentration of titanium is higher compared to all other metals present in the oil. In used engine oils titanium is followed by calcium and bismuth whereas in the virgin oil of both bikes and cars, titanium is followed by zinc.

Table 2 Used oil sample with distilled water and warm water

Element and Its wavelength	with distilled water (ppm)	with warm water (ppm)
Ag 3280	0.003409	-0.006890
Al 1670	0.03125	0.02852
B_ 2497	0.02773	0.06620
Ba 4554	0.008977	0.1261
Bi 2230	1.598	0.3022
Ca 3968	0.4383	2.258
Ca 4226	0.4272	2.191
Cd 2288	0.001607	0.0001870
Co 2286	0.002807	-0.00007900
Cr 2835	0.009896	0.004099
Cu 3247	0.001734	0.001046
Fe 2382	0.1750	0.08229
Ga 2943	0.05370	-0.008996
Li 6707	**0.004156**	**0.0009890**
Mg 2802	0.08251	0.1774
Mg 2852	0.07344	0.1683
Mn 2576	0.009719	0.004262
Ni 2216	-0.0004780	-0.007669
Pb 2203	-0.01735	-0.02045
Ti 3349	4.351	2.730
Zn 2138	0.08475	0.1776

From the results it is clear that the concentration of lithium in the used engine oils is very low and is not worth extracting it. So, lithium cannot be recovered from these used engine oils. Lithium can be extracted from other sources such as brines or sea.

Results for artificial Sea water

Seawater can act as one of the next generation of lithium resources for the future lithium mining industry.(Sixie Yang et al 2018). The concentration of lithium in Sea water is 0.17mg/l.

Table 3 Concentration of lithium in artificial sea water

Sample no	Concentration (ppm)
1	0.1428
2	0.3077
3	2.028
4	0.2736
5	1.394
6	10.63

Lithium concentration on adding the adsorbent material

Adsorption capacity:

Adsorption capacity which is also known as loading is the amount of adsorbate that is taken up by adsorbent per unit volume or mass of adsorbent. Adsorption capacity is commonly represented as 'q' and is expressed in terms of the volume(V) of the adsorbate adsorbed by the adsorbent of unit mass.

Efficiency of Bentonite clay

Table 4 Lithium concentration after addition of bentonite clay

Weight (mg)	Initial lithium concentration (ppm)	Final lithium Concentration (ppm)	% of lithium added in Excess
10	10	11.79	17.9
50	10	11.27	12.7
100	10	11.24	12.4
250	10	10.22	2.2
500	10	9.149	8.51 (adsorbed)

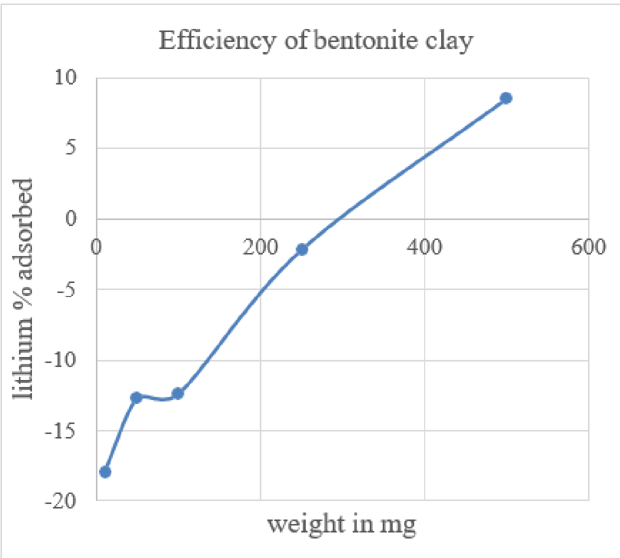

Fig 2 Efficiency of Bentonite clay

The concentration of lithium in the above solutions increased because of the presence of lithium in the bentonite clay. But at addition of more quantity of the adsorbent, the final lithium concentration has reduced which means some of it was adsorbed by the clay but very little.

