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Medicinal Plants the Key Bio-Adsorbents for Anionic Surfactant (SDS) From Waste Water

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Abstract
The pollutant binding capacity of seeds of Embelia ribes, Celastrus paniculatus was investigated in a batch system under varying conditions. The results indicate that sorption equilibrium was established in about 60 minutes. The anionic surfactant sorption is highly dependent on pH and maximum removal was observed at pH 2 - 6. It was also observed that sorption of surfactant decreases with increase in temperature. The experimental results were analyzed in terms of Langmuir and Freundlich isotherms. The Freundlich isotherm model fitted well to data with 0.94 regression co-efficient (R2). Evaluation of experimental data in terms of biosorption kinetics showed that the biosorption of surfactant on both the biomass followed pseudo-first order kinetics. The results showed that biosorbent are an attractive low cost alternative for the treatment of wastewaters containing lower concentrations of anionic surfactant.

Introduction: Rapid industrialization has led to increased discharge of chemicals, that causes environmental and public health problems. Among the noteworthy group of chemicals, surfactants are widely used in many application which pose a serious threat to biolife and environment.Surfactants are widely used in industrial processes for their favorable physicochemical characteristics such as detergency, foaming, emulsification, dispersion and solubilization effects (1-4). Surfactants have become a very important group of compounds in modern life. They are present in chemical industry, hi–tech devices, paints and leather (5). Attending to last statistical data, more than 15 million tons per year (6) are used, so surfactants can be considered as a first important chemical group. In domestic waste water produced by the households, surfactants invariably exists in significant amount due to the enormous use of detergents for washing purpose. Ionic surfactants constitute two third of all surfactants and anionic constitute more than 90% of all ionics (7). Anionic surfactants, having high degree of foaming capacity, are extensively used in the production of tooth paste, soap, shampoo and many industrial detergents (8).

They may be useful and needed compounds, but they are also considered dangerous and undesirable substances because of their impact on water, animal and vegetal life. The main aspects in which surfactants modify on environmental equilibrium involve(9) ground water and lakes pollution, pharmaceutical products binding (so pollution activity of these kind of chemical compounds is considerably increased), animal and human toxicity and biopersistance. Furthermore, they can act synergistically with some other toxic chemical which may be present in waste waters increasing their negative effects on the environment (7). Therefore, the amount of surfactants present in waste waters of many industries, especially detergent and textile, (Photograph - 1-Bilaspur) must be reduced at least to acceptable levels before discharging to the environment. Many techniques have been used for the removal of surfactants in aqueous solution. Among these biological degradation, ozonation and extraction are often costly and may possibly create secondary pollution because of excessive use of chemicals (3, 10-11). Among the physico-chemical processes, adsorption technology is considered to be most effective and proven technology having wide potential for application in both water and waste water treatment (12). Adsorption is considered to be superior compared to other techniques for waste water treatment in term of cost, simplicity of design, ease of operation and insensitivity to toxic substances (13). These adsorption process also proven to be an effective method in the case of low concentrations of surfactant. Numerous adsorbents such as activated carbon, layered double hydroxides and natural biomasses, have been extensively investigated (14-16). Activated carbon has been water industries standard adsorbent for the reclamation of municipal and industrial waste water for almost three decades. Since cost is an important parameter in most developing countries, efforts have been made to explore the possibility of various low cost adsorbents such as sugar cane bagasse, coconut coir pith, saw dust (17) wood charcoal, eucalyptus bark, rice husk, chitin and chitosan (18,19) wheat straw (20). In these sense we have researching natural product as a water treatment agent for several years. The power of using natural product lays on the fact that it is not technologically difficult to operate by non-qualified personal, it is easy to work with and it presents not a external dependency of reagents, as it would happen with other products ($Al_2(SO_4)_3$, $FeCl_3$ etc.). Because of these reasons, it has been recommended by the Food and Agricultural Organization (FAO) as a proper and advisable way for treating water.

