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Natural Adsorbent: Removal of Anionic surfactant from grey water and its comparison with chemical adsorbent

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Abstract

The study aims at comparing removal method of Anionic Surfactant from grey water using natural and chemical adsorbent. The study focused on the comparison of various parameters of the method. The comparison was effectively done by performing batch adsorption experiment in grey water. The chemical adsorbent selected was alum and lime whereas the natural bioadsorbent was powder of karanj seed and tulsi leaves. The optimum adsorbent dose, equilibrium time, pH condition and contact time was determined. In the Batch study a series of 10 mL samples of AS bearing waste water (100 μg mL^{-1}) were shaken for 1h with adsorbents at varying doses. Isotherm data at $27^{0}C$ were fitted to Freundlich model better than to Langmuir model. The R^2 value for CA-1, CA-2, NA-1 and NA-2 was calculated and compared. The Q_{max}. for CA-1 & CA-2 ,BA-1 & BA-2 were found to be 0.6, 0.9, 34.48 and 64.66 mg/g. Maximum adsorbent capacities (Q_{max}.) was obtained by the natural adsorbent than chemical adsorbent. The natural adsorbents showed very good correlation.

1. Introduction :

Human kind has a large foot print on Earth. Overexploitation and misuse of resources has led to problems such as water scarcity and polluted water bodies, with severe consequences for human health and welfare. Almost half of the world's population faces water scarcity of some sort. Furthermore, over half of the world's hospital beds are occupied with people suffering from illnesses linked with contaminated water and 1.8 million children die every year from a water related disease. The World Health Organization reports that 9 % of the global disease burden could be prevented by increasing the access to safe drinking water, improving sanitation and hygiene and improving wastewater management (Pruss- Ustun *et al*.2008). Our lifestyle is largely dependent on the chemical products that are mass produced. About 300 million tons of synthetic compounds are annually produced for industrial processes or consumer products (Schwarzenbach *et al*.2006). As a result, trace xenobiotic organic compounds (also known as organic micropollutants) are commonly present in the aquatic environment. Concerns have been raised about the occurrence of pharmaceuticals, hormones and personal care products in the environment (Daughton & Ternes 1999), (Heberer & Ternes, 2002). Although present in the range of ngL^{-1}- μ gL^{-}these compounds are biologically active and may influence aquatic organisms (Heberer & Ternes 2002). Recovery of resources from waste is a well established practice in the industrial sector. Process water is being recycled, heat exchangers are used to recover energy from process streams and raw materials are recovered from waste streams. Concepts of decentralized sanitation and reuse apply the same logic to household wastewater, no longer seen as a waste stream but as a source of nutrients, energy and water. (Otterpohl 2002). In this way, wastewater management can become more efficient and potentially more successful than conventional wastewater management to increase access to safe drinking water and improve sanitation and hygiene.

In most developing countries, discharges from point sources have increased significantly as a result of industrialization and high living standards. Additionally, an excessive nutrient load to rivers in these countries has been accompanied by untreated wastewater discharges (Smith *et al*.1999. The Global Environmental Monitoring System (GEMS) of the United Nations Environmental Program (UNEP) reported heavy pollution in several rivers around the World (Bichi & Anyata 1999). Synthetic surface active agents (synthetic surfactants) or detergents are used in many industries and in everyday life. The main hazard of detergent pollution lays in their effect on water ecosystems as a whole. In the first instance, surfactants may adversely affect microalgae at the lowest tropic level and impact on their function as major suppliers of oxygen to water bodies (Patin 1985). Surfactants are a group of compounds used daily in huge amounts mainly in household applications and as industrial cleaning agents. According to the Council of European Surfactants Producers Statistics the total quantity of surfactants (without soaps) consumed in Western Europe in 2002 was more than 2.5 million tons (Gonzalez *et al*.2007). Nowadays, the role of surfactants and surfactant detergents a factor of surface and ground water pollution is comparable to that of oil pollution of the world oceans. If the 10 million tons of surfactants annually manufactured worldwide were spread in adsorption layers, they could cover the surface of our planet with nearly 15 monolayers (Sineva *et a*l.2007). An appealing alternative to these procedures for remediation of anionic surfactants is the use of adsorption technologies. In fact, adsorption protocols of anionic surfactants from water have been extensively studied and a wide range of adsorption materials have been tested. A number of adsorption systems have been explored for the removal of surfactants in aqueous solution. Numerous adsorbents, such as activated carbon, layered double hydroxides, silica, mineral oxides and natural biomass, have been extensively investigated (Pavan *et al*.2002, Brown & Zhao 1993, Vanjara & Dixit 1996). Recently research has focused on low cost and easily available materials such as waste activated carbon and rubber granules. (Sandeep *et al.* 2003, Paritosh *et al*.2002). This study aims at comparing removal method of AS from grey water using natural and chemical adsorbent .The study focused on the comparison of various parameters of the method. The comparison was effectively done by performing batch adsorption experiment in grey water. The chemical adsorbent selected was alum and lime whereas the natural bioadsorbent was powder of karanj seed and tulsi leaves. The optimum adsorbent dose , equilibrium time, pH condition and contact time was determined .The natural adsorbent was found to be more effective than the chemical adsorbent.

