

ADSORPTION STUDY OF A NATURAL PRODUCT INTO THE OIL PRODUCING POROUS MEDIA OF UPPER ASSAM BASIN

Borkha Mech Das¹

Assistant Professor,
Department of Petroleum Technology,
Dibrugarh University, Dibrugarh-786004, Assam, India

Subrata Borgohain Gogoi²

Associate Professor,
Department of Petroleum Technology,
Dibrugarh University, Dibrugarh-786004, Assam, India

ABSTRACT

This paper deals with the systematic investigation of adsorption of a natural product, Black Liquor (BL) on porous media obtained from oil producing horizons of Upper Assam Basin by highlighting the crude oil recovery profile after adsorption of the natural product on to the porous media. BL an effluent from paper and pulp mills is a surfactant, which is renewable and abundantly available in this region. The experimental data obtained from the adsorption experiments were then interpreted from the well known models of Langmuir, Freundlich and Redlich-Peterson and was found that the Langmuir model fits the better fit of pH, salinity and temperature data over the entire range of variables studied in this work. This work reveals that with increase in salinity, adsorption increases due to increase in ionic charge of the aqueous medium and with increase in pH, adsorption decreases due to increase in negative charge of the aqueous phase and clay being negatively charged particles it will repel the anionic surfactant (negatively charged). Finer the grains of the porous media more will be the adsorption, since better will be the surface area of the porous media. The work is a supplementary study for the Surfactant based Enhanced oil recovery of the depleted fields of Upper Assam Basin.

Keywords: Black Liquor, Adsorption, Salinity, pH, Enhanced oil Recovery

Introduction:

Success or failure of a Micellar flood depends on the degree of retention of surfactants during flooding. The possible mechanism of the surfactant retention is the solid-liquid interface. Several papers dealing with the retention by way of adsorption of commercially available surfactants have been published (Bae JH and Petrick CB, 1977, Lawson JB, 1978, Trogus FJ et. al. 1979, Langmuir I, 1916, Freundlich HMF., 1906, Redlich O and Peterson DL, 1959) but meaningful comparison of reported data was quite difficult since surfactants of various degree of purity have been used.

Equilibrium relationships in adsorption process between adsorbents and adsorbates are described by adsorption isotherms. Linear regression is frequently used to determine the best-fitting isotherm. The linear least-squares method with linearly transformed isotherm equations has also been widely applied to confirm experimental data and isotherms using coefficients of

determination. In this study, the linear least-squares method and a non-linear method of three widely used isotherms, the Langmuir (1916), Freundlich (1906), and Redlich-Peterson (1959), were compared in an experiment where the surfactant SLS present in BL is adsorbed onto silica.

Surfactant molecule adsorb well at solid interfaces, such as rock surfaces found in petroleum reservoirs. The petroleum reservoirs in upper Assam are sandstone reservoirs, so the dominant mineral is silica (Borgohain P et. al., 2011). The adsorbed layers may represent both an additional resistance to flow by decreasing the absolute permeability of the porous media, as well as loss of surfactant and are therefore of fundamental importance in EOR operations that involve the flow of surfactant solutions through porous media. Adsorption minimizes the loss of high equivalent-weight fraction that is most efficient in lowering the IFT (Shalaby MR et. al., 2013). Adsorption of surfactant considered for EOR applications have been studied extensively over the few years (Gogarty WB, 1977, Gogoi SB, 2012, Krumrine PH et. al. 1982, Paria S and Khilar KC, 2004) as it have convincingly shown that it was possible to develop surfactant systems which displace oil from porous media almost completely when used in large quantities. Surfactants are more expensive than crude oil, development of a practical EOR technique depends on how much surfactant can be economically sacrificed in recovering additional crude oil from a reservoir (Glover CJ et.al., 1979). Further it was learnt that Pulp and Paper industry produces BL that were highly polluting and difficult to biodegrade (Trogus FJ et. al., 1979) but is effective in EOR operations. Clays in the rock have high surface area that can affect the surfactant flood in many ways. Bernard (Anderson GA, 2006) has suggested that by ion-exchange divalent ions were transferred to the surfactant solution from the clays resulting in precipitation of surfactant and loss of surfactant in the displacing fluid. Holm and Josendal (Sharma, VK et.al, 1998) have demonstrated that surfactant solutions will extract Ca^{++} and Mg^{++} . It was found that for a particular surfactant the minimum tension between salt solutions containing the surfactant and an intermediate-paraffinic crude oil like in the case of indigenous Assam crude would occur at high NaCl concentrations and lower surfactant concentrations in the reservoir brine than for typical naphthenic crude (Bernard GW, 1975).

