ISSN NO. 2320-5407

***Journal homepage: http://www.journalijar.com***
***Journal DOI: 10.21474/IJAR01***

***INTERNATIONAL JOURNAL OF ADVANCED RESEARCH***

**RESEARCH ARTICLE**

# Intrusion Of Sulphide In Fresh Water Along The Coir-Retting Areas Of The South West Coast Of India.

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## *Manuscript Info*

***Manuscript History:***

Received: 18 May 2016
Final Accepted: 19 June 2016
Published Online: July 2016

***Key words:***
Retting, pectin, accumulation, de-nitrification, deterioration, anoxic.

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## *Abstract*

Conventional retting of coconut husk has caused serious threats to the coastal eco system. Pectinolytic activity of micro organisms like bacteria, fungi and yeast releases large amount of pectin, polyphenols and tannin which account for the formation of high levels of sulphide, phenol and ammonia, apart from nitrate and nitrite in the medium. Presence of *Desulphovibrio, Micrococcus, Pseudomonas, Clostridium, Bacillus,* and *Aspergillus Niger* has confirmed the microbial interference in the pectin degradation. There are strong indications of retting-related toxins, to have intruded into the fresh water system along the coastal belt.



## Introduction:-

Retting of coconut husk for the production of fibre is widespread throughout the coastal areas of Cape Comorin, the southern tip of peninsular India, in view of their economic importance. The retting process brought about by the pectinolytic activity of micro organisms like bacteria, fungi and yeast normally produces large quantities of organic substances such as pectin, pentosan, polyphenols and tannin (Manoj *et al*., 2014; Immanuel *et al*.,2014). The release of organic acids like poly phenols and tannin into the retting effluents make the entire medium acidic(Cholarajan *et al*.,2011). Sulphate-reduction and nitrification too contribute to acidity. Water quality of the nearby resources has deteriorated with the accumulation of toxic organic compounds (Sundararaj *et al*.,2015).

Depletion of dissolved oxygen and production of $H_2S$ are the most important factors associated with the water quality of retting zones (Nirmala *et al*.,2004). The depletion of oxygen leads to anaerobic degradation with the emission of $H_2S$, thereby increasing the pollution indices of the surroundings(Lahav *et al*.,2006). The anoxic conditions during summer in the retting zones are due to restricted circulatory process and heavy breathing by the organic matter in the medium (Kadeeja Beevi *et al*., 2004) and during this time, oxidation- reduction potential falls in effluent and the sediments. Bacterial sulphate- reduction is a potential source of high sulphide concentration in sediment (Dan *et al*.,2007) and the rate of sulphate- reduction is actively controlled by the supply of organic matter.

$$SO4^{2-} + 8e^- + 10H^+ \rightarrow H_2\,S + 4H_2O \qquad E^0 = --221mv$$

The sulfurous odour is a marker for the presence of sulfate-reducing bacteria (*Dexter et al*.,2003) and the organic carbon used by these bacteria are limited to a few single organic molecules such as lactate and pyruvate which are partly oxidised to acetate (Alvarez,2005; Kolmert,1999; Vallero,2003). In the anoxic sediments, hydrogen sulphide precipitates black metal sulphides affecting soil redox, metal concentration and oxygen availability (Holmer *et al*., 2011). Manoj *et al* (2014) have indicated the presence of sulphide in the water sources of Kodungallur retting zones which may be due to the intrusion of sulphide from the retting zones due to the microbial decomposition of organic load.

The microbial denitrification process taking place as part of the nitrogen cycle, leads to a steady decline in nitrate-nitrogen accompanied by a progressive increase in ammonia. However, nitrification of ammonia too, is associated with micro organisms and this proceeds rapidly in the sediments under favourable pH conditions. The yield of nitrite from ammonia is slow and is relatively low, compared to the amount of oxygen consumed by the converting micro organisms(Tiwari,2009).

During different stages of retting of coconut husk, large amount of pectin, lignin and tannin are released from the husk into the surrounding medium. Studies on the poly phenols and phenolytic bacteria in coir fibre steep ecosystem, have revealed the presence of resorcinol and catechol in addition to phenol in the coir fibre steep liquor (Bijoy Nandan,2004) and these poly phenols come mostly from lignin during its biodegradation(Van Schie and Young,1998; Arts *et al*.,2005). The phenolic effluents released into the environment also contribute to further deterioration of the health of water sources. The present study was undertaken to assess the water-sediment characteristics associated with the impact of pollution along the retting zones.