2. Methodology

2.1 *Materials & Reagents* :

Acridine orange (ACO),SDS, glacial acetic acid, toluene were from BDH(AR grade) and were used as received. Crystal violet (CV), orthophosphoric acid, Benzene was from MERCK and were used without further purification.

2.2 *Adsorbents* :

Alum($Al_2(SO_4)_3.24H_2O$) and Lime $Ca(OH)_2$was supplied by S.D Fine Chemicals and were used as received.
Karanj seed and Tulsi leaf was available from the college campus .

2.3 *Method* :

The determination analysis was done by spectrophotometric method. Systronics 105 with 1cm quartz cell was used for spectrophotometric analysis. Standard Solution of Sodium dodecyl sulphate (SDS) Sodium dodecyl sulphate (sigma, purity > 99.0 %) was dried at 50^0C under reduced pressure until a constant mass was achieved before weighing. The critical micelle concentration (CMC) of SDS is 8.1×10^{-3} M (~ 2333 ppm) SDS working solutions were prepared by appropriate dilution of the stock solution with doubly distilled water. However, the concentration of a diluted stock solution decreases after allowing it to stand for one day. Therefore, the working solution was prepared immediately prior to use by accurate dilution of the stock solution. The stock and working solutions were kept in refrigerator to avoid probable biodegradation .Doubly distilled de-ionized water was used throughout. Crystal violet (CV), the cationic dye (M.wt.407.9) was dissolve in doubly distilled water to give 5×10^{-3} M stock solution. The solution was stored under cold and dark condition. The stability of solution was monitored by measuring absorption spectra in the visible region. Standard Solutions of SDS 10 mL aliquots having varying concentration from 0.6 to 10 ppm (mgL^{-1}) were taken in the separating funnel. In the Separating funnel Crystal violet and orthophosphoric acid (100µL) each are added followed by the addition of 5mL benzene. The contents are shaken for 1 min. and then allowed to settle for 5 min. The aqueous layer is discarded. The benzene layer is collected and 2.5 mL of this solution is used. The coloured benzene layer is directly used for the absorbance measurements at 565nm against the reagent blank and prepared the Calibration graph by plotting absorbance versus concentration of SDS. The concentration of SDS in the sample was computed by using the calibration graph prepared under similar condition.

2.4 *Bio-Adsorbents* :

The preparation process of the bio-adsorbents was carried out in the following way; The raw materials were washed first with tap water and then with distill water to avoid the presence of any foreign materials. Moisture contents of seeds were estimated as percentage water of fresh weight. Five replicates with five seeds each were taken and their moisture content was determined by hot air oven method. Seeds were kept for 72 hours at 103^0C (ISTA 1996). The weights were taken before and after oven drying. The moisture content was calculated as follows and expressed in percentage. The moisture content of seed was determined by the following formula:-

$$\%\ \text{Moisture Content}\ (\%\ \text{MC}) = \frac{\text{Seed fresh weight - Seed dry weight}}{\text{Seed fresh weight}} \times 100$$

$$\text{Water Content}\ (g\ H_2O\ g^{-1}\ \text{DM}) = \frac{\text{Seed fresh weight - Seed dry weight}}{\text{Seed dry weight}}$$

Karanj seeds are oily seeds and the water content was recalculated for zero amount of lipid (Sacandé *et al*. 2000) and expressed as follows as g H_2O g^{-1} DM

$$\text{Water Content (g } H_2O\ g^{-1} \text{ DM) (at Zero oil Content)} = \frac{\text{Seed Fresh Weight - Seed Dry Weight}}{\text{Seed Dry Weight - Seed Oil Content}}$$

Water content expressed as g H_2O g^{-1} DM hereafter is actually water content calculated with zero oil unless otherwise mentioned. When the seeds attain a constant weight they were reduced into powder by a domestic mill. No pH modification was needed, as natural pH 7 was achieved.