Celastrus paniculatus (Malkangni) belong to family Celastraceae. This plant has been used for sharpening the memory, increasing intellect and improving concentration. Massage of the Seed oil of this plant is used sciatica, lumbago, paralysis, arthritis etc. Embelia ribes (Vaividang) belong to family Myrsinaceae. It is medicinal woody climber with long slender brittle stem, it is a climbing creeper shrub and flexible. (21). It is considered to be vulnerable due to excessive harvesting and because of its many uses (22). It is highly valuable medicinal plant with carminative, antibacterial, antibiotic, hypoglycemic and anti fertility properties.

After a preliminary screening on surfactant removal ability of several natural agents, this paper aims to characterize interesting capacity of Embelia ribes and Celastrus paniculatus in surfactant removal. Due to its proteinic nature and flocculant activity it works very well removing surfactants from surface water. Further throughout the paper the Embelia ribes and Celastrus paniculatus seeds will be given the terms as Bio-adsorbate -1 (BA-1) and Bio-adsorbate -2 (BA-2).

Reagents : Crystal Violet (CV), SDS (Sodium dodecyl sulphate), Benzene, Orthophosphoric acid were from BDH (AR) grade and were used as received. All other chemicals used in this study were of high purity and used without further purification.

Adsorbents : The extraction process was carried out in the following way; The seeds of the two medicinal plants were shade dried at room temperature in a clean environment to avoid contamination for few days and powdered in a domestic grinder. The powdered samples were stored in air tight bottles at room temperature for further analysis.

General Surfactant Removal Assay: A sodium lauryl sulphate ($CH_3(CH_2)_{11}OSO_3Na$) (1-100 ppm) solution was prepared. Different volume of this solution were put into recepients and controlled quantity of adsorbents dosage was added. A vigorous shaking was applied for 60 minutes using a REMI shaker of 120 rpm until a equilibrium was achieved. Then a sample was taken and it was centrifuged. Surfactant removal was determined by visible spectrophotometer.

Surfactant analysis : In order to analyse surfactant concentration, a rapid and reliable method has been developed for the determination of Anionic Surfactant. Crystal violet(23) has the potential for being used as an ion – pairing agent with AS. The ion – pair formed between AS and CV is extractable in benzene. Sample solution (10 ml) containing SDS in the range of 0.7–10 ppm was transferred into a 25 ml separating funnel. CV (5×10^{-3}) and orthophosphoric acid 100µL each was added. Then 5mL of benzene was added to it and shaken for 1 minute. The aqueous layer was then discarded and the benzene layer was used for absorbance measurement at 565 nm.

Batch Mode Adsorption Study:

Batch adsorption experiment was carried out at room temperature (25-30^{0}C). In each experiment 250 mL SDS solution of known initial concentration (1mg/L-100mg/L) was treated with a specified known amount (by wt.) of biomass (10mg/L to 200mg/L), and known pH for a specified period of time. Batch kinetic studies were conducted using fresh biomass to determine the time needed for Sodium dodecyl sulphate binding process to reach the equilibrium state. Based on Kinetic experiment results all experiments were conducted for a period of 60 minutes. After the equilibrium was reached the adsorbent was separated from the SDS solution by using whatman's filter paper No.42, then visible spectrophotometer (Systronics-105) measured the concentration of SDS remaining in the solution.

The adsorbtion capacity of surfactant on the adsorbent, qe (mg/g), was calculated by *a mass balance relation*

$$qe = (Co - Ce) V/W \quad - \qquad (1)$$

where

Co and Ce are the initial and equilibrium concentrations of surfactant respectively. (mg/L) V is the volume of solution (L) and W is the weight of the adsorbent used.

Similar experiments were also carried out to evaluate the effect of process parameters such as pH (2-10) biosorbent dosage (10 -200g/L), initial concentration of SDS (2-200 mg/L). The Industrial waste water contaminated with SDS were treated with biomass in a batch experiment. The experiments done without biomass were treated as blanks.

Result and Discussion:

1-*Effect of pH on Biosorption:*

pH values were varied between 2 and 10 in order to determine its influence on surfactant removal. Experimental data series is shown in figure no.1. As it can be appreciated a fixed dose of 25g/L of BA-1 and with a surfactant dose of 10 ppm tends to be less effective as pH becomes higher i.e. towards the alkaline medium. The graph between pH and bioadsorbent shows a marginal increase from 2 pH to max. at 5 pH and then it decreases moving from 6 pH to 9 pH. BA-1 remove sodiumdodecyl sulphate upto 80-96 %.