## Study Area:-

The study area lies between $8^0$ 2' and $8^0$ 4' N latitudes and $77^0$ 26' and $77^0$ 30'E longitudes along the South-West Coast of peninsular India, encompassing Cape Comorin which receives heavy rain during South West and North East monsoons. The present study was undertaken between June 2010 and May 2012, spreading over south west monsoon, north east monsoon, post monsoon and summer. Thousands of retting ponds are situated along the coastal regions of Kanyakumari. Effluent and sediment samples were collected from the retting ponds from the strategic locations falling within 40 km area from Manakudy (1), Eathamozhi (2), Rajakkamangalam (3), Ganapathipuram (4), Thickurichy (5), Manavalakurichy (6), Puthur (7), Kottilpadu (8), Colachel (9) to Thengapattinam (10) along the South West Coast of India.

Coconut husks are normally allowed to ferment in retting ponds adjoining the estuaries and allied water bodies, for a minimum period of three months in previously-used fermentation ponds. Effluent samples, sediments from the respective retting ponds and water from the nearby ponds and wells were collected in triplicate. The effluent and water samples were collected using dried polythene bottles and kept at the freezers.

## Materials and Methods:-

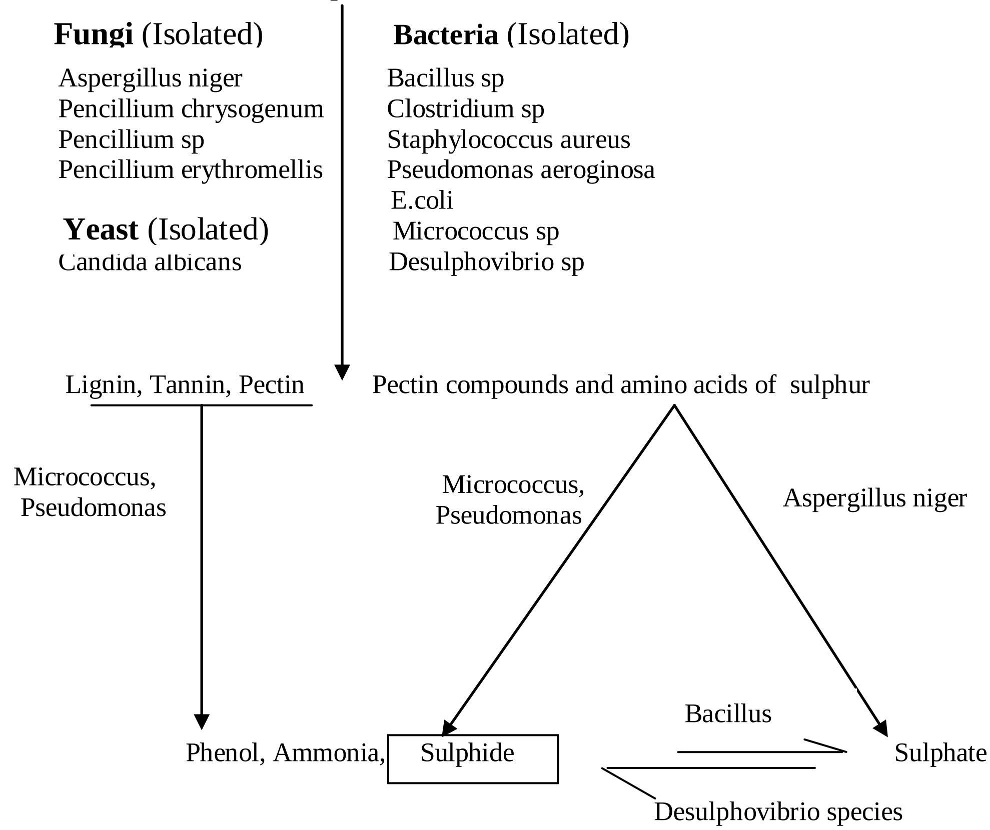
The samples were analysed for the relavant physico-chemical parameters including sulphide, sulphate, phenol, ammonia, nitrate and nitrite. Analyses were carried out as per standard procedures (APHA, 2005).The concentration of ammonia and hydrogen sulphide in the surrounding air were also recorded using digital VS70-$NH_3$ and VS70-$H_2S$ gas monitors.

