Chapter- 4

Tamarugite production using organic solvent precipitation

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4.1 Introduction

In the previous sections, the synthesis of tamarugite has been described. To achieve tamarugite as the product, the leaching of white aluminium dross with aq. NaOH solution and then the addition of H_2SO_4 has been done. The solution was allowed to crystallize to generate tamarugite. However, the presence of other phases like $Na_3H(SO_4)_2$ and $NaHSO_4$ was also detected.

In order to prepare tamarugite with greater purity, an alternative method has been developed. In the present chapter, the generation of tamarugite has been carried out using organic solvent precipitation. This method involves the utilization of organic solvents alongside the aqueous solutions.

As explained later in this chapter, the major factors contributing the precipitation of solute from aqueous medium are the difference in the dielectric constants for the organic solvents and the difference in the solubility of the solute in the two media. The saturation of the solution, the addition of the required ions in the required stoichiometry and the temperature difference between the aqueous solutions and the organic solvent, play important roles in the precipitation of tamarugite. The method of organic solvent precipitation is well known in the pharmaceutical industries. It is used to produce a specific phase from the aqueous solution.

The precipitated tamarugite has been subjected to jar test and a comparative examination of the coagulation property has been done. This is done to study the coagulation tendency of organic solvent precipitated tamarugite with respect to crystallized tamarugite (described in the previous chapter), poly aluminium chloride (PAC) and commercial alum. The comparison of the turbidity change with the dosage has been illustrated, along with the change in the pH of the water.

To analyse the recovery of the organic solvents, tamarugite has been precipitated using the recycling the organic solvents. For this, ethanol has been taken as an example. The precipitation of tamarugite has been repeated four times. The characterization of the recycled ethanol has been provided. Also, the characterization results of the precipitated tamarugite samples have also been provided.

A comparison of the two methods of preparation of tamarugite has been given. The differences in the resultant products and their characteristics have been described. The changes in the coagulation properties have been discussed.

In the end, the major conclusions drawn from this chapter have been elucidated. This chapter connects the waste utilization to the water recycling, along with an alternative method of producing tamarugite.

4.2 Synthesis of tamarugite using organic solvent precipitation

The chief source of aluminium content in tamarugite is white aluminium dross. As mentioned in the chapter 2, the initial step involved is the leaching of raw feed with sulphuric acid solution. The parameters are mentioned previously. This leads to the reaction of aluminium and alumina with sulphuric acid.

The formation of aluminium sulphate proceeds as shown in eq. (4.1- 4.2) [58].

$$2\ Al + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ H_2 \qquad (4.1)$$

$$Al_2O_3 + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ H_2O \qquad (4.2)$$

The leaching experiment has been done to extract aluminium content into the leach liquor. The liquor obtained post leaching is filtered to separate the unreacted solid residue from the leach liquor. To determine the aluminium content in the solution, the complexometric titrations have been done. For this, the EDTA salts, EBT-indicator and $ZnSO_4$ aqueous solutions are used. The method used for the titrations are described in Chapter 2. The titrations have been repeated twice and the average values have been calculated.

With a feed of 2 g white aluminium dross powder, approximately 1.31 g of aluminium gets extracted into the solution. This amounts to nearly 0.048 moles of aluminium. To ensure the composition of the resultant product, an equivalent amount of sodium ions need be supplied to the solution. For this, aq. NaOH solution is prepared such that the aluminium and sodium ions become equal in amount.

The method of synthesizing tamarugite described in the previous chapter has one drawback. The amount of sodium present in the resultant product was fairly high. This led to the generation of the other sulphate phases. Even after multiple alterations of the parameters, the amount of sodium remained higher than aluminium, ultimately generating the sulphate phases. To ensure that the exact composition of tamarugite is achieved, the leaching of white aluminium dross with sulphuric acid is carried out, instead of sodium hydroxide.

With the addition of aq. NaOH solution to the leached filtrate, the solution mixture contains Na^+, Al^{3+} and SO_4^{2-} ions. However, the formation of tamarugite does not take place in this case. As shown in Figure 4.1, the solution is saturated and thermostated at 45 °C for 4 hours.

While the organic solvents (Acetonitrile, Tert-butyl alcohol, Propan-2-ol and Ethanol) are thermostated at higher temperature, the saturated solution mixture is maintained at 20 °C. Figure 4.1 shows the transfer of small volume of the solution (2.5 mL) to these organic solvents (47.5 mL).

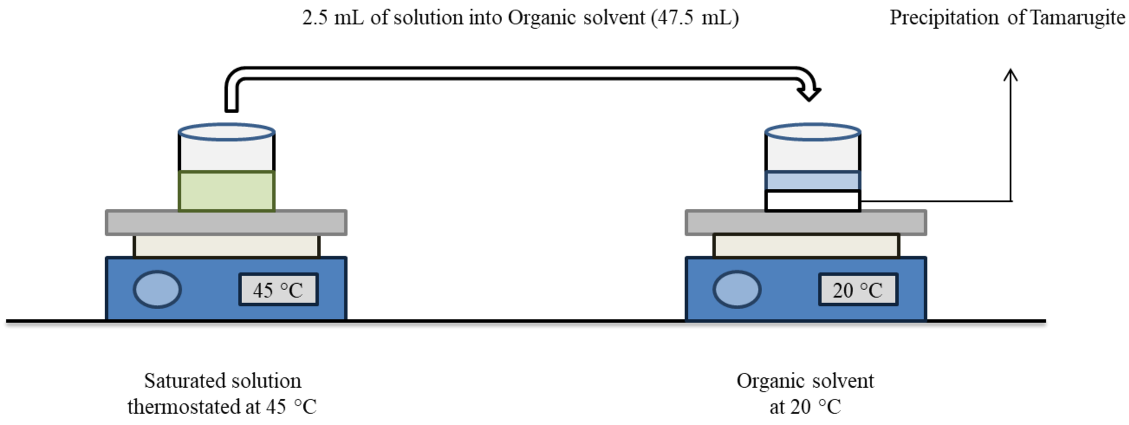


Figure 4.1: The schematic diagram for the precipitation of tamarugite using the organic solvents

With the addition of the saturated solution to the organic solvents, white tamarugite is precipitated. For complete precipitation of tamarugite from the solution, the organic solvent is stirred at 400 rpm for 10 minutes.

Table 4.1: Various organic solvents used for the experiments and their dielectric constants compared to water

Organic Solvent	Dielectric constant
Acetonitrile	36.55
Ethanol	25.02
2 – Methyl – 2 – Propanol	12.50
Propan – 2 – ol	20.07
Water	79.99

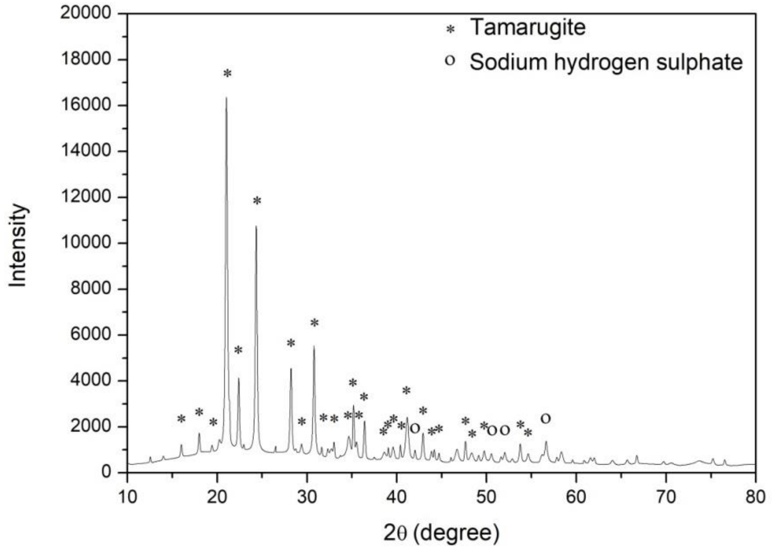
It is essential to understand why these organic solvents were chosen. These organic solvents have dielectric constant lower than water and these solvents are completely miscible with water. The difference in the dielectric constants of the organic solvents causes the rejection of the solute dissolved in the aqueous solution. The dielectric constants are mentioned in the Table 4.1.

After the precipitation of tamarugite, the beaker containing the organic solvents with tamarugite is left undisturbed for around 15 minutes. After this, the decantation of organic solvent is carried out, leaving behind the crop of tamarugite that settles down. A slurry is prepared by adding methanol to the beaker. This slurry is transferred to the centrifugation tubes and subjected to centrifugation.

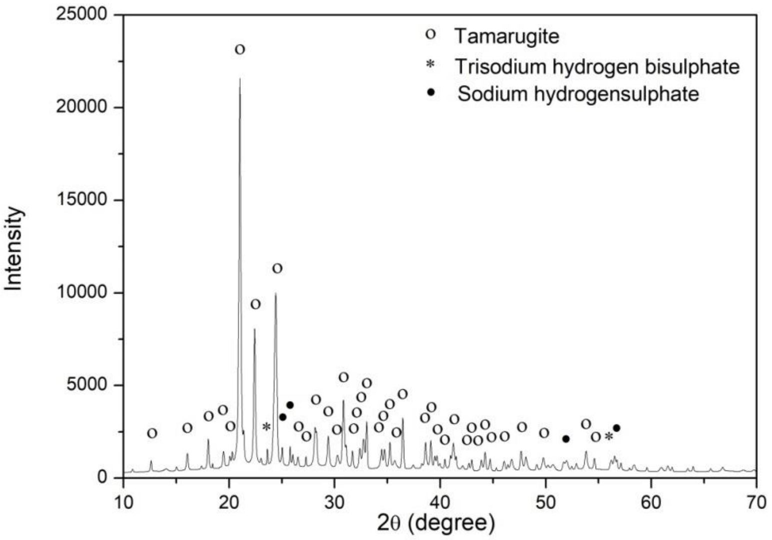
The process of centrifugation is repeated multiple times to ensure the reduction of the pH of the methanol. After this, the samples of tamarugite have been stored in the desiccator to dry. All the samples obtained in the end of the experiments were white fine powders. The sogginess of the samples was completely removed. The washing with methanol and drying in desiccator facilitates the removal of the sogginess. These samples have been characterized; the results are described in the next sections.