Leaves of Ocimum Sanctum were dried in shadow for several days. Dried leaves were ground and sieved to 50 mesh sizes. It was then washed with distill water. Washing was continued till the pH of filtrate became neutral. And filter cake was first dried at room temperature and then in an oven at 105°C to attain constant weight. No other chemical and/or physical treatments were used prior to biosorption experiments. The biomasses were then stored in the dessicator to protect it from moisture. The adsorbent applied are Lime (CA-1), Alum (CA-2),Karanj seed (NA-1) and Tulsi leaf (NA-2). Further throughout the chapter for convenience the Pongammia pinnata seeds and Ocimum sanctum leaves will be expressed as Natural adsorbate -1 (NA-1) and Natural adsorbate -2 (NA-2).

3. Result and Discussion

3.1 *Effect of adsorbent dosage* :

In the Batch study a series of 10 mL samples of AS bearing waste water (100 µg mL^{-1}) were shaken for 1h with adsorbents at varying doses (1– 900g/L).In batch study it is very necessary to find optimum adsorbent dose of the adsorbent and the result was shown in the figure – 1

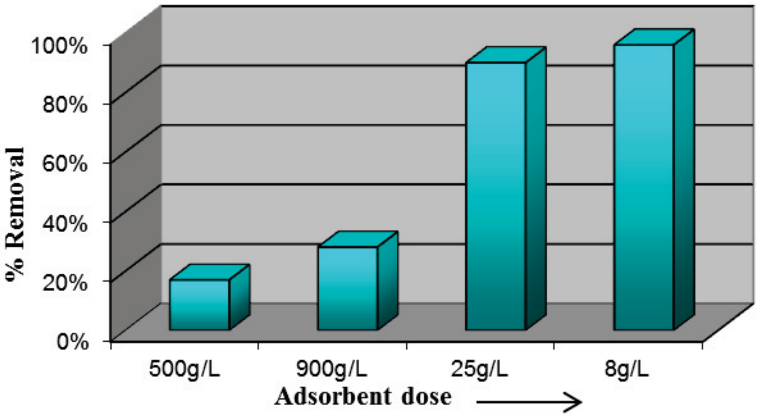


Figure -1 Effect of adsorbent dose on AS removal by Chemical adsorbents (CA-1 & CA-2) and Bio adsorbents (NA-1 & NA-2).

3.2 *Effect of pH* :

pH values were varied between 4 and 9, in order to determine its influence on surfactant removal. Experimental data series is shown in Figure 2. A fixed dose of 5g/L of adsorbent with a surfactant dose of 10 ppm was taken. The chemical adsorbents (CA-1 & CA-2) are found to be in the alkaline medium as there would have been increase of anions (OH^- & SO_4^{2-}) and the natural adsorbents (BA-1 & BA-2) are found to be in the acidic medium as the proteinic nature of the natural adsorbents makes the medium cationic. The electrostatic attraction between the natural adsorbent and negative – charge surfactant active centers is reinforced. The adsorption of the AS was found to be efficient by the natural adsorbent shown in Figure -2