## Results and Discussion:-

There are significant seasonal and station-wise variations in parameters such as sulphide, phenol, ammonia as well as nitrate and nitrite while comparing the effluents with those of the fresh water sources. The values presented here are the mean of the two monsoon and summer seasons of 2011 and 2012.

High levels of sulphide concentration are recorded in the retting yards, ranging from 5.26 ppm-max(monsoon) to 10.97ppm-max(summer); mean(8.12ppm), in the sediment and 3.14ppm-max(monsoon) to 5.95 ppm-max(summer); mean (4.55ppm)in the retting effluent. There is a corresponding increase from 715 ppb-max(monsoon) to 1780 ppb-max(summer); mean(1250 ppb) in the water sources; as well as the $H_2S$ concentration in the atmosphere (740 ppb-max(monsoon) to 950 ppb-max(summer); mean:850ppb) near the retting yards (Fig-1a). The high correlation ($R^2$ =0.88) observed between well water and effluent (Fig-1b) is an indication of the source. The bacterial decomposition of organic matter utilizes large amount of dissolved oxygen resulting in near-anoxic condition (mean DO:0.91 ppm) in the effluent(Fig-1c) and ultimately produces $H_2S$ in acidic pH levels. Microbial degradation of pectin with the help of *Micrococcus* (plate-1),*Clostridium* and *Pseudomonas* sp favours the formation of hydrogen sulphide from the decomposition of organic compounds containing sulphur. The sulphates(mean:47.54ppm) formed through the action of *Aspergillus niger* (plate-2) from the released compounds are also reduced further to sulphide through *Desulpho-vibrio* sp (gram negative rods,plate-3) during summer and during this time the redox potential falls(effluent:-52 to 72 mv, sediments: -152 to 30 mv).

**Microbial Decomposition of Husk**




$$(CHO)_{106}(NH_3)_{16}H_3PO_4 + 53SO_4^{2-} \xrightarrow[\text{Sulphate reduction}]{\text{Desulphovibrio}} 106CO_2 + 106H_2O + 16NH_3 + H_3PO_4 + 53S^{2-}.$$

The sulphide ion produced, establishes an equilibrium with hydrogen ions to release hydrogen sulphide.

$$S^{2-} + H^+ \rightarrow HS^-$$
$$HS^- + H^+ \rightarrow H_2S$$

The black colour of the sediments in the retting areas is an indication of the sulphides of iron(Thomas *et al.*,2002). The concentration of iron ranges from 3.65ppt-max(monsoon) to 4.63ppt-max(summer); mean(4.14 ppt) in the retting sediment and 423ppb-max(monsoon) to 834 ppb-max(summer); mean (628.5 ppb) in the retting effluent. The fresh water sources indicate leaching of iron (170ppb-max(monsoon) to 420 ppb-max(summer); mean:295ppb) probably released from the sediments containing iron sulphide. In the anoxic reducing environment of the retting zones, hydrated ferric oxide is reduced to ferrous form which combines with $H_2S$ producing iron sulphide.

Nitrate is of great importance in assessing the self purification properties of water system and nutrient balance in surface water (Rump and Krist, 1992). In the retting yards, nitrate concentration in the sediment varies from 20.11ppm-max(monsoon) to 24.33ppm-max(summer); mean(22.22ppm) whereas, in the effluent it ranges from 19.56 ppm-max(monsoon) to 58.26 ppm-max(summer); mean (38.91ppm) and. in the fresh water sources from 2.91ppm-max(monsoon) to 5.95ppm-max(summer); mean(4.43ppm). High nitrate concentrations observed in the sediment as well as in the effluent in the retting areas is especially from nitrification taking place in the sediment as well as in water column, as reflected by the corresponding increase in the fresh water sources(Fig-2a,2b).

$$NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$$
$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$$

The rise in nitrite concentration results from the continuous nitrification-de nitrification processes occuring in the medium. The nitrite concentration ranges from 7.28 ppb-max(monsoon) to 9.95ppb-max(summer) in the retting sediment; mean(8.62ppb) and 6.15 ppb-max(monsoon) to 8.85ppb-max(summer) in the effluent; mean (7.5ppb) which is reflected in the fresh water sources (2.75ppb-max(monsoon) to 3.13 ppb-max(summer),mean: 2.94ppb) during summer(Fig-3). Comparatively higher levels of nitrite in nearby fresh water sources is reported in a few stations.