Black liquor can be used as a surfactant for enhanced oil recovery from the oil producing horizons of Upper Assam Basin. Gogoi S.B & Das B.M also reports the effect of using black liquor and spent sulfite liquors, which emanate as effluent from Nowgong Paper Mill, Jagiroad, Assam, in enhanced crude oil recovery from Naharkotiya porous media. They have showed that addition of Na-lignosulfonate to crude oil emulsions gives rise to ultra-low inter-facial tensions between the oil and the aqueous phase, which are very much in demand in enhanced oil recovery projects. Reduction of interfacial tension leads to the release of residual oil droplets from the capillaries in the porous media, thereby increasing substantially the amount of petroleum obtainable from a given porous media (Gogoi and Das, 2012).

Accordingly, a complimentary study on adsorption of the BL onto the porous rocks was carried out in order to assess its effect on EOR. This study was confined to adsorption equilibrium and the results were interpreted from the well known theoretical models.

Experimental Analysis:

Materials

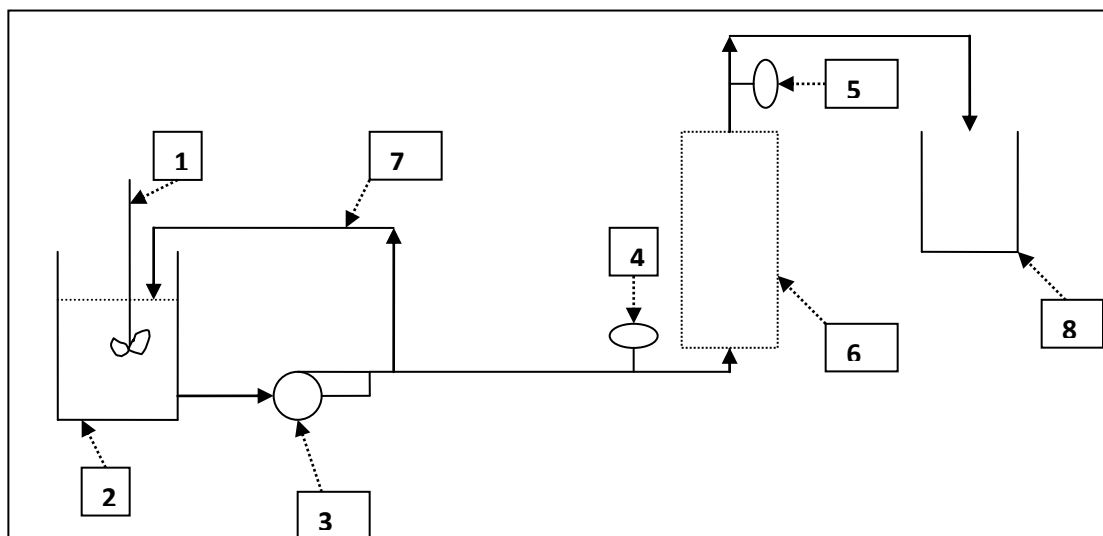
The porous media were selected from Bhogpara and Nahorkatiya oil fields from a depth of 3827 - 3837 m and 3836 – 3839 m respectively which were used as adsorbents. Paraffin oil of viscosity (μ_o) 115 cp & brine solution, 3000 ppm of NaCl in DW having viscosity (μ_w) of 1 cp are used respectively. The surfactant used is BL whose main constituent is Na-Lignosulfonate, which is cheap and locally available as waste from Nowgong Paper Mill, Jagiroad.

Method employed:

Flooding Operation

Trapping and release of fluids from porous media is the subject of extensive study during the last several decades and are currently of greater interest as a result of the critical need to improve oil recovery efficiency from petroleum reservoirs. Multiphase flow in porous media is an area pragmatically to study the basis to visualize an EOR process by Micellar flooding. The emulsions may either be oil-in-water type or water-in-oil type. These emulsions have drop sizes of few a micrometers (μm) which transport in the reservoir rock with permeabilities ranging from a tenth to several Darcys. In order to evaluate how emulsions flow through porous media and how addition of certain chemicals to the aqueous phase of the emulsion, enhances oil recovery from the porous media, it is therefore essential to develop a mathematical model based on the Filtration theory and simulate the flow behaviour in order to deduce implication for the design and optimization of MAP-EOR processes.