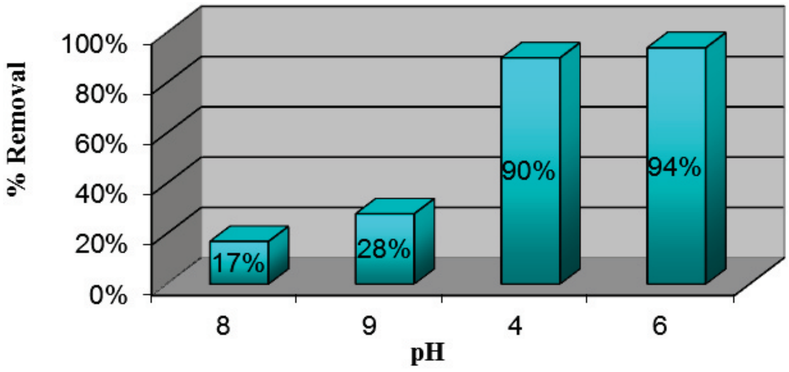


Figure -2 pH influence on surfactant removal

3.3 *Effect of Effect of contact time :*
Waste water (10 mL) with fixed adsorbent dose and pH was shaken for 1h. In all cases, after shaking, the sample were allowed to settle for 5 min. and then filtered through whatmann paper no.42. The results are depicted on Figure -3

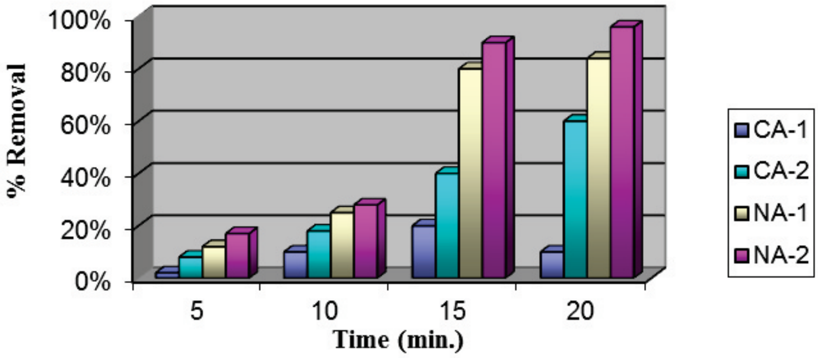


Figure -3 Effect of Contact time

3.4 *Isotherm studies* :
If it is assumed that the uptake of SDS by the adsorbent is the result of physical attraction or chemical co-ordination between the SDS and chemical moiety on the adsorbents then the maximum number of such sites would be finite. When the adsorbent and adsorbate come in contact with each other, dynamic equilibrium is established between the adsorbate concentration in both the phases. The state is dynamic in nature, as the amount of adsorbate migrating onto the adsorbent would be counter balanced by the amount of adsorbate migrating back into the solution. When all the sites available achieve equilibrium,the adsorptive capacity would be maximum (Weber & Morris 1963). A plot of equilibrium concentration (C_e) and adsorptive capacity (Q_e) was drawn for each adsorbent. The adsorption isotherms for different adsorbents are shown in Figure 4 – 11. To estimate maximum adsorption capacity ($Q_{max.}$) linearized forms of Langmuir and Freundlich isotherms were prepared based on the following equations,

$$\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{b} Q_{max}\left(\frac{1}{C_e}\right) \tag{1}$$

$$\log q_e = \frac{1}{n} (\log C_e) + \log K_f \tag{2}$$

where C_e is the solute concentration at equilibrium in aqueous phase in mg/L, q_e is the solute adsorbed per unit weight of adsorbent in mg/g. Q_{max}. is the maximum solute adsorbed per unit weight of adsorbents in mg/g and b, n. K_f are constants. Separate curves were drawn for all adsorbents by plotting $1/q_e$ against $1/C_e$ to get the corresponding Langmuir isotherms, and from the equations Q_{max}. was obtained.