4.3 Characterization of organic solvents precipitated tamarugite

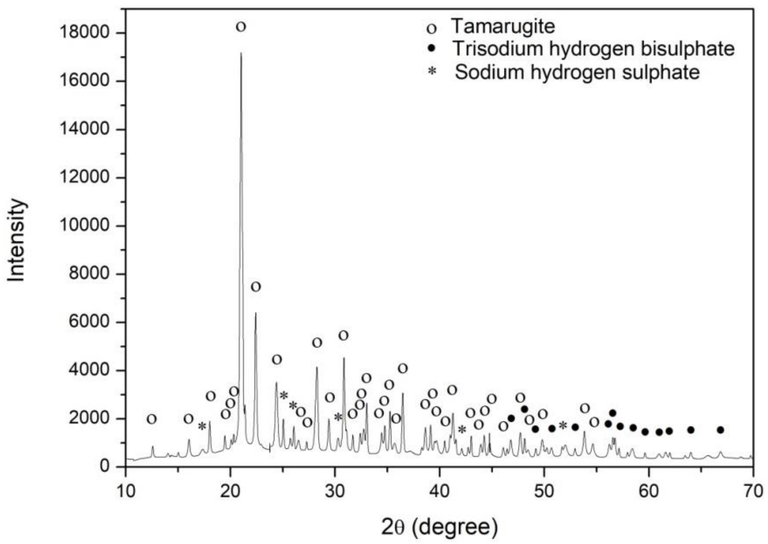
The precipitated tamarugite samples have been characterized using XRD and SEM-EDS facilities. The XRD patterns of the samples are shown in the figure 4.2.



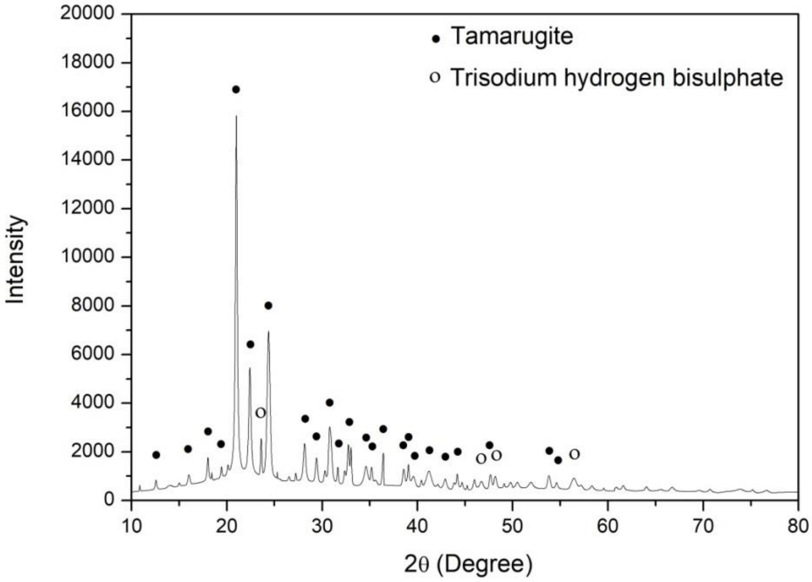
Acetonitrile



Ethanol



Propan-2-ol



Tert-Butyl Alcohol

Figure 4.2: X – ray diffraction pattern of Tamarugite precipitated from: a. Acetonitrile, b. Ethanol, c. propan-2-ol and d. Tert-butyl alcohol

As observed from the XRD patterns, the major phase identified is tamarugite, which was the primary objective of the present research. The other phases, $Na_3H(SO_4)_2$ and $NaHSO_4$ are present in lesser quantities, the peaks of these phases are very less in numbers and intensities, compared to that of tamarugite.

The major peaks identified for tamarugite precipitated from acetonitrile are at 21.03°, 22.40°, 24.31°, 28.27° and 30.80°. Sodium hydrogen bisulphate was identified at 42.12°, 50.56°, 52.06° and 56.65°. For tamarugite precipitated from ethanol, the major peaks for tamarugite were 21.06°, 22.49°, 24.49° and 30.87°. Trisodium hydrogen bisulphate has been identified at 23.58° and 56.17°, whereas sodium hydrogen bisulphate is at 25.07°, 25.71°, 51.80° and 56.65°.

Similarly, for tamarugite precipitated from propan-2-ol, the major peaks are at 21.04°, 22.46°, 24.34°, 28.26° and 30.80°. Trisodium hydrogen bisulphate has a few minor peaks at 46.85°, 48.22° and 56.54°. Some peaks of sodium hydrogen sulphate are at 25.10°, 26.07° and 30.34°. Tamarugite precipitated using Tert-butyl alcohol had peaks at 21.01°, 22.42°, 24.34° and 30.83°. Trisodium hydrogen bisulphate was identified at 23.59°, 46.75°, 48.11° and 56.40°.

Comparing the patterns of tamarugite samples precipitated using the various organic solvents, it can be observed that tamarugite is clearly the dominant phase and trisodium hydrogen bisulphate and sodium hydrogen sulphate are minor phases. The peak positions of tamarugite are quite consistent and the intensities of the peaks are also similar. As described in the literature, the organic solvents have the capacity to precipitate a particular phase from the aqueous solution [132]. This method is exploited in producing drugs. A similar trend is observed for the precipitation of tamarugite.

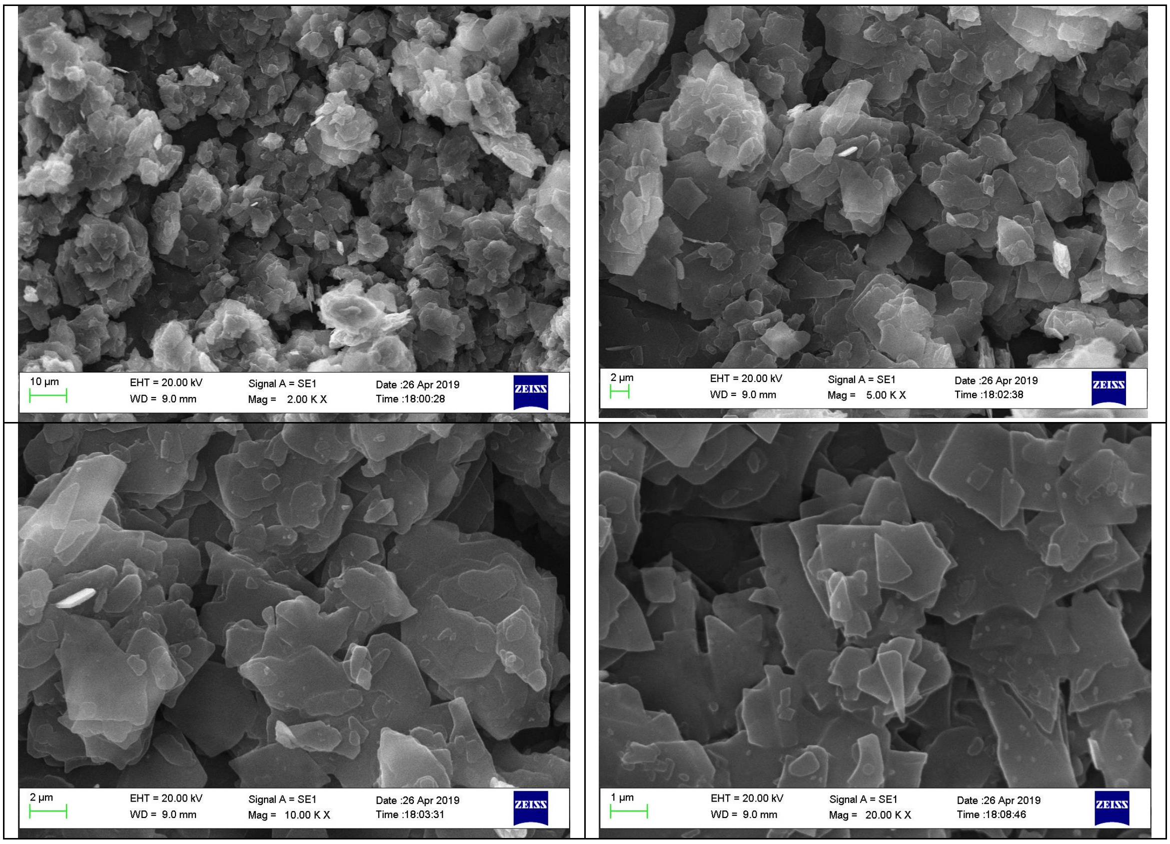
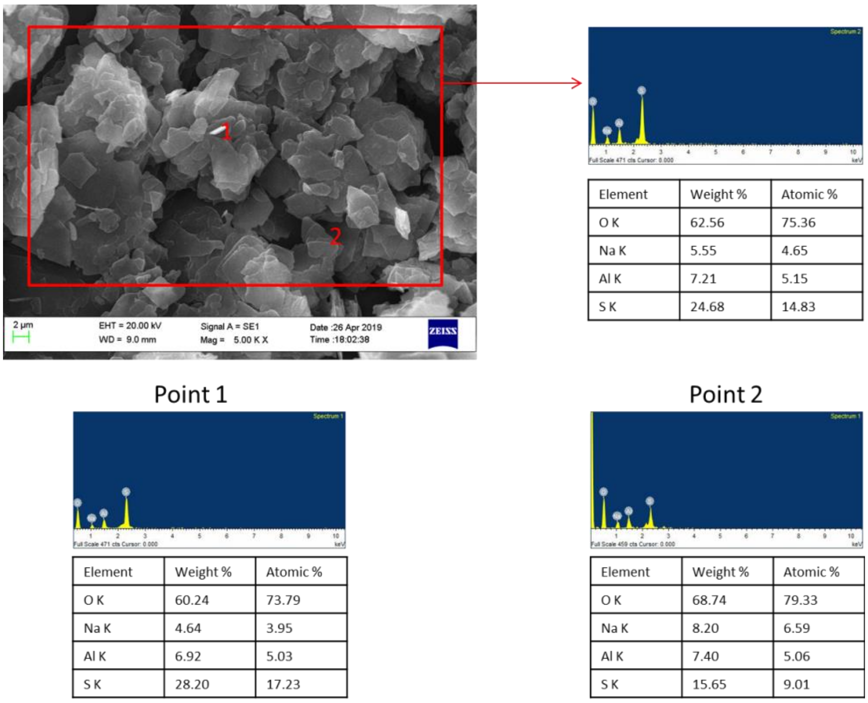


Figure 4.3: SEM images of tamarugite precipitated using Acetonitrile at 2000x, 5000x, 10000x and 20000x



Element	Weight %	Atomic %
O K	62.56	75.36
Na K	5.55	4.65
Al K	7.21	5.15
S K	24.68	14.83

Point 1

Element	Weight %	Atomic %
O K	60.24	73.79
Na K	4.64	3.95
Al K	6.92	5.03
S K	28.20	17.23