2- *Effect of Biosorbent dosage* :A graph was plotted between the different dosage of biosorbent of Embelia ribes and Celastrus paniculatus powder. The study of effect dose of adsorbent is necessary and very useful to find out the optimum amount of adsorbent required for the removal of SDS. The effect of adsorbent dose studies is observed from 5-100g/L for BA-1 and 1g/L-100g/L . A graph was plotted between the different biosorbent dosage (1-100g/L) with percentage removal of SDS were shown in Fig - 2. The graph shows a marginal increase in SDS removal with increasing biomass concentration which ranged between 60% to 90%.

3- *Effect of adsorbate concentration*: The effect of adsorbate concentration is studied taking a range of solution (5-200mg/L) with an optimum pH value. The rate of SDS adsorption on BA-1 as given in Fig. 3. The percentage removal remains constant after a particular increase of initial concentration of the SDS solution. This may be due to the lack of available active sites for the adsorption of high initial concentration of SDS solution and also it is known that increasing the total amount of surfactant (and particularly anionic one) may lead to a de-naturation of proteins.

Effect of contact time: In the adsorption system contact time plays a vital role. The effect of contact time on the percent removal of SDS was investigated at the optimum initial concentration of SDS and it is presented in Fig.4. It was found that the removal of SDS increases with contact time to some extent. The removal of SDS (in terms of SDS adsorbed i.e. qe) by the adsorbent BA-1 increases, reaches maximum value and then remains constant with the increase in contact time (may be due to desorption process). The relative increase in the extent of removal of SDS (qe) after 20 minutes of contact time is negligible and hence it is the optimum contact time.

Adsorption isotherms: Adsorption isotherms are essential for the description of how SDS will interact with the natural bio-adsorbate surface and are useful to optimize the use of natural bioadsorbate as adsorbents for the removal of SDS removal. Two important physicochemical aspects of evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the Kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationship between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. Most often Biosorption equilibria are described with adsorption isotherms of Langmuir or Freundlich types.

The linear form of Freundlich theorem is:

$$\text{Log } qe = \log k_f + 1/n \log C_e \qquad (2)$$

The linear form of the Langmuir theorem is:

$$qe = a\, b\, Ce / (1+b\, Ce) \qquad (3)$$

where log K_f is a measure of the adsorption capacity and 1/n, is an indicator of adsorption effectiveness; qe is the amount of SDS adsorbed per unit mass of adsorbent (mg/g), a and b are Langmuir constant which are the measures of monolayer (maximum) adsorption capacity (mg/g) and energy of adsorption g/L respectively.

The values of Freudlich and Langmuir parameters were obtained respectively, from the linear correlations between the values of (1) log qe and log Ce and (2) Ce/qe and Ce.
The adsorption isotherms parameters along with the correlation coefficients are presented in the table - 1

Freundlich and Langmuir isotherm plots are shown in Figures -5 (a) and Fig–6 (a).

Kinetics of adsorption:

The two important physical and chemical aspects for parameter evaluation of the sorption process as a unit operation are kinetics and the equilibria of sorption. Kinetics of sorption, described the solute uptake rate, which in turn governs the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption.
The sorption kinetic data obtained from natural bioadsorbate - SDS system was studied with different kinetic models). The kinetic of adsorption of SDS and BA1 and have been studied by applying the following kinetic equations proposed by Lagergren based on the solid capacity

Lagergren equation:

$\text{Log}\ (qe - q) = \log qe - (k_{ad.}\ t)/2.303$ (5)

All the linear correlations were found to be statistically significant (as evidenced by r-values close to unity) at 95 % confidence level and indicate the applicability of these kinetic equations and the pseudo first order nature of the adsorption process of SDS on BA-1 and BA-2 .