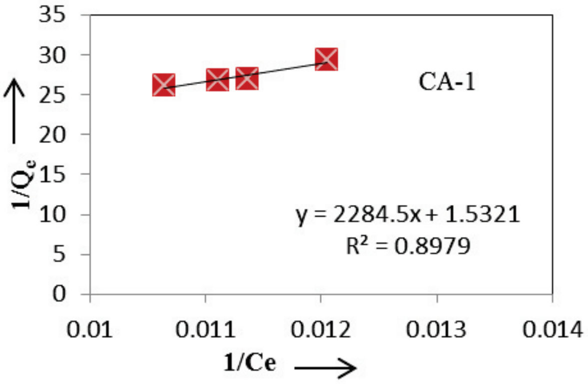


Figure - 4 Langmuir Isotherm of CA-1

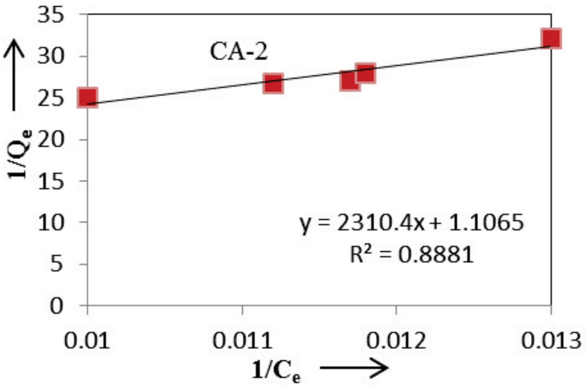


Figure - 5 Langmuir Isotherm of CA-2

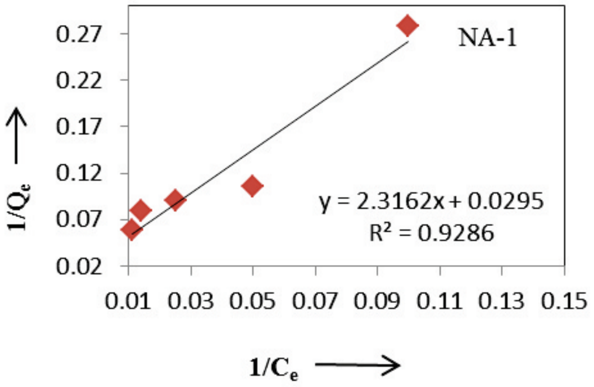


Figure-6 Langmuir Isotherm of NA-1

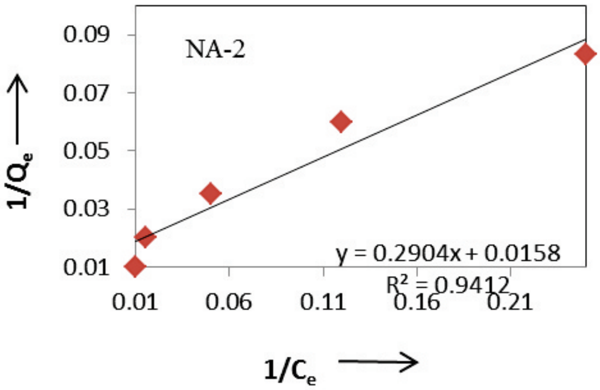


Figure-7 Langmuir Isotherm of NA-2

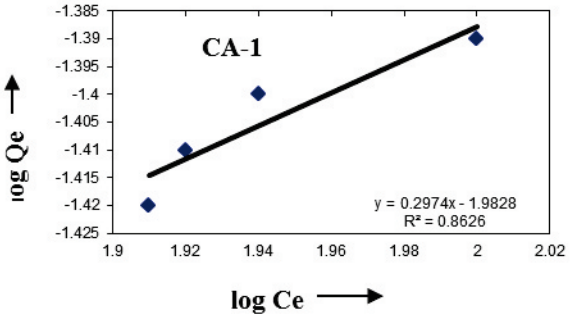


Figure-8 Freundlich Isotherm of CA-1

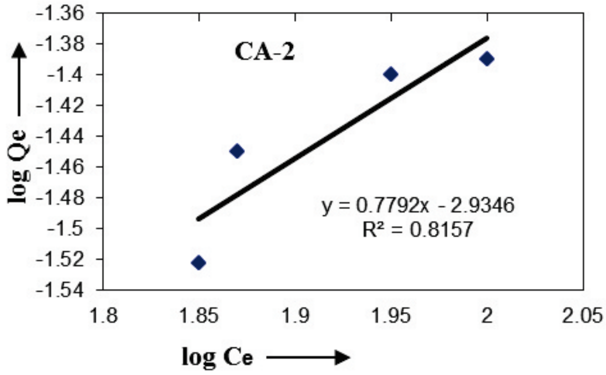


Figure -9 Freundlich Isotherm of CA-2

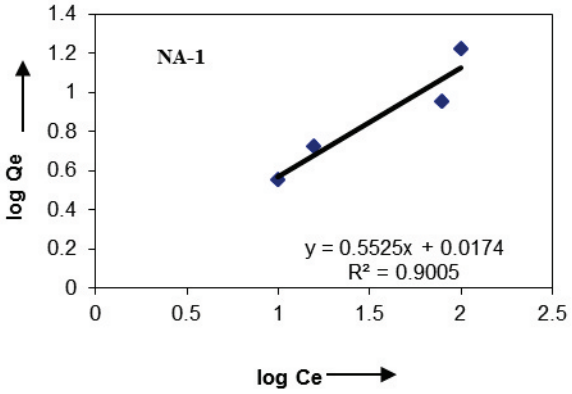


Figure - 10 Freundlich Isotherm of NA-1

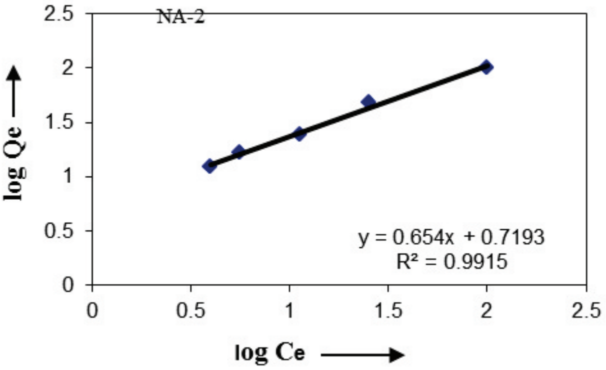


Figure - 11 Freundlich Isotherm of NA-2

The equations obtained for Langmuir and Freundlich adsorption isotherms for the chemical and natural adsorbents are shown in table – 1

Table 1. Langmuir and Freundlich adsorption isotherms parameters for the chemical and natural adsorbents

Adsorbent	Equation for Langmuir model	Equation for Freundlich model
CA-1	$1/q_e = 2284.(1/C_e) + 1.532$ (0.897)*	$\log q_e = 0.297 \log C_e - 1.9982$(0.862)*