Point 2

Element	Weight %	Atomic %
O K	68.74	79.33
Na K	8.20	6.59
Al K	7.40	5.06
S K	15.65	9.01

Figure 4.4: SEM-EDS of tamarugite produced using Acetonitrile

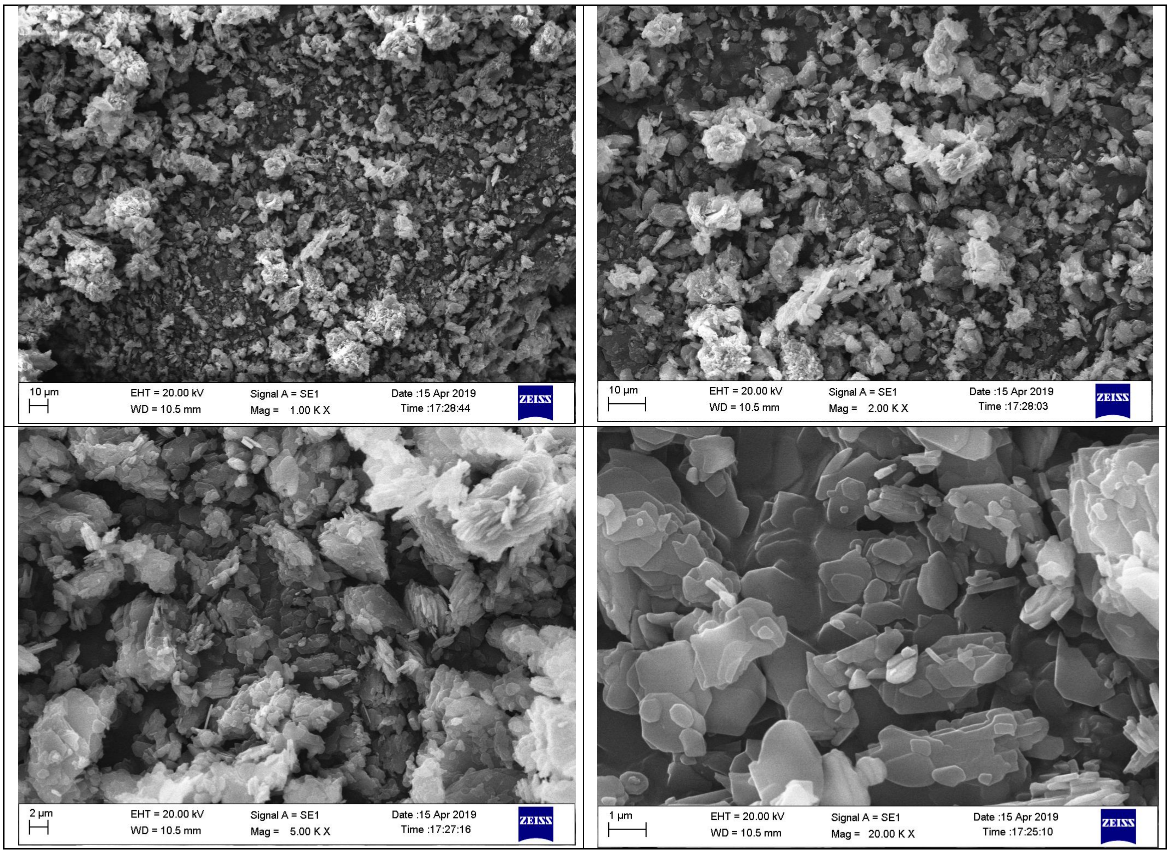
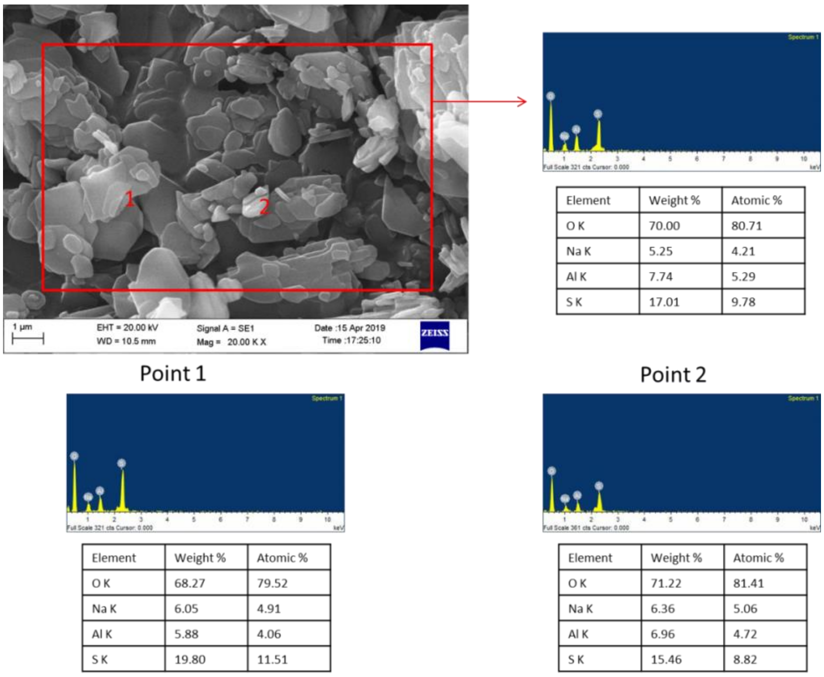


Figure 4.5: SEM images of tamarugite precipitated using Ethanol at 1000x, 2000x, 5000x and 20000x



Element	Weight %	Atomic %
O K	70.00	80.71
Na K	5.25	4.21
Al K	7.74	5.29
S K	17.01	9.78

Point 1

Element	Weight %	Atomic %
O K	68.27	79.52
Na K	6.05	4.91
Al K	5.88	4.06
S K	19.80	11.51

Point 2

Element	Weight %	Atomic %
O K	71.22	81.41
Na K	6.36	5.06
Al K	6.96	4.72
S K	15.46	8.82

Figure 4.6: SEM-EDS of tamarugite produced using Ethanol

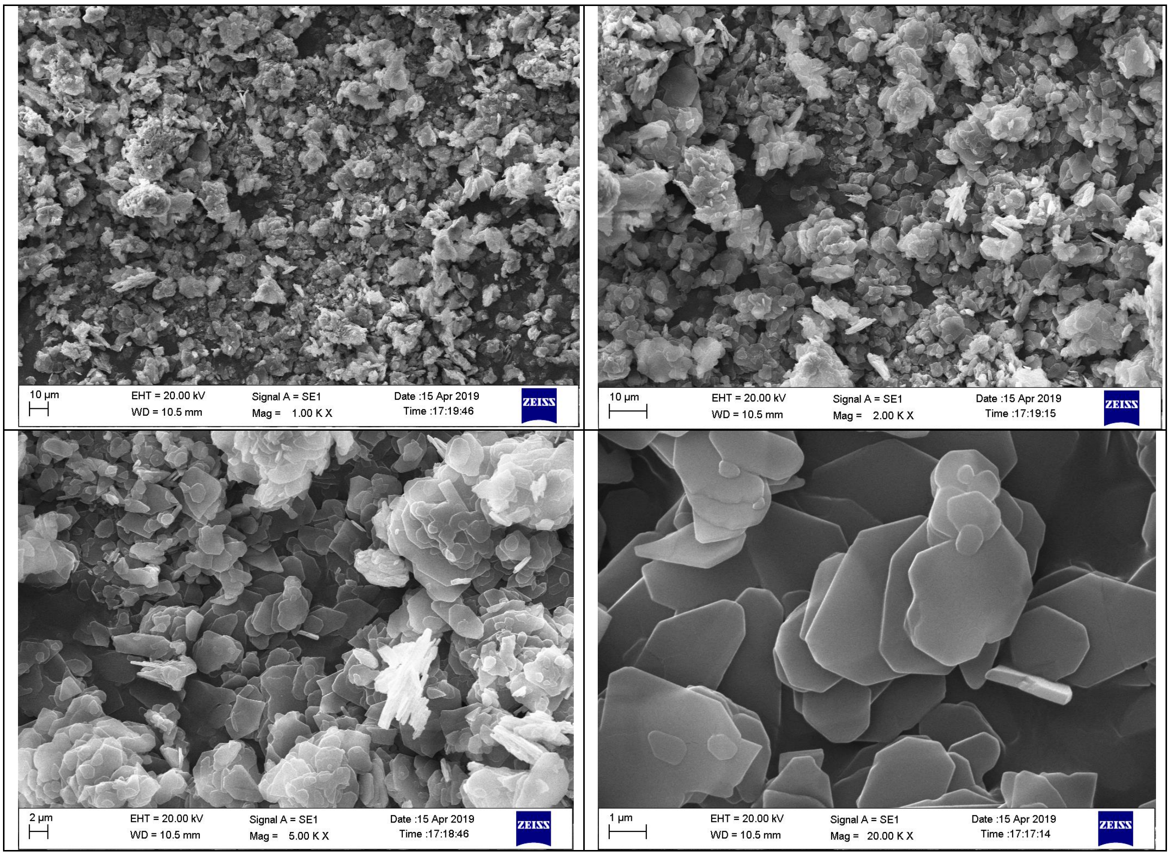
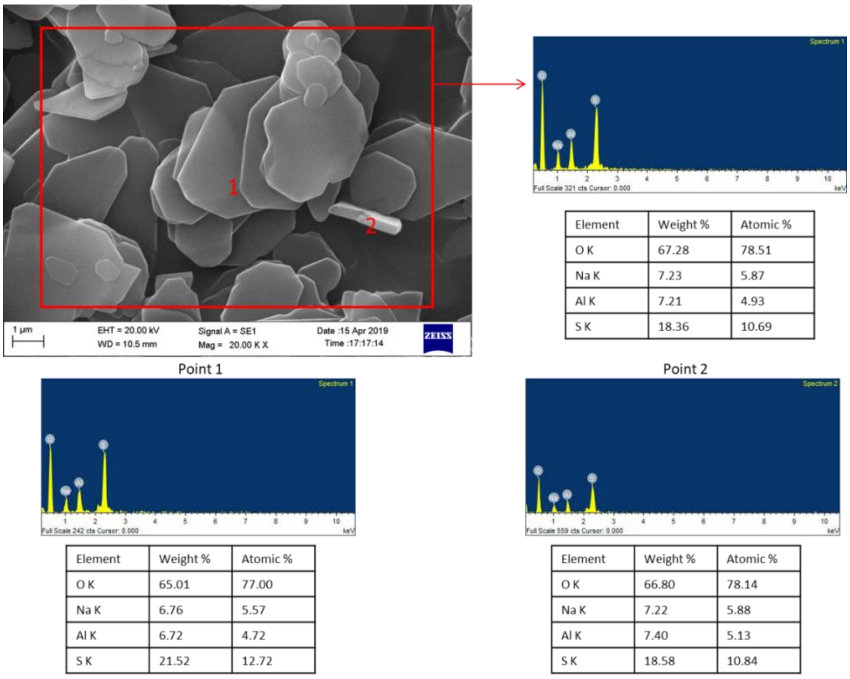