FTIR Analysis of the Seeds

The intense bands occurring at 3350.14 cm-1, 2925.38cm-2, 2854.31 cm-1, 1746.29 cm-1, 1461.55 cm-1, 1371.76 cm-1 ,1231.08 cm-1, 1162.83 cm-1 , 718.39 cm-1 corresponding to N-H/ C-H/ C=O/ phenol C-O str/ C=N/ C-H aromatic str/ stretching, bending, vibrations respectively indicate the presence of amines, amides, C-H bond of alkanes, ester, ether, phenol C-O bond,O-H aromatic mono substituted compounds in the seeds of Celastrus paniculatus (Malkangni).
The intense bands occurring at 3438.40 cm-1, 3311.49 cm-1, 2923.04 cm-1, 2852.69 cm-1, 2360.56 cm-1, 1616.52 cm-1, 1459.62 cm-1, 1329.43 cm-1, 1197.20 cm-1 and 699.35 cm-1 corresponding to O -H / N-H / O-H / C-H / N-H /C=O/Phenol O-H / C-Cl / stretching, bending , vibrations respectively indicate the presence of alcohol,amines,carboxylic acid , ester ,C-H bond for alkanes , amino acids etc in the seeds of Embelia ribes (Vaividang).

Conclusion:

The experimental results indicate that adsorption on the seeds of Embelia ribes and Celastrus paniculatus can be used as a effective way of removing anionic surfactant from waste water. The results of adsorption equilibrium and adsorption kinetics depend on initial concentration of surfactant, pH, adsorbent dose and contact time. A commercial based natural products have been found as an effective anionic surfactant removal agents in aqueous solutions. Langmuir and Freundlich models fit well to experimental data so surfactant removal phenomena can be explained through adsorption hypothesis. Experimental series fits better to Freundlich and then to Langmuir, according to r^2 determination parameter value it is possible to prove the goodness of this fitting by showing linearized graphics. A detailed study on column adsorption is under progess. 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 hydrophilic end of the surfactant.Numerical values may differ in other operational conditions or working with different surfactant.

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FIGURE – 1 : Effect of pH on percentage removal of SDS