CA-2	$1/q_e = 2310.(1/C_e) + 1.106$ (0.888)*	$\log q_e = 0.779 \log C_e - 2.394$(0.815)*
NA-1	$1/q_e = 2.316.(1/C_e) + 0.029$ (0.928)*	$\log q_e = 0.552 \log C_e + 0.017$ (0.900)*
NA-2	$1/q_e = 0.290.(1/C_e) + 0.015$(0.941)*	$\text{Log } q_e = 0.654 \log C_e + 0.719$(0.991)*

*R^2 values of CA-1 and CA-2, NA-1 and NA-2

The Q_{max}. for CA-1 & CA-2, NA-1 & NA-2 were found to be 0.6,0.9,34.48 and 64.66 mg/g. Maximum adsorbent capacities (Q_{max}.) was obtained by the natural adsorbent than chemical adsorbent. The natural adsorbents showed very good correlation. The natural adsorbents are found to be a potential adsorbent for AS.

3.5 *FTIR and SEM images* :

Further characteristics of the natural adsorbents were analyzed using SEM (scanning electron microscopy) and Infrared spectrum was analyzed. The images are shown in Figure 12-15. The presence of cavities in the SEM images shows the binding sites of the adsorbent. In the FTIR spectrum the presence of peaks at 3348 and 1678 cm^{-1} indicates the presence of –COOH and /or –OH groups which also contributes to some extent to the removal of SDS.