Figure 4.7: SEM images of tamarugite precipitated using Propan-2-ol at 1000x, 2000x, 5000x and 20000x



Element	Weight %	Atomic %
O K	67.28	78.51
Na K	7.23	5.87
Al K	7.21	4.93
S K	18.36	10.69

Point 1

Element	Weight %	Atomic %
O K	65.01	77.00
Na K	6.76	5.57
Al K	6.72	4.72
S K	21.52	12.72

Point 2

Element	Weight %	Atomic %
O K	66.80	78.14
Na K	7.22	5.88
Al K	7.40	5.13
S K	18.58	10.84

Figure 4.8: SEM-EDS of tamarugite produced using Propan-2-ol

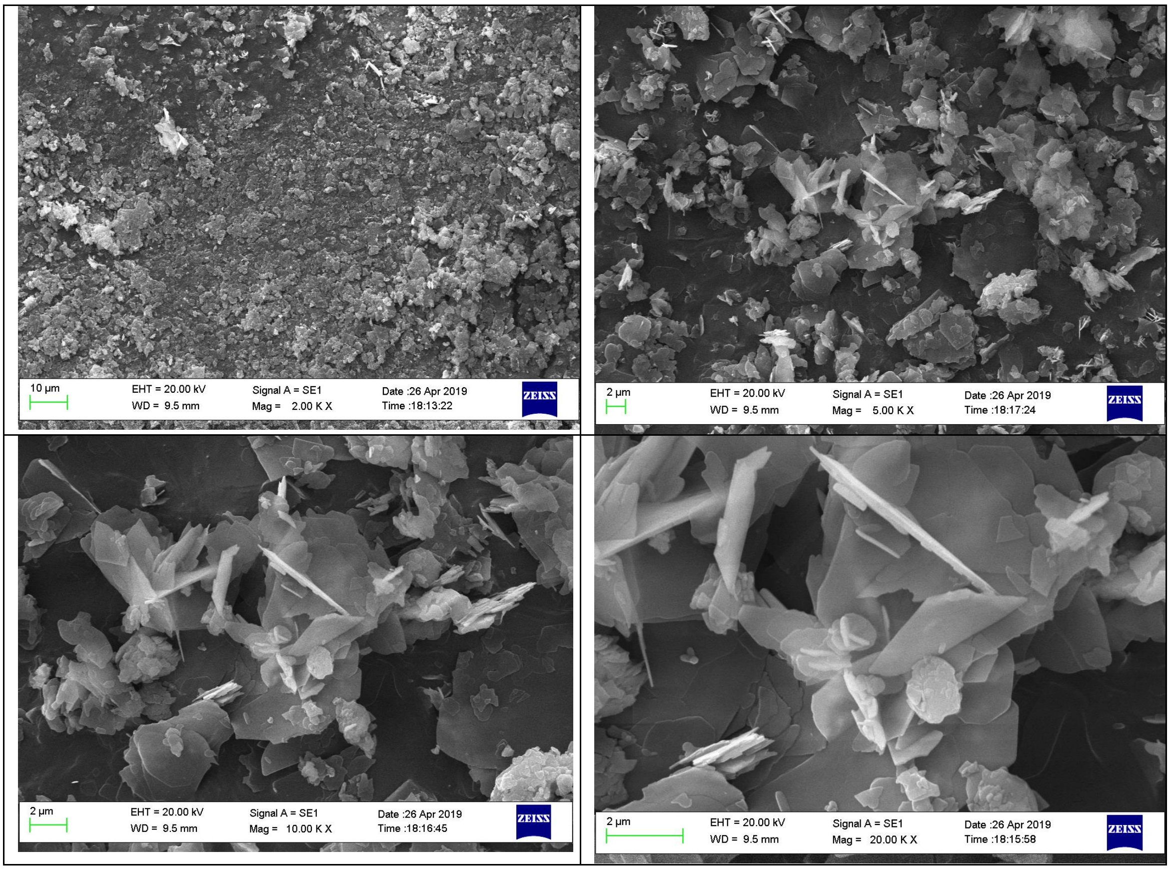
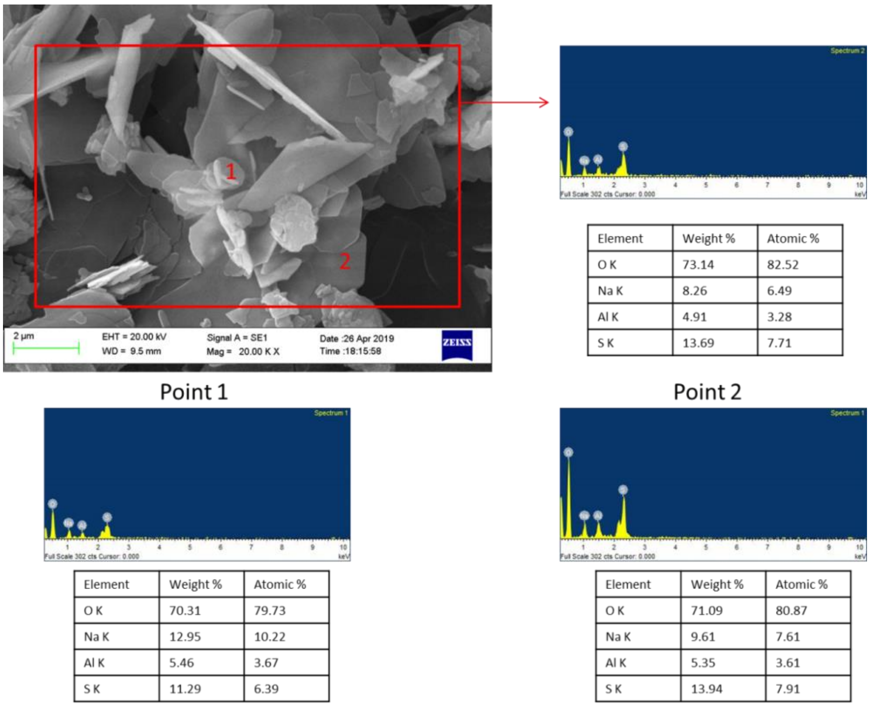


Figure 4.9: SEM images of tamarugite precipitated using Tert-butyl alcohol



Element	Weight %	Atomic %
O K	73.14	82.52
Na K	8.26	6.49
Al K	4.91	3.28
S K	13.69	7.71

Point 1

Element	Weight %	Atomic %
O K	70.31	79.73
Na K	12.95	10.22
Al K	5.46	3.67
S K	11.29	6.39

Point 2

Element	Weight %	Atomic %
O K	71.09	80.87
Na K	9.61	7.61
Al K	5.35	3.61
S K	13.94	7.91

Figure 4.10: SEM-EDS of tamarugite produced using Tert Butyl Alcohol

The SEM images of tamarugite depicted from figure 4.3 to figure 4.10 illustrate the expected morphology of plate-like structures as described in literature [125]. This plate-like morphology is consistent in all the samples precipitated from the four organic solvents used during the experiments. When observed at lower magnifications, the fine powder shows the clusters and agglomerations of the particles. As the magnification is increased, the actual morphology of the sample appears.

The stacking of plates over each other and the growth of perpendicular plates is clearly seen. This pattern is also seen in the crystallized tamarugite and naturally isolated tamarugite samples. The elemental composition of the samples has been determined using the EDS.

As shown in Table 4.2, the calculated weight % of the elements and the values obtained in the EDS are in close agreement, although the EDS provide a localized characterization report. However, it is noted that around 3.17 % weight comprising of hydrogen present in the samples is not detected by the EDS, as it is unable to detect light elements

Table 4.2: The calculated weight percentage of the elements present in Tamarugite vis-à-vis as observed values in the EDS. These values are average values.

Elements	**Ethanol**	**Acetonitrile**	**2 – Methyl, 2 – Propanol**	**Propan – 2 – ol**	**Calculated value**
Sodium	5.88	6.13	10.27	7.07	6.59 %
Aluminium	6.86	7.17	5.24	7.11	7.73 %
Sulphur	17.42	22.67	12.97	19.46	18.33 %
Oxygen	69.83	63.84	71.51	66.36	64.18 %

In order to study the composition of the tamarugite sample precipitated using organic solvents and compare it to the crystallized tamarugite, the elemental analysis is performed using ICP-OES. It has been found that nearly 0.862 mg/L sodium and 0.578 mg/L aluminium are detected in the tamarugite samples precipitated using organic solvents. As opposed to the composition of crystallized tamarugite, it is seen that the amount of sodium is lesser in the present case. The lesser amount of sodium implies the lower amount of other phases present in the resultant product.

The studies for the thermal analysis have also been carried out, to compare the products obtained previously. Just like the tamarugite produced by crystallization, the temperature drop is observed in two ranges in the TGA plot, 100 – 400 °C and 600 – 720 °C. As illustrated in the literature the two temperature ranges mark the removal of water of crystallization linked to tamarugite and the decomposition of the aluminium sulphate to release SO_3 gas [125]. The analysis has been performed to study the temperature transitions using Origin software (version 8.0724). The important transition temperatures are found to be 126 °C, 160.8 °C, 241.2 °C and 343.7 °C.

The number of water of crystallization associated to tamarugite sample has been calculated using the mass reduction in the temperature range of 100 – 400 °C. This has been done by equating the mass reduction with the stoichiometry of the phase (molar mass of the water present). Upon calculation, the number of water molecules was found to be 6, which was the expected value for tamarugite. The TGA plot is shown in the figure 4.11. The total mass at the end of the experiment is nearly 35 % of the initial mass taken.