The experiments are conducted on the description of the multiphase flow in porous media based on Darcy's law (Darcy H. 1856) and JBN method (Johnson EF et. al. 1959) for unsteady – state displacements.



[1=Stirrer, 2=Sample reservoir, 3= Pump, 4 & 5= Pressure gauge, 6= Porous media, 7= By-pass, 8= Sample collector]

Figure 01 - Permeability apparatus

The setup for permeability test essentially comprises a cylindrical section of 0.3048m length and 0.0381m packed with crushed rock sample, pressure gauges, sample reservoir, sample collector, stirrer and a pump all connected by pipes of 0.0127 and 0.022225m outside diameter as shown in the above figure. The core sample was crushed in such a way that the grains were not broken. The crushed grains were made into a pack by using emseal, purchased locally and compressed uniformly in order to obtain a pack of uniform packing characteristics and packed into the test cylinder. The permeability experiment was not carried with the actual core obtained from the oil field because the clay minerals in the actual core samples encountered problems like swelling and also to gain further understanding of the physical mechanisms of emulsion flow in porous media. The measured effective porosity by saturation method before flooding was found to be in between

18.78-21.90%. The pack was covered with a sieve of 320 mesh size at the top and the bottom. Flooding solutions were stirred in the reservoir and injected at the bottom of the cylindrical section at a constant volumetric flow rate of 0.0002m/s by self priming monoblock 186.425watt (0.25HP) pump supplied by Telco, Coimbatore, India. The inlet and outlet pressure of the cylindrical section was recorded from pressure gauges. According to Babu, D.R. et.al. (1984), a constant superficial velocity of 7.3×10^{-5} m/s $\pm 1.62 \times 10^{-6}$ m/s and 3.472×10^{-6} m/s was maintained during the brine and surfactant flooding steps respectively. Experiments were conducted at room temperature of $301.15 \pm 275.15^\circ\text{K}$. The permeability of the porous media was varied by adjusting the sand grain distribution by the clay mineral through washing and settling.

The absolute permeability (K_o) of the porous media to brine was measured during initial brine flooding flow rate and pressure was constant. Paraffin oil was injected into the test sample saturated with brine and brine was displaced until the initial brine saturation (S_{wc}) was reached and the relative permeability (K_{ro}) of oil at S_{wc} was calculated. The test sample becomes saturated with S_{wc} and S_{oi} was flooded by secondary brine. During secondary brine flooding the breakpoint i.e. the point at which the first drop of brine comes out was noted and the brine with oil that flows out from the test sample was collected in graduated test tubes. The difference in pressure was noted at about 5×10^{-6} m³, 10×10^{-6} m³, 20×10^{-6} m³, 40×10^{-6} m³, 80×10^{-6} m³, 130×10^{-6} m³ and 260×10^{-6} m³ effluent emulsion collection. Simultaneously the relative permeabilities of the test sample to oil and water was also calculated. Oil was separated by adding deoiler Catflo (Catalytic Polyelectrolyte) supplied from Oil India Limited, Duliajan, with constant agitation by means of a stirrer. Secondary brine flooding was carried till residual oil saturation (S_{or}) was reached, which was discontinuous. Finally, surfactant flooding was done till residual oil saturation after surfactant flooding (S_{ors}) was reached and there was no further production of oil from the test sample.

Adsorption

Adsorption test was done using Shimadzu UV VIS Spectrophotometer UV-1700 calibrated at 190 to 900 nm wave-length. Initially, water is placed in a 1 mL plastic cuvette in the holder to obtain a baseline correction (F1).