There is considerable release of ammonia in summer following a similar pattern observed in nitrate and nitrite levels. The value ranges between 234ppb-max(monsoon) and 567ppb-max(summer) in the effluent (mean:400.5ppb), the maximum value being observed at stations 3 and 4. The corresponding high levels of ammonia in the fresh water sources (196.5 ppb-max(monsoon) to 324ppb-max(summer); mean:60.25ppb) and atmosphere (89.5ppb -max(monsoon) to189ppb-max(summer); mean:139.25ppb) is an indication of the source (Fig-4a) as revealed by the high correlation ($R^2$=0.82) observed between well water and effluent (Fig-4b). There exists a definite link between the three parameters nitrate, nitrite and ammonia which could be due to the de-nitrification process which is active during summer, under a near-anoxic condition under the influence of *Bacillus (*plate-1) and *Pseudomonas.*

Phenol is another major pollutant in the water sources surrounding the retting units. The concentration in the effluent ranges from 1.36ppm-max(monsoon) to 1.96ppm-max(summer); mean (1.66ppm) and in the adjoining water sources it ranges from 65ppb-max(monsoon) to 140ppb-max(summer); mean(103ppb). Obviously the phenolic substances have intruded from the effluents to the surrounding medium(Fig-5a) as revealed by the high correlation ($R^2$=0.87) observed during summer(Fig-5b).Organic matter like pectin, pentosan, polyphenols and tannin from the retting areas have increased the organic pollutants in the surrounding medium making it acidic. Phenols such as catechol, resorcinol, pyrogallic acid which are soluble to certain degree especially in the deprotonated form, contribute to the higher phenolic concentration of the retting medium. Bacterial species like *Pseudomonas* (reported as gram negative rod) and *Micrococcus* species(gram positive cocci) are associated with the leaching of poly phenols and such phenol degrading bacterial strains were isolated earlier by Aresta *et al* (2010) in the polluted waters.

It is increasingly clear that high levels of sulphide, phenol and ammonia from the coir-retting units have intruded in to the surrounding water sources and have exceeded the maximum permissible levels of EPA(Nitrate and nitrite concentrations are well within the prescribed levels,,Table-1).

**Table-1**:- Permissible and reported levels of various parameters.

| Parameters | Permissible levels (EPA) | Reported levels(Maximum) |
|---|---|---|
| Sulphide | 0.2ppm | 1.23ppm |
| Phenol | 0.005ppm | 0.11ppm |
| $H_2S$(Air) | 0.1ppb(Ambient) | 0.95ppm |
| Ammonia(Air) | 0.14ppm | 0.16ppm |
| Nitrite | 1ppm | 1.40ppb |
| Nitrate | 10ppm | 3.40ppm |