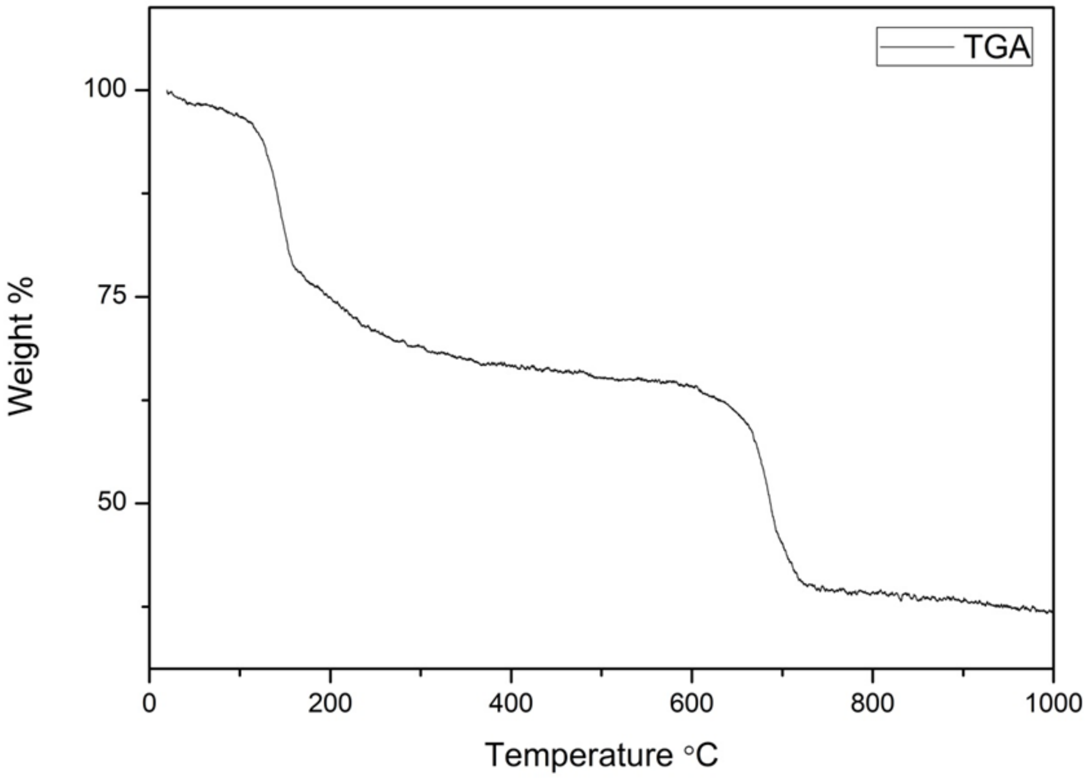


Figure 4.11: Thermogravimetric analysis of tamarugite describing the mass loss with the rise in temperature

In the previous chapter, the decomposition of aluminium sulphate has been discussed. A similar result is observed in the temperature range of 600 – 720 °C. The literature also describes the release of SO_3 gas in this temperature region [125, 129, 130]. The DSC analysis of the tamarugite sample is also done to analyse the energy transitions when the temperature variation is provided.

The temperature range for the DSC analysis is from room temperature to 500 °C. Figure 4.12 describes the DSC curve for tamarugite. As observed from the plot, it can be seen the set of peaks are endothermic and at the end of the plot, the exothermic trend is observed.

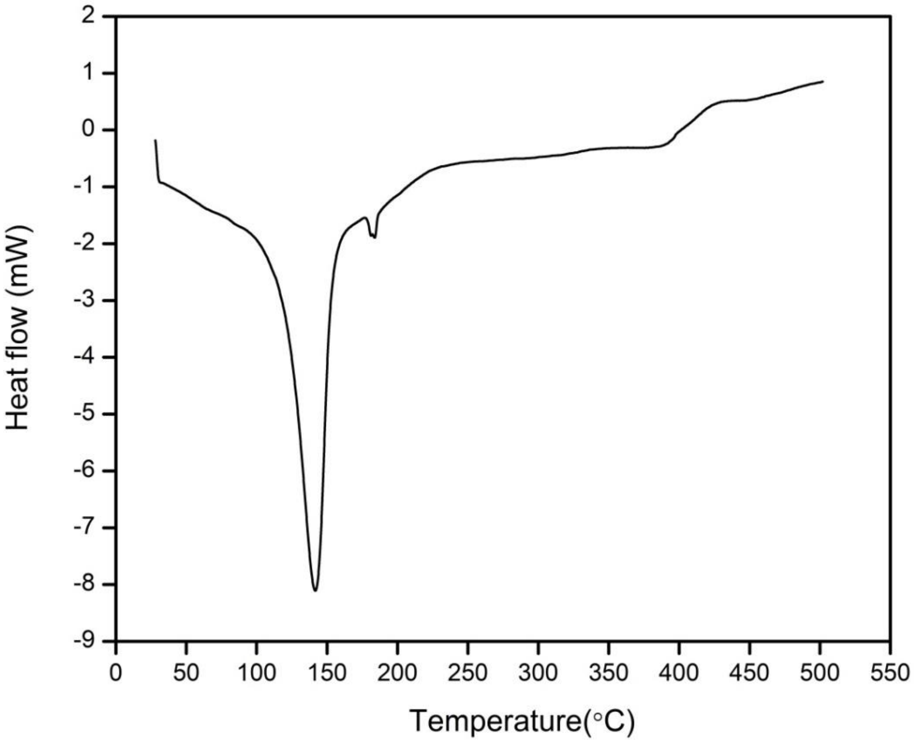


Figure 4.12: DSC curve of tamarugite sample during heating

Major endothermic peaks are seen between the temperature 50-250 °C, which is linked to the removal of water molecules from the samples. This has also been confirmed with the literature [125]. Just like the analysis of the natural samples, the strong endothermic peak is at 141.5 °C, followed by a minor peak at 183.2 °C.

4.4 Understanding Organic-Solvent Precipitation

To understand the mechanism of organic solvent precipitation better, a greater insight in this process is essential. As mentioned previously, the pharmaceutical sectors are the major areas exploiting the organic solvent precipitation to synthesize the required phase from the aqueous solution. The phases in question may have sensitivity towards heat and may have polymorphic occurrence. To successfully isolate the required phase, this method is used [133]. The multiple phases can regularly be produced, but with the use of organic solvents, the required phase can be precipitated.

For this process, an anti-solvent is chosen. Anti-solvents are usually organic solvents that are highly soluble in the solvent in consideration. When such liquids are mixed with the solvents (in our case aqueous solution), the solubility of the solute reduces sharply. The choice of the anti-solvent also depends on the dielectric constants. As illustrated in the introduction part of the chapter, the dielectric constants of the four organic solvents were less compared to that of water. Also, these experiments are usually performed at ambient temperatures. High temperature operations are not required in these processes.

In the present case, the aqueous solution has been saturated properly, before maintaining the temperature at 45 °C. The total volume of the saturated solution added to the solvents dictates the overall precipitated products. The temperature, as described before, is also important. The organic solvents are at lower temperature (20 °C).

These factors result in the precipitation of tamarugite. The final yield of the precipitates is governed by the degree of saturation of the solution and the temperature gradient between the solution and the solvent. There is also the factor of additional seeding, but in the present research the seeding is not done.

The super saturation required to precipitate tamarugite is achieved by the thermal gradient and solubility difference between the aqueous solution and organic solvents. This method has been well documented in the literature [134]. The precipitation is further assisted by agitating the organic solvent during the precipitation. This method is used to produce spherical agglomerates of potash alum [134]. Designing a method for tamarugite production, the precipitation using the four organic solvents has been done.

Usually the recycling of the organic solvent is possible in the pharmaceutical industries, as it will be very expensive if a large amount of organic solvent is lost after a single use. The recycling of ethanol is studied to examine its properties after precipitation of tamarugite. This has been discussed in the later sections of the chapter. In the next section, the application of tamarugite as a coagulant is studied.

4.5 Coagulation studies for various coagulants

Impurities in present in water are of various types. Some impurities are dissolved in it, some suspended and some are colloidal in nature. The suspended particles present in the water will settled down, when water is left undisturbed for a long period of time. This will help in removing the larger particles from the water, as at the end of the settling, the larger suspended particles settle. However, the impurities are still present in water. These are much smaller in size and are stable in the water. Usually, these are negatively charged colloidal particles.

As described in the previous chapter, the negatively charged colloidal particles have a positive charge cloud around them, making them repel each other. This repulsion is due to the Zeta potential of the particles. The agglomeration of the colloidal particles is possible when the van der Waals forces overcome the repulsion between the particles [135]. With the addition of the coagulants in appropriate amount, the energy barrier is broken. This is done by destroying the charge cloud around the colloidal particles, followed by the formation of the microflocs and macroflocs.

With the introduction of the coagulant dosage to the raw water samples, the charge neutralization takes place. When the water samples are rotated at high rpm, the coagulant comes into the contact with the water molecules. As explained in the previous chapter, the formation of amorphous aluminium hydroxide takes place. This leads to the two main methods of coagulation.

The colloidal particles may be enmeshed within the amorphous hydroxide particles or may be entrapped in the particles. The sweeping of the particles due to the turbulence of the water can also take place. The formation of microflocs and macroflocs is observed when the rotation speed of the water is reduced [136]. The destabilized particles turning into flocs lead to the increase in the mass of the agglomerates. These flocs grow in size and settle due to gravity, as the rotation of the water is stopped and the jars are left undisturbed [131].

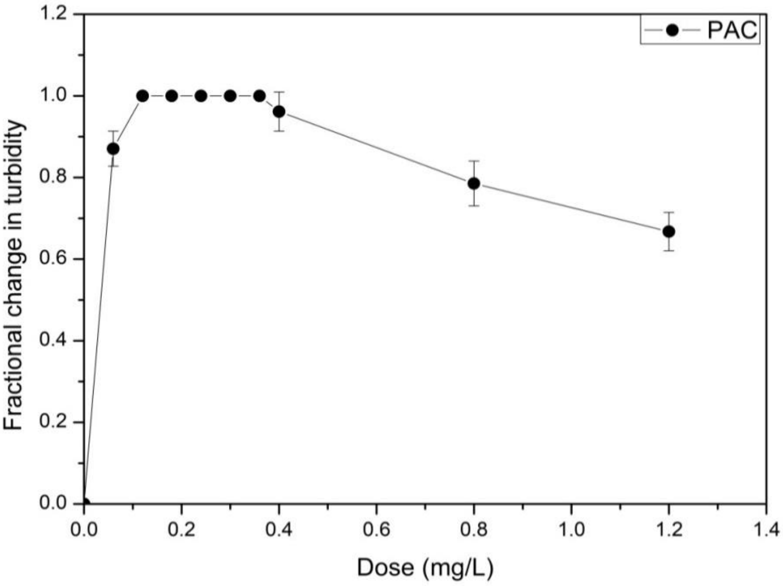
To collectively examine and analyse the coagulation properties of the two tamarugite samples (crystallized and organic solvent precipitated), PAC and commercial alum, the jar test was done. The water samples have been collected from Assi Ghat, River Ganga. The details of the experiment are mentioned in the chapter 2. Similar to the previous study, the fractional change in turbidity is calculated by determining the initial and the final values of turbidity by using Nephalometer. The test has been done to determine the optimum coagulant dose for the given raw water sample using various coagulant.