Table 5 Efficiency of Reduced graphene oxide

Weight (mg)	Initial lithium concentration (ppm)	Final lithium concentration(ppm)	% Adsorbed
10	10	9.92	0.80%
20	10	9.24	7.60%
30	10	9.01	9.90%
40	10	8.62	13.8%
50	10	8.32	16.8%

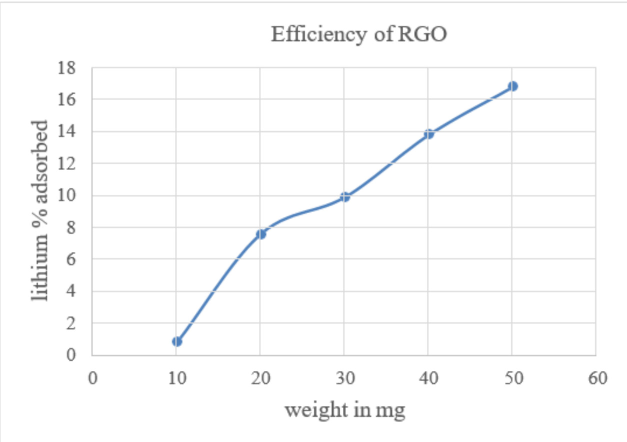

Fig 3 Efficiency of reduced graphene oxide

In case of reduced graphene oxide, with increase in the quantity of the material, the final concentration of lithium is reducing slightly which means greater quantities of this material reduces the final concentration of lithium in the solution which implies large quantity of RGO adsorbs higher lithium.

Efficiency of Graphene Oxide

Table 6 Lithium concentration after addition of GO

Weight (mg)	Initial lithium concentration (ppm)	Final lithium concentration (ppm)	% Adsorbed
10	10	9.46	5.40%
20	10	9.24	7.60%
30	10	8.84	11.6%
40	10	7.90	21.0%
50	10	6.60	34.0%

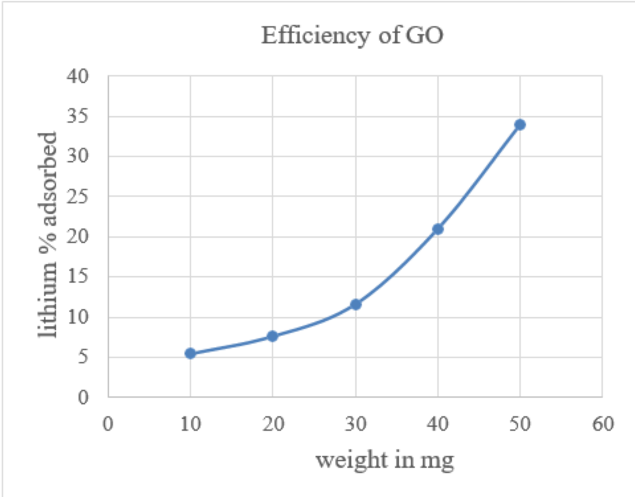

Fig 4 Efficiency of graphene oxide

In case of GO, with the increase in the quantity of the material, the final concentration of the lithium has decreased more than and RGO which suggest that this isn't a better adsorbent than RGO.

Efficiency of RGO and Aluminum hydroxide complex

Table 7 Lithium concentration after addition of reduced graphene oxide and Aluminum hydroxide complex

Weight (mg)	Initial lithium concentration (ppm)	Final lithium concentration(ppm)	% Adsorbed
10	10	9.86	1.40%
20	10	9.21	7.90%
30	10	8.72	12.80%
40	10	7.46	25.40%
50	10	7.14	28.60%

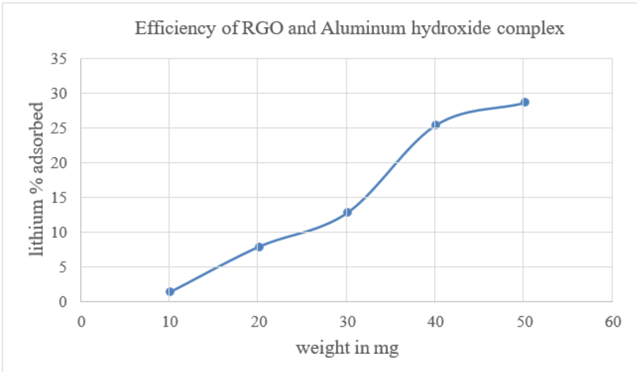

Fig 5 Efficiency of RGO and $Al(OH)_3$ complex

With the increase in the quantity of the adsorbent, the adsorption capacity is increasing but not very effectively. As it was previously seen that RGO is not an effective adsorbent of lithium. Hence its complex is also not so efficient.