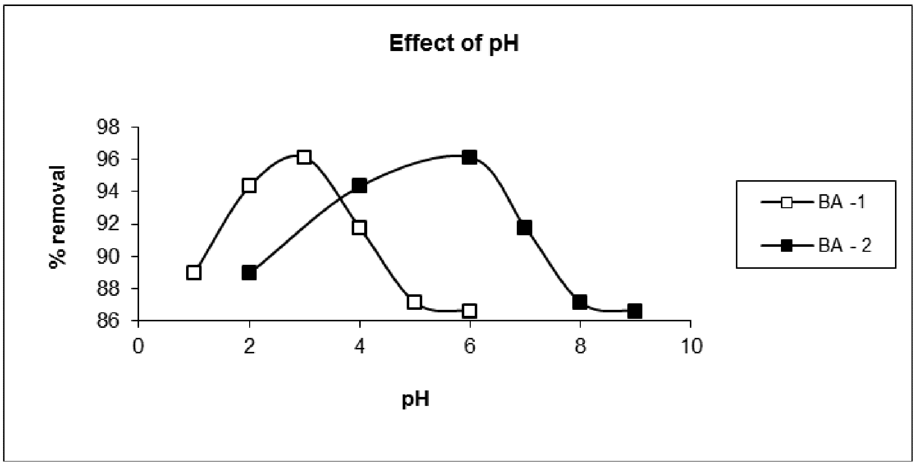

FIGURE – 2 : Effect of adsorbant dose on percentage removal of SDS

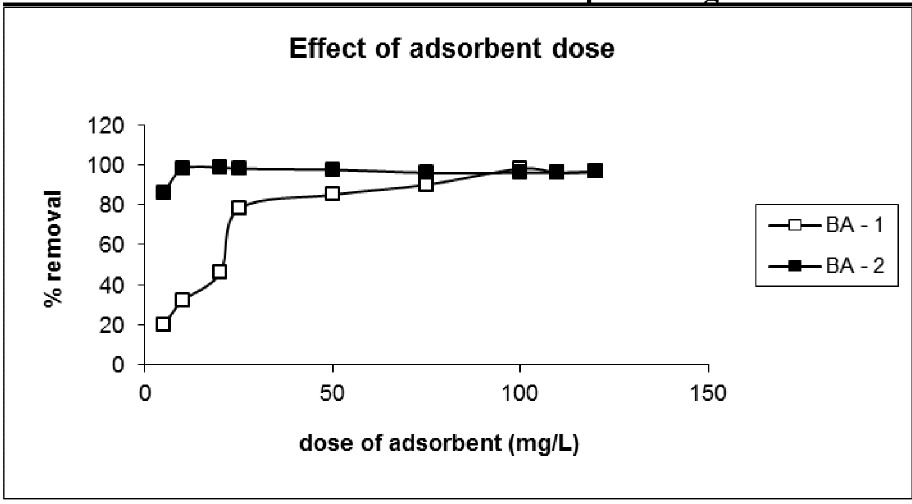

FIGURE – 3 : Effect of SDS concentration (ppm) on percentage removal

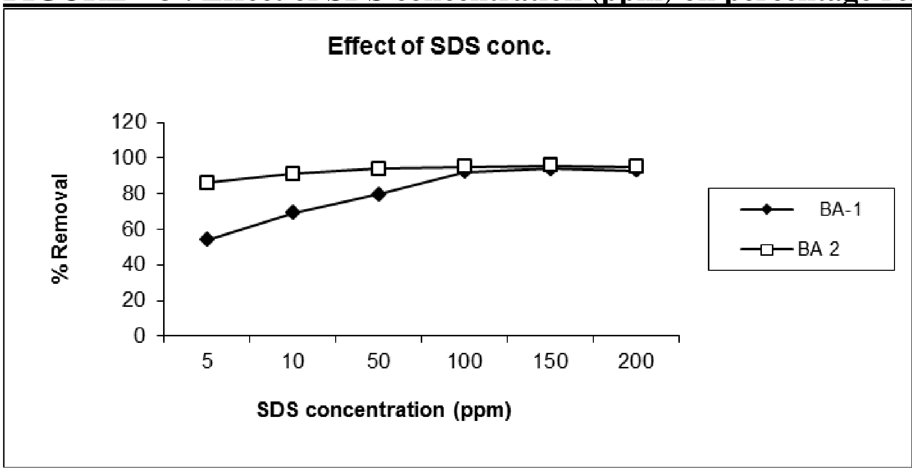

FIGURE – 4 : Effect of contact time on percentage removal of anionic surfactant SDS

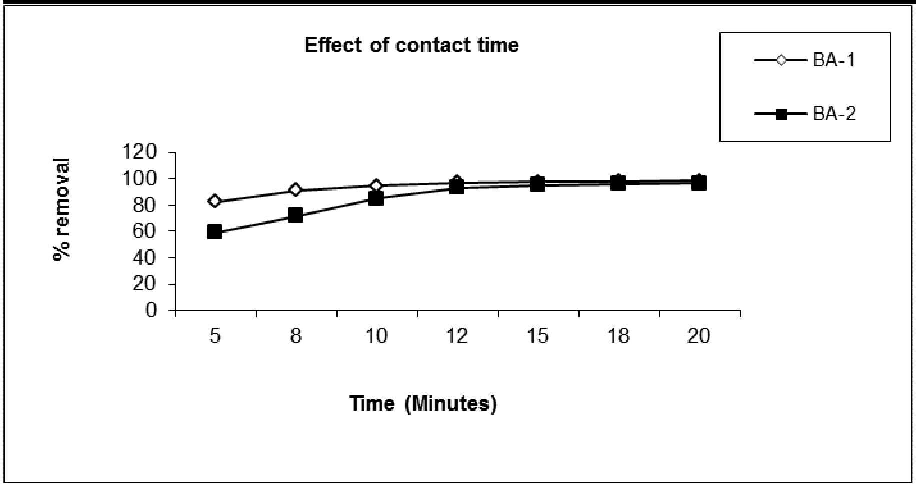

Table – 1 :