The fractional change in turbidity is already discussed in the previous chapter. Using the same concept of measuring the capacity of the coagulant, the results of the Jar test are illustrated in the figure 4.13. The first plot is the fractional change in turbidity with respect to the dosage of the coagulant for PAC. The chemical formula for PAC is $\{Al_n(OH)_mCl_{3n-m}\}_x$. It should be noted that the raw water was collected from the same source and the initial turbidity for every jar was similar in all tests. This is important because the amount of poly aluminium chloride coagulant was very less to bring the fractional change in turbidity to unity.

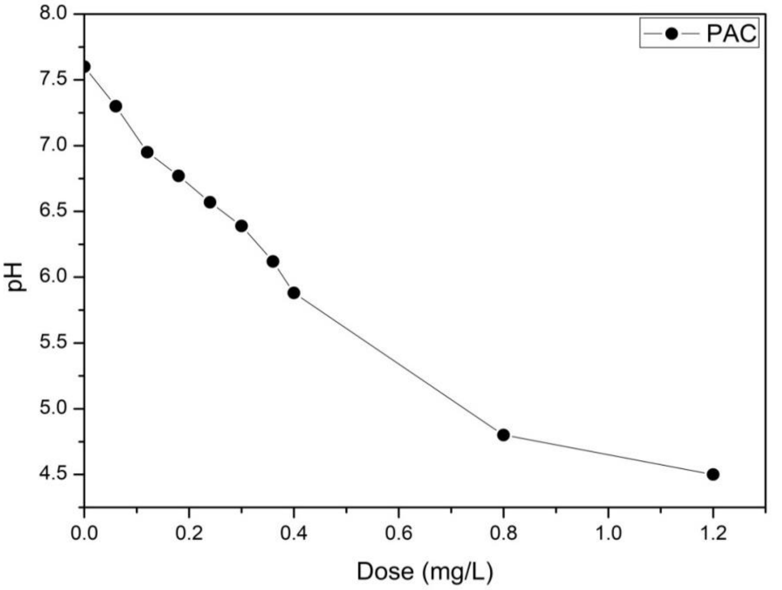
As observed from the plot, 0.2 mg/L of coagulant was sufficient to bring the value of Δt of the raw water to 1. With further rise in the coagulant dosage, Δt remained constant till 0.4 mg/L. As the dosage is increased even further, the value of Δt starts to drop again. The optimum value of the dosage for poly aluminium chloride as a coagulant was 0.2 mg/L for the raw water sample. The increase in the turbidity is simply due to the charge reversal and stabilization of the colloidal particles.

An interesting phenomenon seen in the figure 4.13.b is the sharp reduction in the value of pH of the raw water with the rise in PAC dosage. The initial pH of the water was nearly 7.60; as the dosage reached just 0.4 mg/L, the pH of water had reduced to around 5.75. With further increase, a steeper reduction is seen. At 1.2 mg/L, it reached around 4.50.

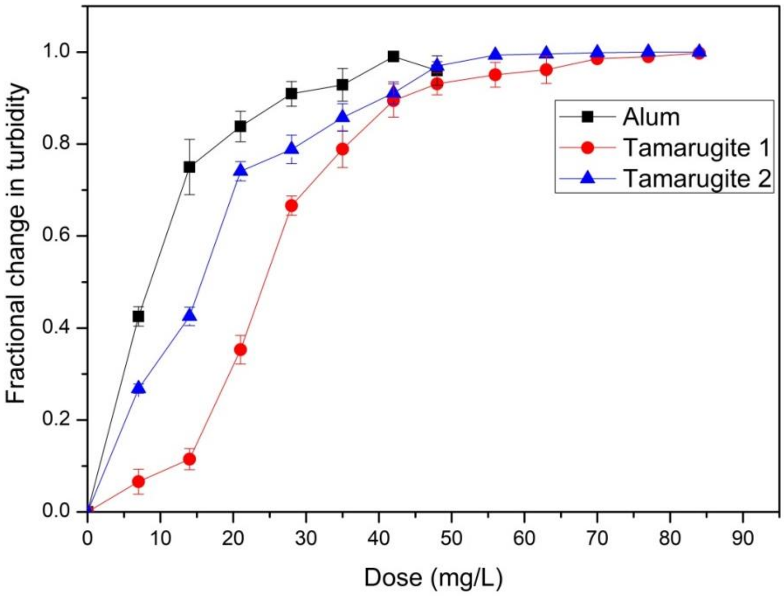
When the pH of the water drops suddenly, the stabilization of the pH becomes necessary. This is achieved with the salts like calcium hydrogen carbonate and lime. It is not possible to use water with very low value of pH, therefore these chemicals are used. The reduction of the pH also affects the functioning of the coagulant. The efficiency of the coagulant is affected adversely [135]. Although PAC is a great coagulant, the cost of the PAC is higher compared to the conventional coagulants commercial alum.


Fractional change in turbidity
Dose (mg/L)
PAC
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

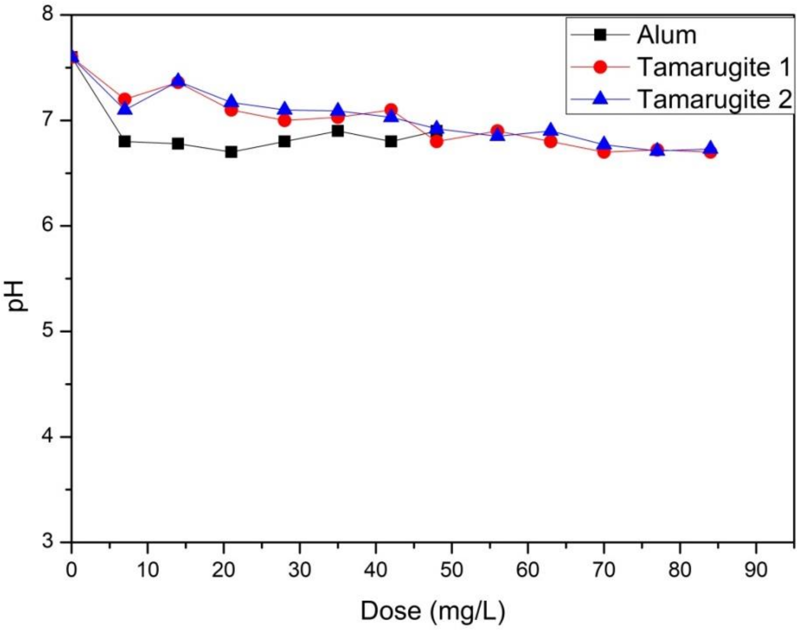
a.


pH
Dose (mg/L)
PAC
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
0.0
0.2
0.4
0.6
0.8
1.0
1.2

b.



c.



d.

Figure 4.13: a. Fractional change in turbidity of water using PAC as a coagulant, b. Variation in pH of the water with the PAC dose, c. Fractional change in turbidity of

water using commercial alum, tamarugite 1 (crystallization) and tamarugite 2 (organic solvent precipitation) and d. Variation in pH of water

A comparison between three coagulants, commercial alum, tamarugite 1 (crystallized) and tamarugite 2 (organic solvent precipitated) is seen in the figure 4.13.c and d. As the dosage of the coagulants is increased, the fractional change in turbidity also increases. Commercial alum is able to bring the value of Δt to unity at around 42 mg/L. Before this value, the coagulation of commercial alum had dominated the plot. After this optimum value, the turbidity increases, just like the case of PAC, due to the reversal of charge and the rise in the stability of the particles.

At this point (beyond 50 mg/L), tamarugite 2 maintains the value of Δt close to unity. This means the optimum dosage for tamarugite 2 was nearly 50 mg/L. It is also observed that tamarugite 1 lagged behind commercial alum and tamarugite 2. Only at severely high dosage of 70 mg/L, the values of Δt for tamarugite 1 and tamarugite 2 reach the maxima.

The next plot shows the change in the value of pH of the water after the jar test. As seen from the plot, the values of the pH remained within a range of 7.60 to 6.80. This trend is consistently observed even at high dosages of the coagulants. This is an advantage over PAC as a coagulant, as the value of pH is well within a specific range and there is no need to maintain the pH due to the excessive addition of the coagulant. This plot is in contrast to the pH variation observed for PAC. Other parameters of water were also measured. The conductivity value for untreated water was 0.478 m℧ and 0.435 m℧ for treated water. Similarly, the alkalinity for the untreated water was found to be 220 ppm, whereas the treated water showed 173 ppm.

4.6 Reutilization of ethanol for the precipitation of tamarugite

If the organic solvents were washed away after a single cycle of precipitation, then it would not be an economical process. Ethanol is one of the most common organic solvent available. It has been observed that ethanol helps in precipitation of tamarugite from the aqueous solution. Therefore, experiments were performed to observe its reusability and determine whether the quality of Tamarugite produced was same after every cycle. The precipitation has been done for four cycles and characterization of the resultant ethanol is done using NMR spectroscopy. The proton NMR spectrum has been obtained for a range of 0 to10 ppm. The solvent used for the characterization of the ethanol sample is dimethyl sulphoxide. The spectrum obtained comprised of quartet, triplet and sextet at approximately 3.5 ppm, 2.5 ppm and 1 ppm. These peaks confirm the composition of ethanol.