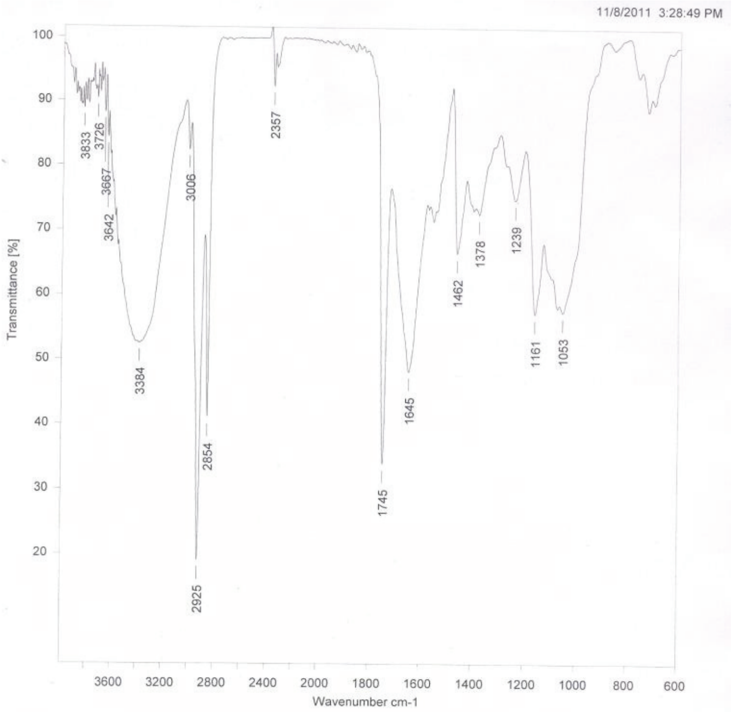


Figure - 12 FT-IR figure of NA-1 (Karanj seed)

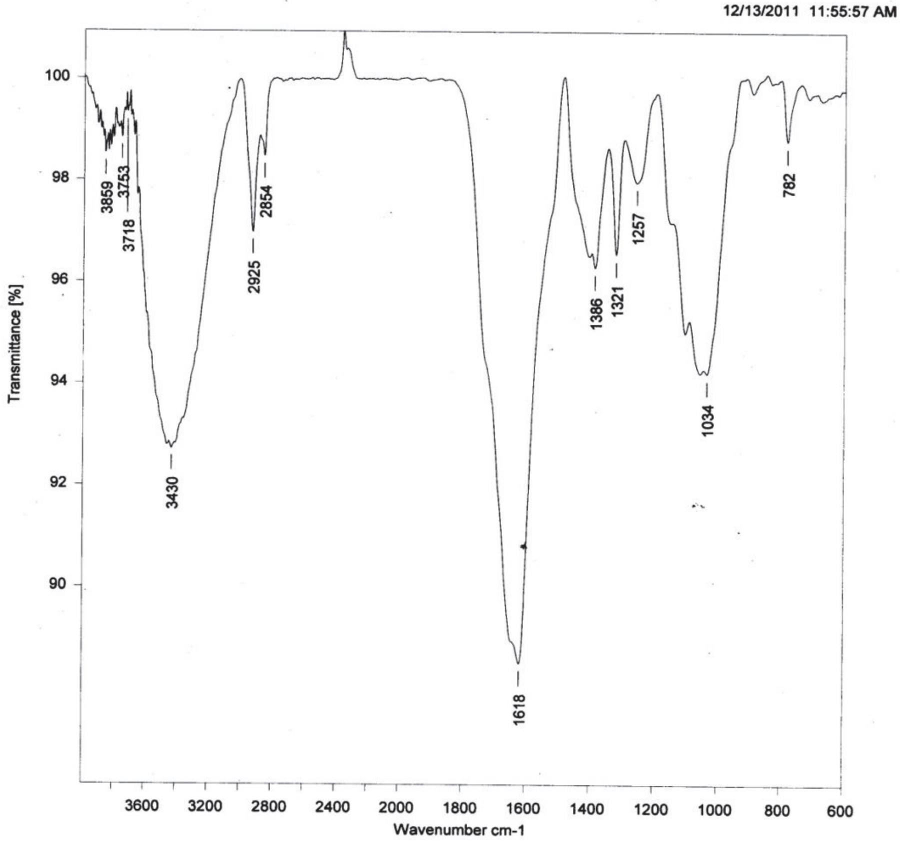


Figure - 13 FT-IR of NA-2 (Tulsi Leaf)

Based on the FTIR studies it can be concluded that the various functional group act as efficient sites for the adsorption of the surfactant which takes place by the substitution of amine, nitro, hydroxyl and carboxylic groups by the hydrophyllic end of the surfactant.

SEM image of Karanj seeds (Figure-14 & 15) were taken in various magnification of 20 μm,50 μm,100 μm and 500μm. The images show cavities which explain the presence of active sites for adsorption present in the Naturaladsorbent-1.