Efficiency of graphene oxide and Aluminum hydroxide complex

Table 8 *Lithium concentration after addition of graphene oxide and Aluminum hydroxidecomplex*

Weight (mg)	Initial lithium concentration (ppm)	Final lithium concentration(ppm)	% Adsorbed
10	10	8.52	14.80%
20	10	8.04	19.60%
30	10	7.84	21.60%
40	10	6.25	37.50%
50	10	5.24	47.60%

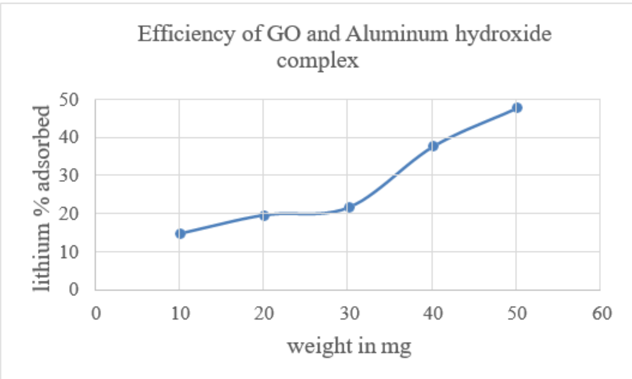

Fig 6 Efficiency of GO and Al(OH)3 complex

from the above results of GO, it is clear that the graphene oxide power is adsorbing the lithium well and Aluminium hydroxide is also a good adsorbent of lithium. So the complex of these two compounds has adsorbed high lithium content compared to all other materials.

Comparison of all the adsorbents

The graph represents the adsorption efficiencies of the four adsorbents namely, Graphene oxide, reduced graphene oxide, graphene oxide and aluminum hydroxide complex and reduced graphene oxide and aluminum hydroxide complex. From the results it is clear that the highest efficiency among the prepared four adsorbents was exhibited by the complex of graphene oxide and aluminum hydroxide which is 47.60%. And the least adsorption efficiency among the four was exhibited by reduced graphene oxide. As reduced graphene oxide showed least efficiency, the complex of this compound with aluminum hydroxide also showed lesser efficiency.

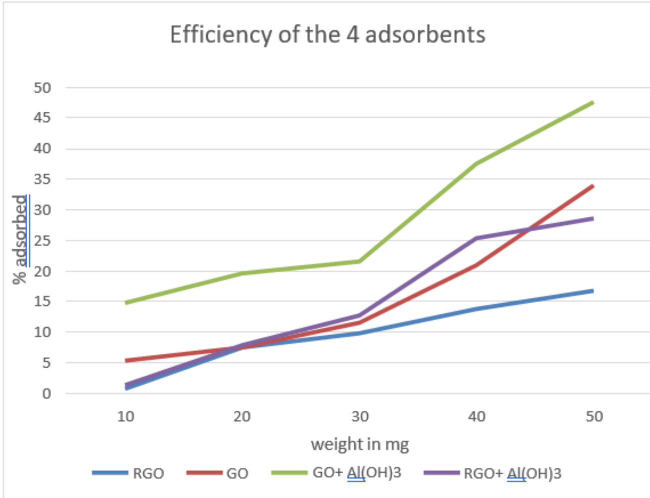

Fig 7 Efficiency of 4 adsorbents

VI. CONCLUSIONS

In the present study, the main element concentrated is lithium. Its high concentration in the water is very toxic. On the other hand this element has vast applications in many fields mainly in the manufacture of lithium ion batteries for electric vehicles and many electric gadgets. India is not producing lithium; it is exporting lithium from other countries like China. The aim of this project is to extract lithium from sources using adsorption mechanism. In this, firstly the concentration of lithium in the lubricating oils was analyzed. Along with many heavy metals, some concentration of lithium was present as it is the main constituent that provides lubrication. These lube oils are very dangerous when discharged into water or soil. So, it is important to recover these elements and reduce the toxicity. Here, the targeted element is lithium. And then, the Sea water was tested for its lithium concentration. Adsorbents were prepared and few of them were analyzed by FTIR and AFM. Before trying the adsorbents on lube oils and sea water, we first tested them on 10ppm lithium concentration solution. Five adsorbents were prepared and were tested. This is just a fundamental idea to find the viability of lithium adsorption mechanism using these adsorbents. We have reduced a minimal percentage of 47% as a result. From this it can be concluded that certain adsorption techniques are not beneficial. But, it is evident that certain mechanisms could help in retrieving higher alkali metals corresponding to lithium characteristics based on their atomic number and hygroscopic in nature.

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