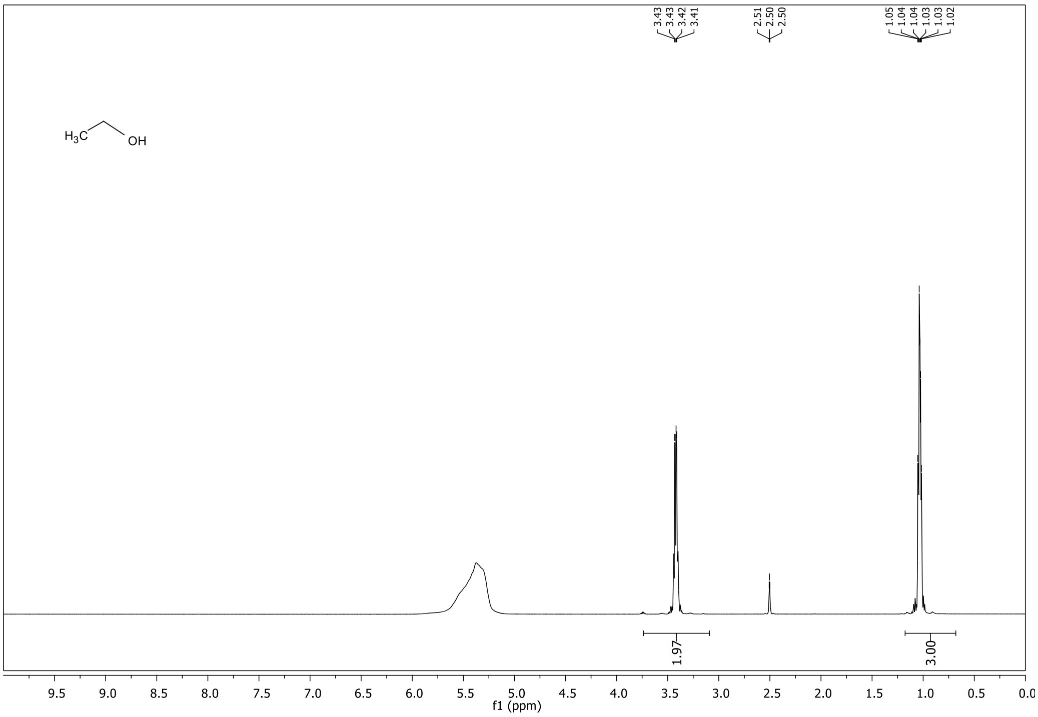


Figure 4.14: Proton NMR Spectra for ethanol after fourth cycle of precipitation of tamarugite

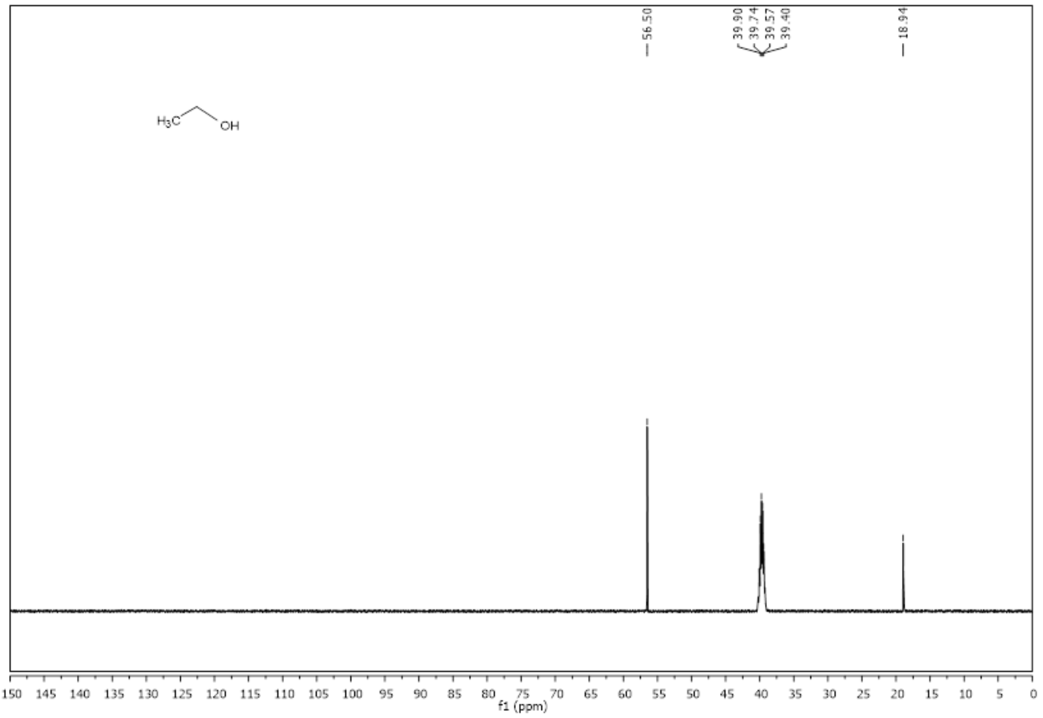


Figure 4.15: ^{13}C NMR Spectra for ethanol after fourth cycle of tamarugite precipitation

The ^{13}C NMR spectrum was obtained for a range of 0 to 150 ppm. Singlet peaks are observed at 18.94 and 56.50 and a quartet is observed at around 39 ppm. From the NMR spectrum of the recycled ethanol, it is observed that the chemical nature of ethanol remained the same. No peaks other than that of ethanol have been identified and it justifies that the final product was indeed ethanol.

The separation of ethanol from the tamarugite after precipitation was done by directly centrifugation process. The washing of the samples was done after the ethanol was removed. This ethanol was recycled again for precipitation. The precipitated tamarugite samples were dried and washed with methanol multiple times and stored in desiccator. The characterization of the tamarugite samples produced from the recycled ethanol is provided in the next section.

4.7. Characterization of tamarugite produced in the recycling of ethanol

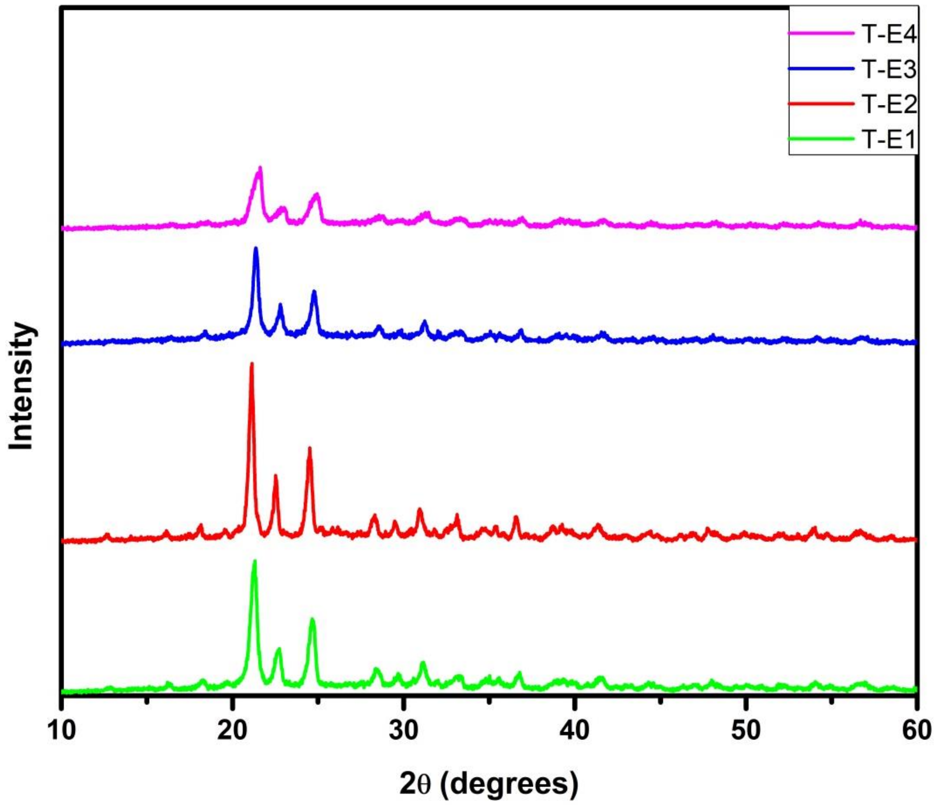


Figure 4.16: The XRD patterns of tamarugite precipitated from ethanol during the recycling

Figure 4.16 shows the XRD pattern of tamarugite precipitated from ethanol in four cycles. T-E1 to T-E4 are tamarugite produced from first cycle to the fourth cycle. As can be seen from the pattern, the peak positions coincide at 21°, 22.4° and 24.4°. The intensities vary to some extent, but the trend remains the same for all the three major peaks. This shows that the resultant products were of similar quality.

In order to see the difference in the precipitated tamarugite, SEM-EDS of tamarugite of the first and the fourth cycle have been done. The same is shown in the Figures 4.17 to Figure 4.20.

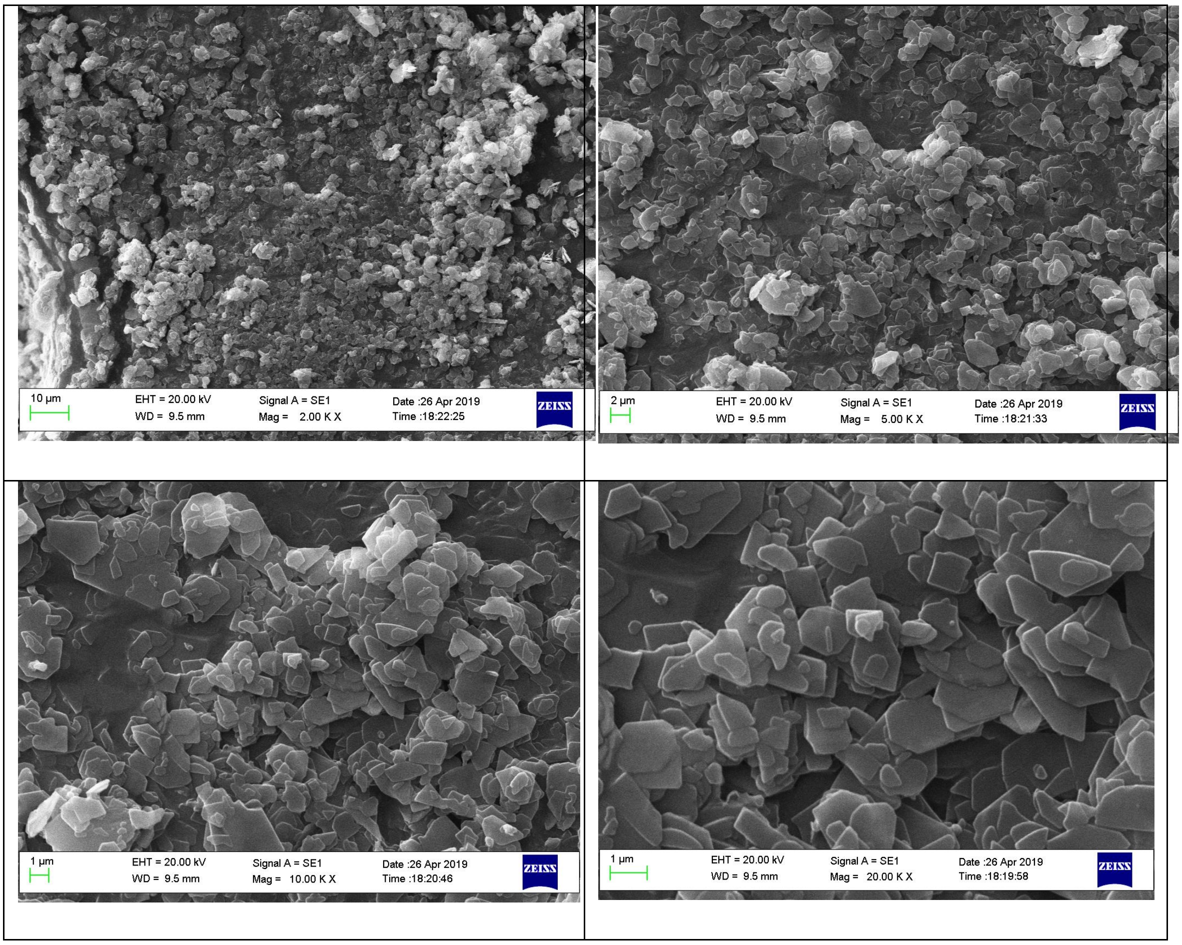
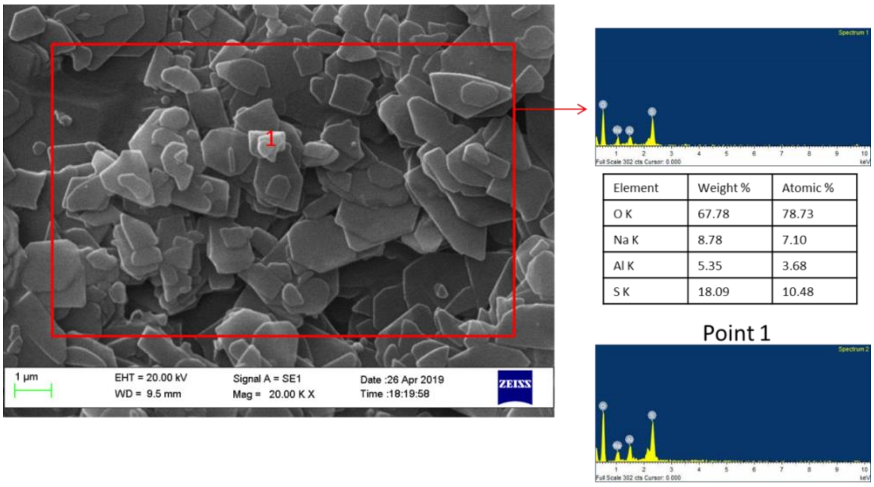