**Figures**

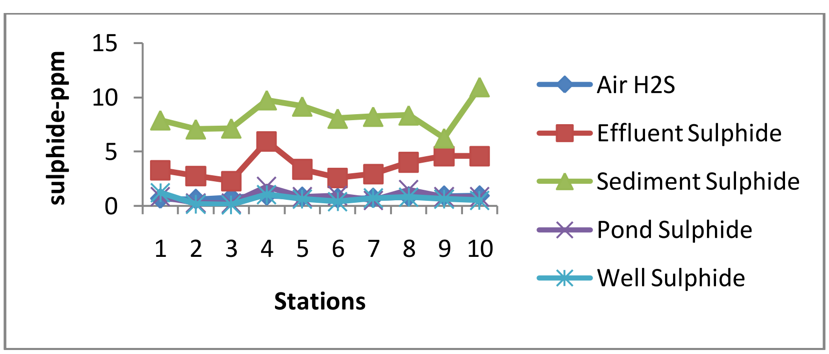



**Fig-1a**:- Station-wise variation of sulphide during summer.

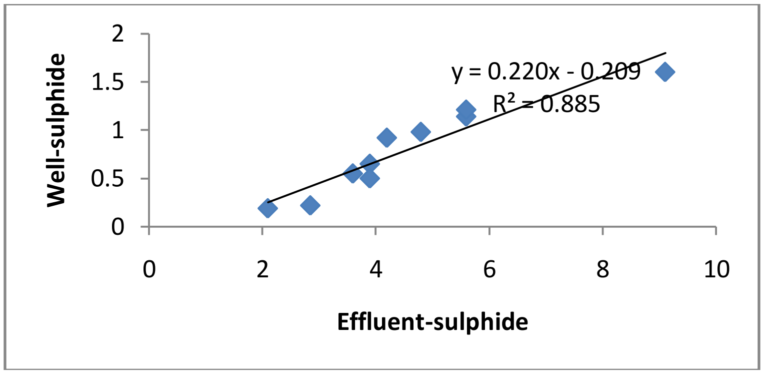



**Fig-1b:-** Variation of sulphide in well water and effluent (2012-summer).

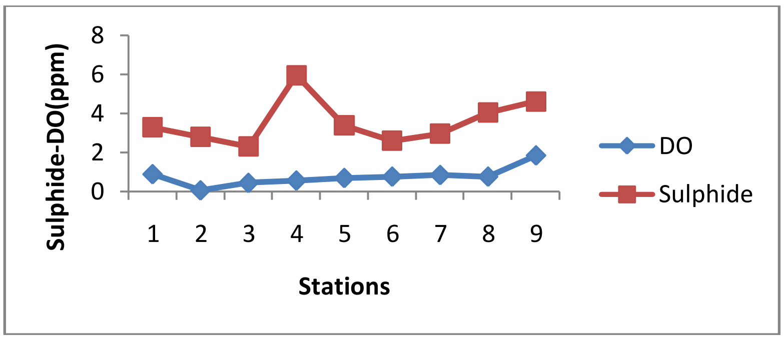



**Fig-1c:-** Variation of DO and Sulphide in the effluent during summer.

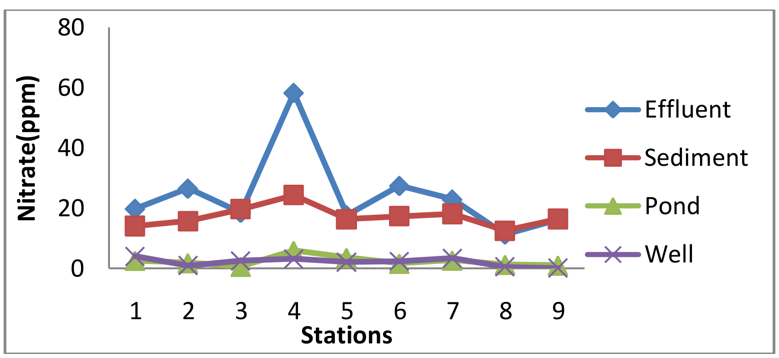



**Fig-2a**:- Station-wise variation of nitrate during summer.

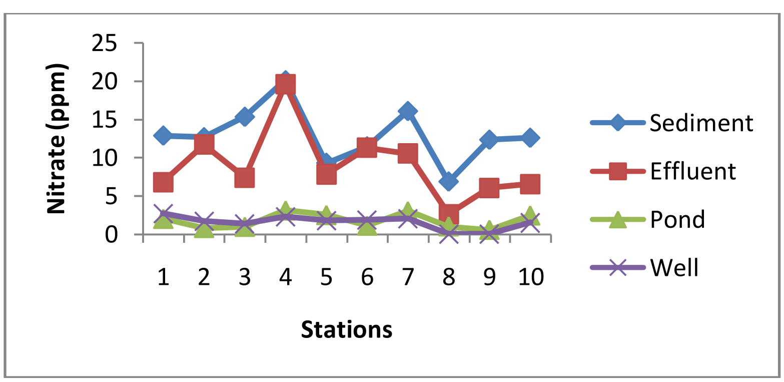