	Freundlich Theorem			Langmuir Theorem		
	K_F (mol/gm)	n	R^2	K_L (mol/gm)	Q_0 (mol/gm)	r^2
BA-1	$3.079x10^{-5}$	2.04	0.99	$0.219x10^{-5}$	$7.06x10^{-6}$	0.903
BA-2	$3.499x10^{-5}$	1.83	0.99	$0.51x10^{-5}$	$7.35x10^{-6}$	0.953

Figure 5(a) – Langmuir Theorem (BA-1)

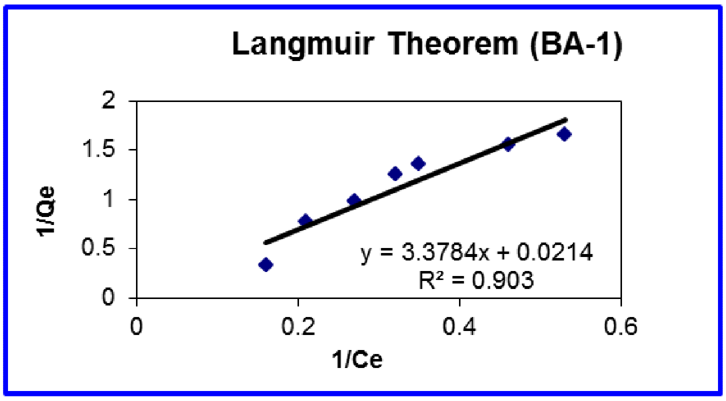

Figure 5(b) – Freundlich Theorem (BA-1)

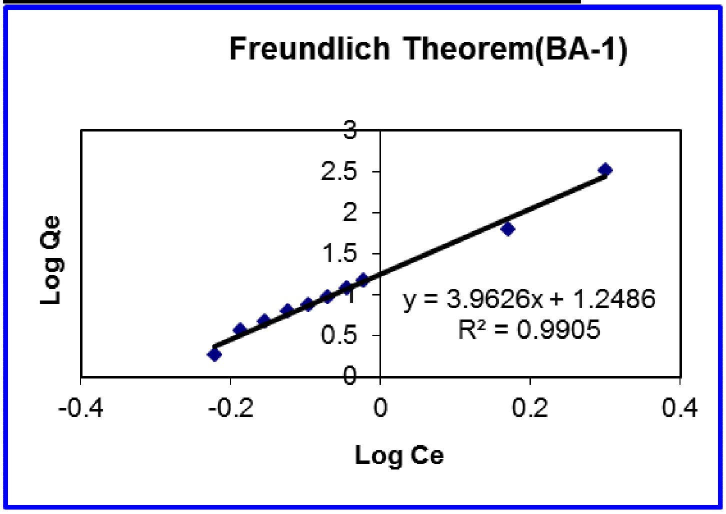

Figure 6(a) – Langmuir Theorem (BA-2)

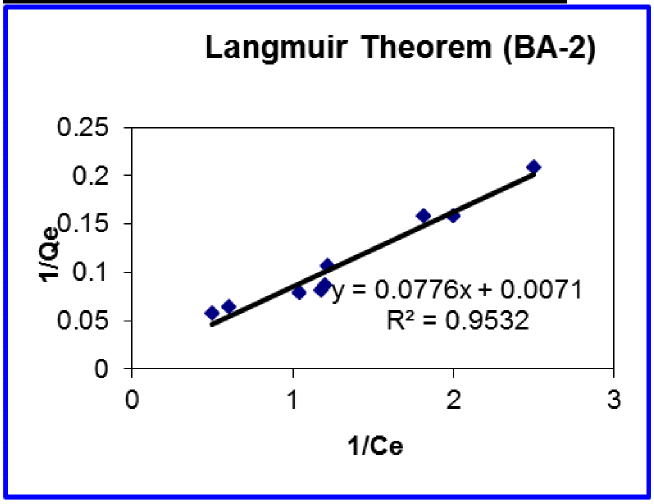

Figure 6(b) – Freundlich Theorem (BA-1)