Figure 4.17: SEM images of tamarugite produced in first cycle of using ethanol



Element	Weight %	Atomic %
O K	67.78	78.73
Na K	8.78	7.10
Al K	5.35	3.68
S K	18.09	10.48

Point 1

Element	Weight %	Atomic %
O K	69.38	80.17
Na K	6.48	5.21
Al K	6.42	4.40
S K	17.72	10.22

Figure 4.18: SEM-EDS of tamarugite produced in first cycle of using ethanol

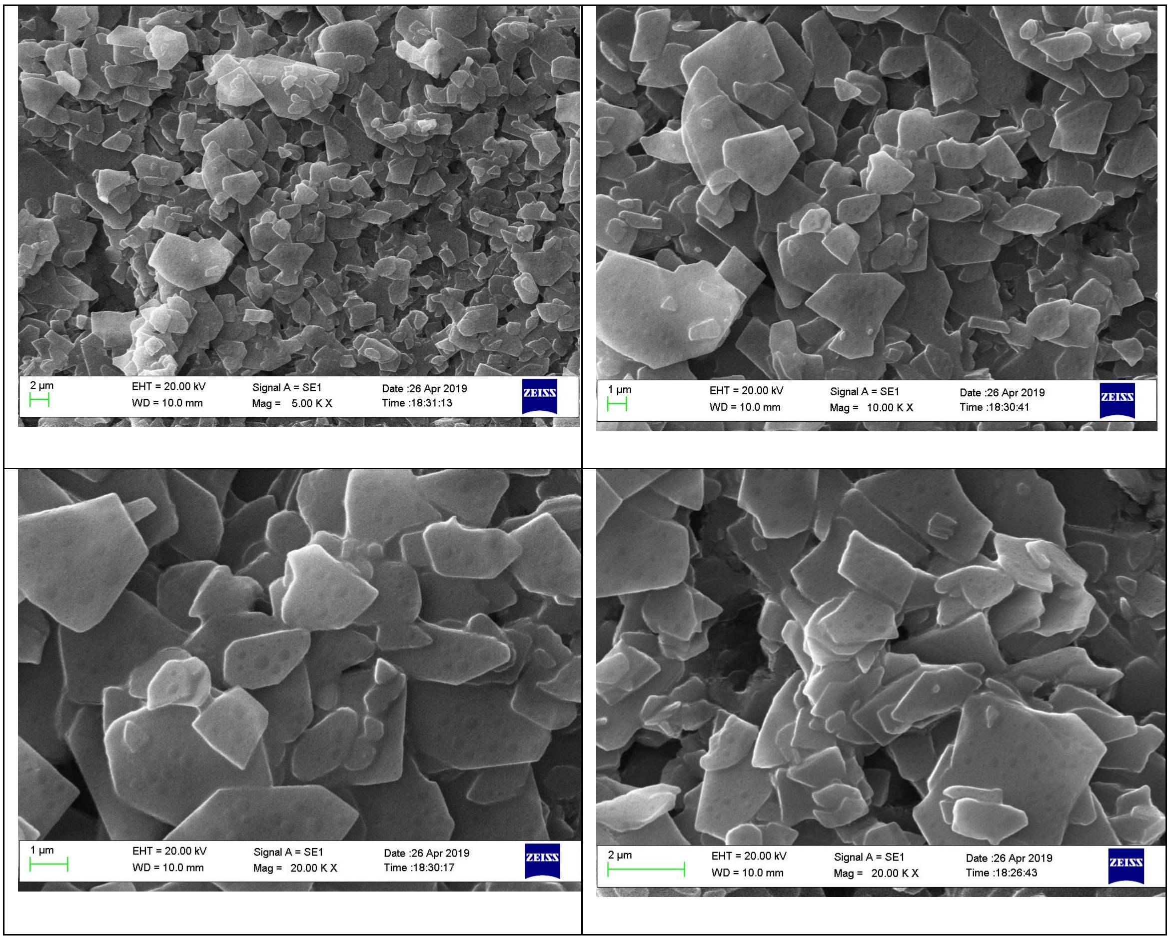
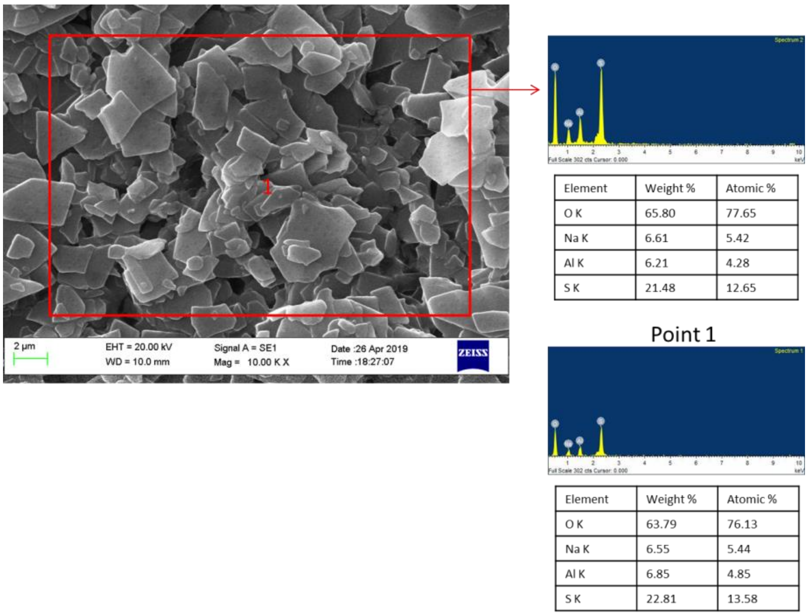


Figure 4.19: SEM images of tamarugite produced in fourth cycle of utilizing ethanol



Element	Weight %	Atomic %
O K	65.80	77.65
Na K	6.61	5.42
Al K	6.21	4.28
S K	21.48	12.65

Point 1

Element	Weight %	Atomic %
O K	63.79	76.13
Na K	6.55	5.44
Al K	6.85	4.85
S K	22.81	13.58

Figure 4.20: SEM-EDS of tamarugite produced in fourth cycle of utilizing ethanol

As observed from the SEM images, the morphology of the tamarugite produced in the first cycle and the fourth cycle were almost similar. The plate morphology is seen in both the samples at higher magnifications. The elemental composition (the weight percentages of the elements) also closely resembles the calculated values.

This indicates that the recycling of ethanol is a good method for repeated precipitation of tamarugite for four cycles. The NMR spectra illustrated in the previous section and the characterizations of the resultant product shown in this section imply that the wastage of organic solvent after a single use is uneconomical. Recycling of the organic solvents is a better method for improved economy of the process.

4.8 Conclusions

This chapter described the organic solvent precipitation of tamarugite using white aluminium dross as a source of aluminium. The extraction of aluminium into the solution is done by the leaching with H_2SO_4 while the aq. NaOH solution provides the sodium ions. The precipitation of tamarugite using organic solvents (acetonitrile, ethanol, propan-2-ol, Tert-butyl alcohol) is done. The characterization of the resultant tamarugite samples is shown.

The phase determination using the XRD patterns show that the major dominant phase is tamarugite, with minor amount of trisodium hydrogen bisulphate and sodium hydrogen sulphate. The SEM-EDS shows that the plate morphology of tamarugite is seen in all the samples. The elemental composition is further confirmed by ICP-OES. The precipitation of tamarugite using organic solvents is discussed.

The application of the precipitated tamarugite for the coagulation of the colloidal particles in raw water is also studied. A comparative study of the coagulants is done. It has been shown that organic solvent precipitated tamarugite performs well in comparison to the crystallized tamarugite and alum. Although poly aluminium chloride is a great coagulant, the reduction in the pH of the water samples is very large for a small dosage. In contrast to this sharp reduction, the pH of water remains stable for alum and both tamarugite, even at severely high doses. This shows that there is no requirement of addition of alkaline salts to stabilize the pH of water, if tamarugite is used as a coagulant.

The recycling of ethanol is also shown to make the process more economical. The tamarugite samples precipitated in the four cycles of ethanol recycling have also been characterized. It is seen that the samples are similar to the regular tamarugite and the quality of the resultant product is maintained. This is done to reduce the wastage of the organic solvents after a single cycle of precipitation.

Therefore, an alternative method of recycling white aluminium dross is described. The production of tamarugite by organic solvent precipitation, its application in water treatment and recycling of the organic solvents for repeated precipitation are the important points discussed in this chapter.