**Fig-2b**:- Station-wise variation of nitrate during monsoon.

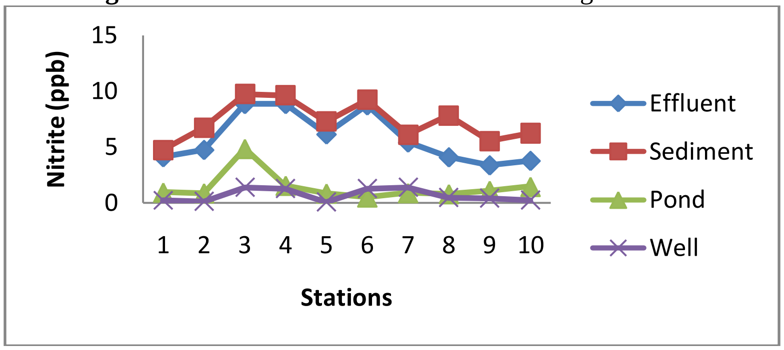



**Fig-3**:- Variation of nitrite among the stations during summer.

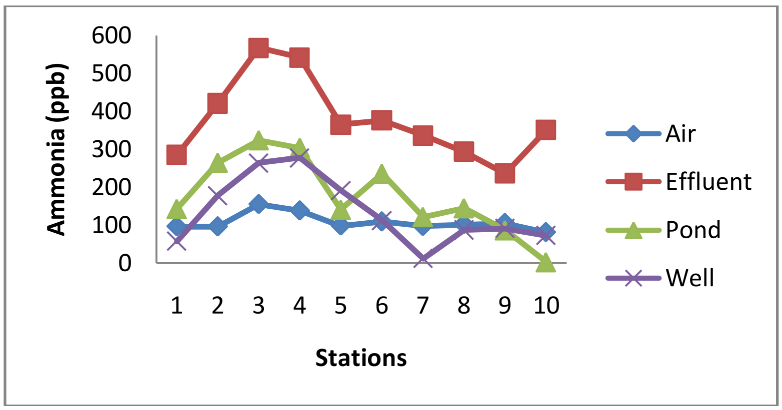



**Fig-4a**:- Station-wise variation of ammonia during summer.

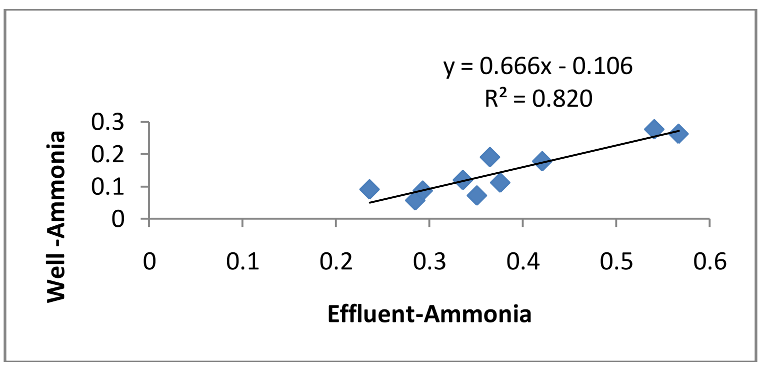



**Fig-4b**:- Summer variation of ammonia in well water and effluent.

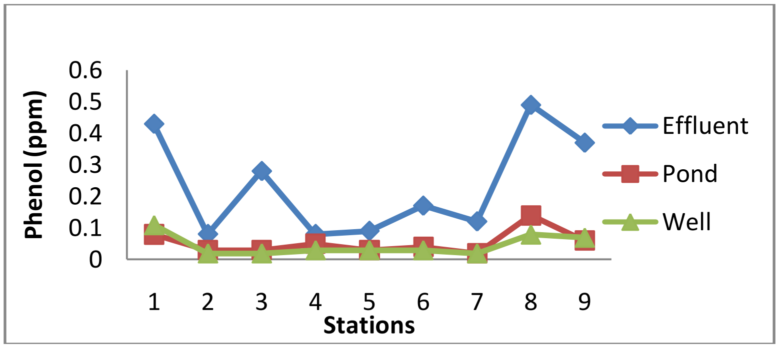



**Fig-5a**:- Summer variation of phenol among the sources.
(Effluent scale is minimised)