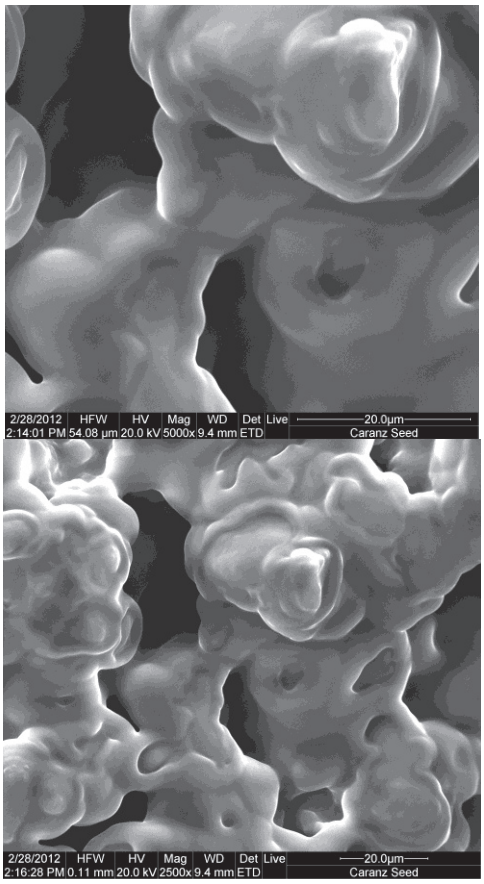
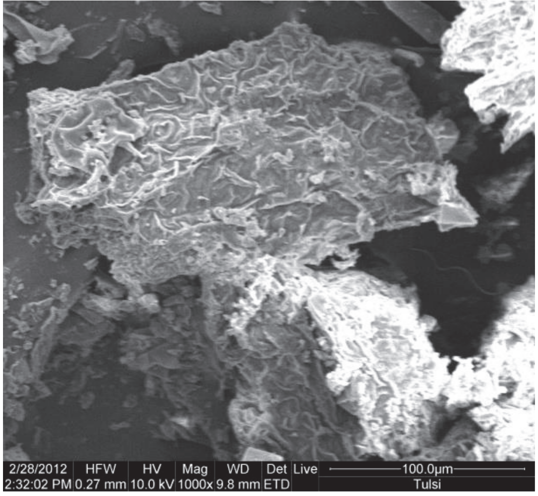


Figure-14 SEM (Scanned Electron Image) of NA-1 Karanj seed

SEM , Image of Tulsi leaf (Figure - 15) was taken in various specifications of 100 μm, 200 μm and 500 μm and was found fine cavities in the Natural adsorbent -2 which explains the adsorption capability of Tulsi leaf.



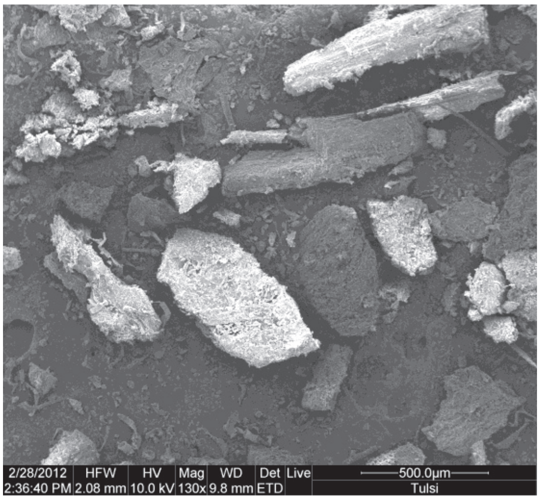


Figure-15 SEM (Scanned Electron Image) of NA-2 Tulsi leaf

4. Conclusion

Four adsorbents –Lime, Alum, Karanj seeds & Tulsi leafs were tried for AS removal. Lime and Alum shows a poor performance. The chemical adsorbent amount is also huge in terms of removal of AS. The natural adsorbents exhibited maximum removal efficiency ranged from 90 % to 94 % As pH increases, efficiency of the process decreases, due surely to the cationic character of the Biomass protein and to the fact that at acidic pH hydrophobic links are enhanced. Temperature does not affect significantly to surfactant removal process. The Qmax.values were compared. Isotherm data at 27^0 C were fitted to Freundlich model better than to Langmuir model. The R^2 value for CA-1, CA-2, NA-1 and NA-2 was calculated and compared. In terms of co-relation coefficient the natural adsorbents are found to be in good agreement. Among both the types of adsorbents the natural adsorbents are found to be free of cost material. These adsorbent leaves scope to study more extensively for their commercial applicability.

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