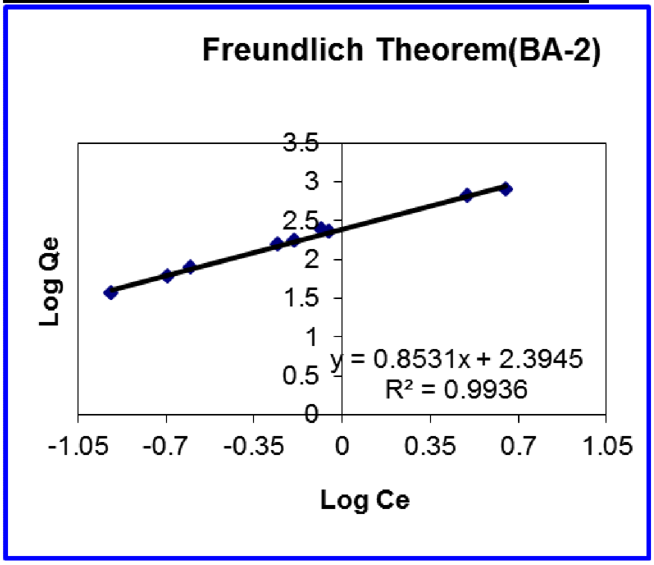

Figure 7 : FTIR spectra of seeds of Celastrus paniculatus(Malkangni)

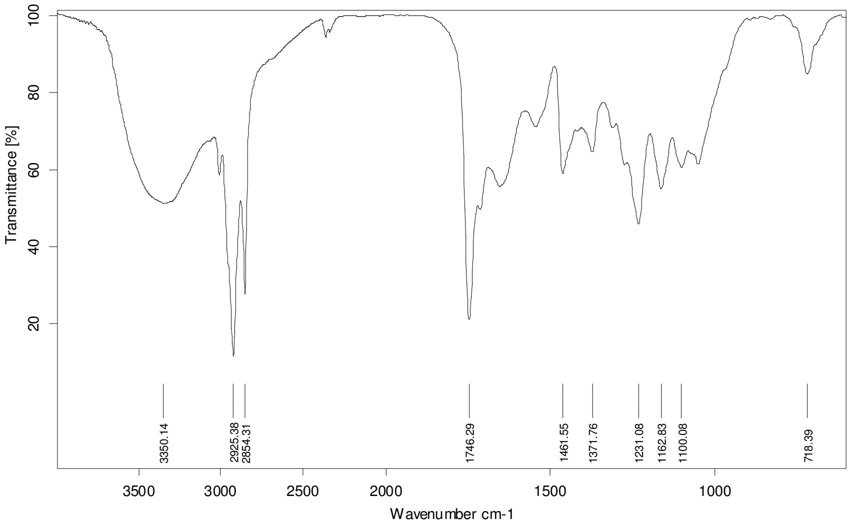

Figure 8 : FTIR spectra of seeds of Embelia ribes (Vaividang)

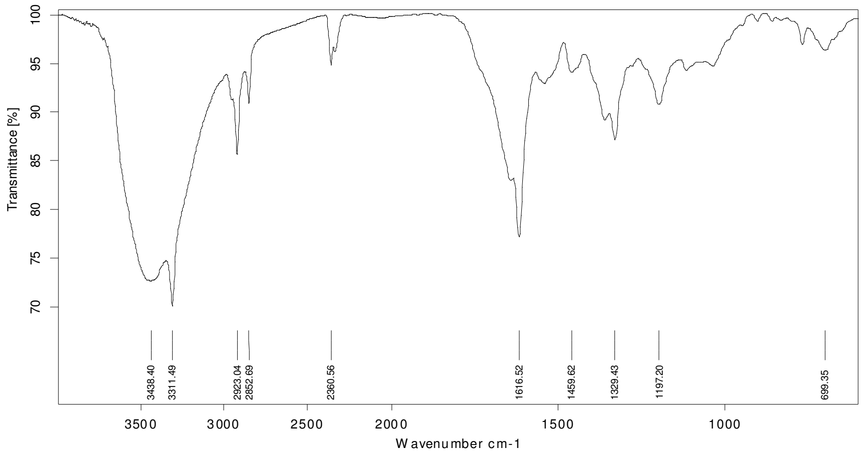

Photo -1 Near M J College Bhilai