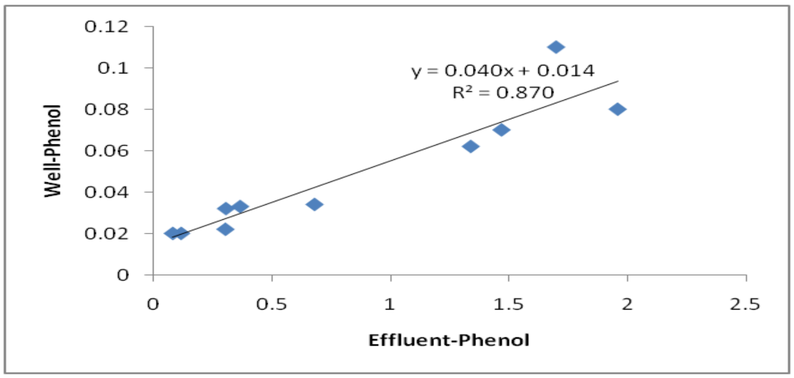



**Fig-5b**:- Variation of phenol in the well water and effluent during summer.

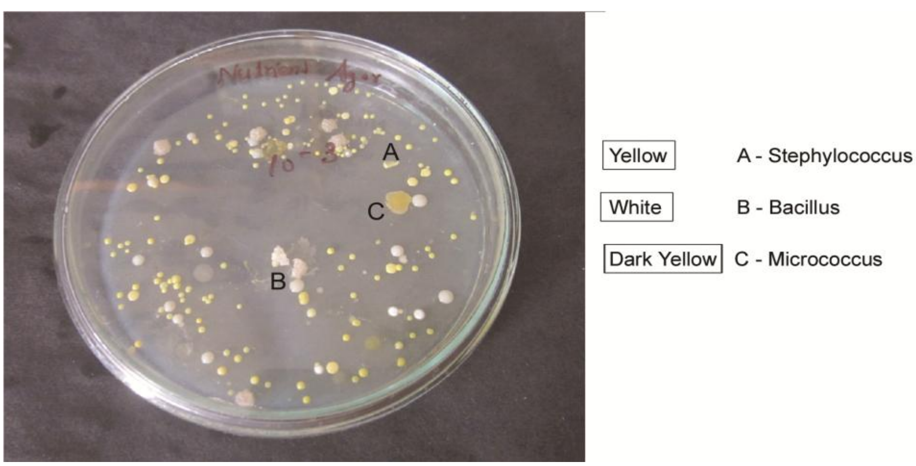



**Plate 1:-** Different types of bacteria in the retting zones

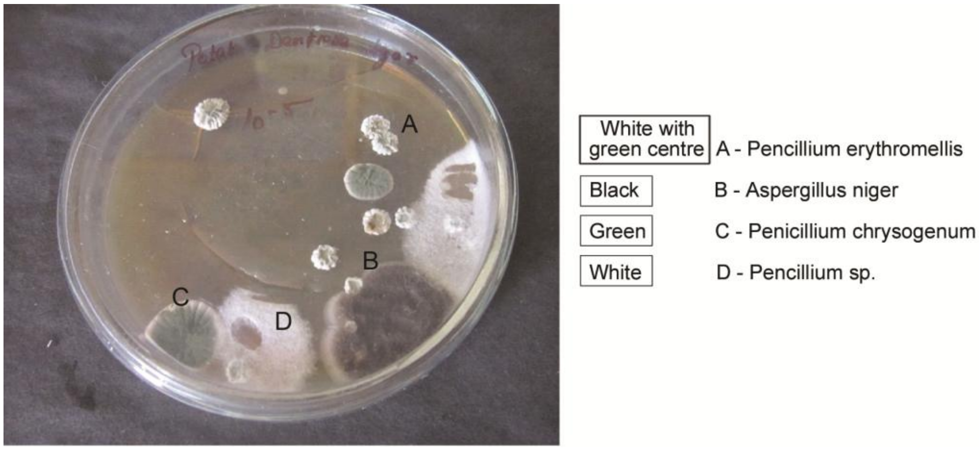



**Plate 2:-** Different types of fungi in the retting zones

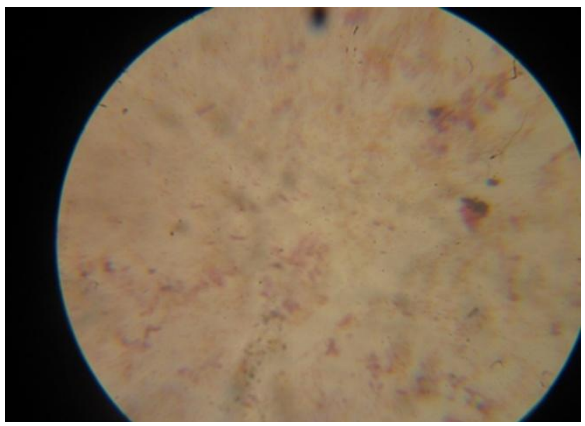


**Plate 3**:- Desulpho-vibrio in the retting zones

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