0.34 ml BL (CMC value) was added to 99.66 ml of DW

Since density of BL = 1.08 gm/ml

$$0.34 \text{ ml} \times 1.08 \frac{\text{gm}}{\text{ml}} = 0.367 \text{ gm}$$

$$\frac{0.34}{0.34 + 99.66} = \frac{0.34}{100}$$

$$\text{Also, Dilution} = \frac{0.34}{0.34 + 99.66} = \frac{0.34}{100}$$

$$\text{and Dilution Factor} = \text{DF} = \frac{100}{0.34} = 294.12$$

Then the cuvette was filled with further diluted BL solutions for determining the UV-VIS spectrum of BL sample. The λ_{max} and other wavelengths of the peaks were recorded in the UV-VIS spectrum. Thanh (2002) found λ_{max} around 198 nm, and in this study it was found to be 196 nm which are reasonable as this difference might be attributed to instrumental error. The calibration curve (Figure 4.2) of BL is obtained by plotting absorbance versus concentration on a graph paper, which was in the form of a straight line [$y = mx + c$].

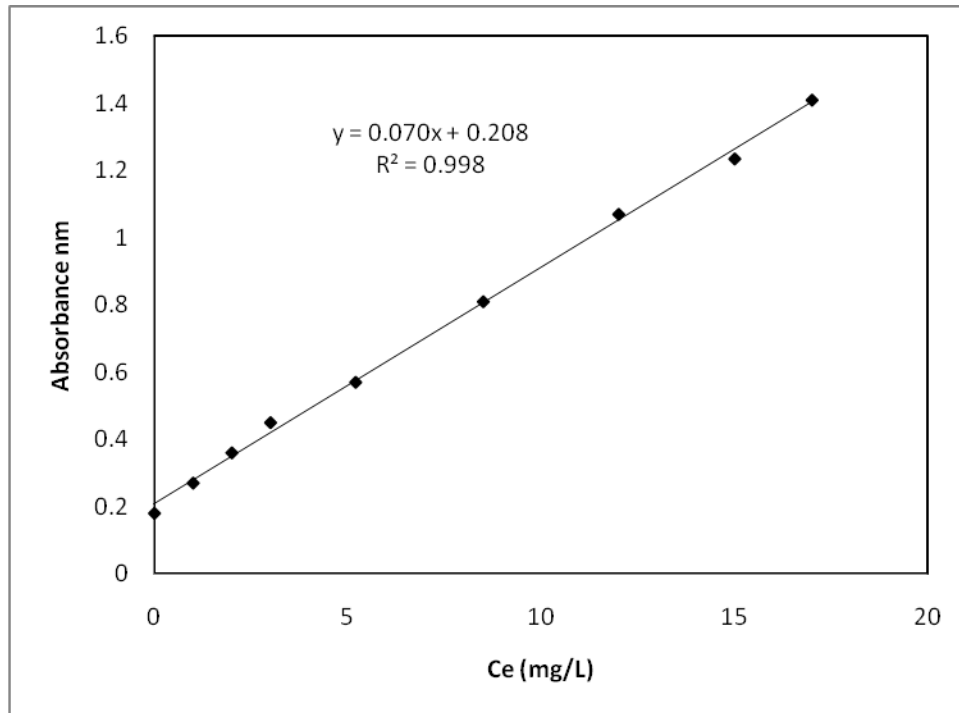


Figure 02: Calibration curve of BL in DW

1 gm of adsorbent (porous media) was taken in each of the 15 ml graduated centrifuge tubes. Different concentrations of the further diluted BL solutions in gm (by multiplying by density of BL) as mentioned above was added to the centrifuge tubes. The samples were prepared as in Table 4.2.

Table 01: Sample Preparation for Adsorption test

Sl.no.	Amount of Adsorbent (gm)	Adsorbate in solution (mg/L)
1	1	after attaining DF of 294.12 these samples were further diluted in DW
2		after attaining DF of 294.12 these samples were further diluted in saline water whose salinity ranged from 1000-4000 ppm
3		after attaining DF of 294.12 these samples were further diluted in water whose pH ranged from 3-9. Different pH solutions were prepared according to Dacie and Lewis (1998).

To obtain the equilibrium isotherms the test tubes with the adsorbate and adsorbent as in Table 4.2 were shaken in a magnetic shaker for 24 hours. After achieving equilibrium, the mixtures were allowed to settle and the supernants were decanted and collected in test tubes. The samples were then centrifuged at 4000 rpm for 5 minutes and then filtered by filter paper. The filtrates were analyzed with Shimadzu UV-VIS Spectrophotometer for the remaining BL concentrations that could

not be adsorbed in the porous media. The amounts of BLs adsorbed at equilibrium (q_e) were calculated from the calibration curve.

Results & Discussion:

Core flooding

The results of the Core flood Experiments are represented graphically below in Figure 3.

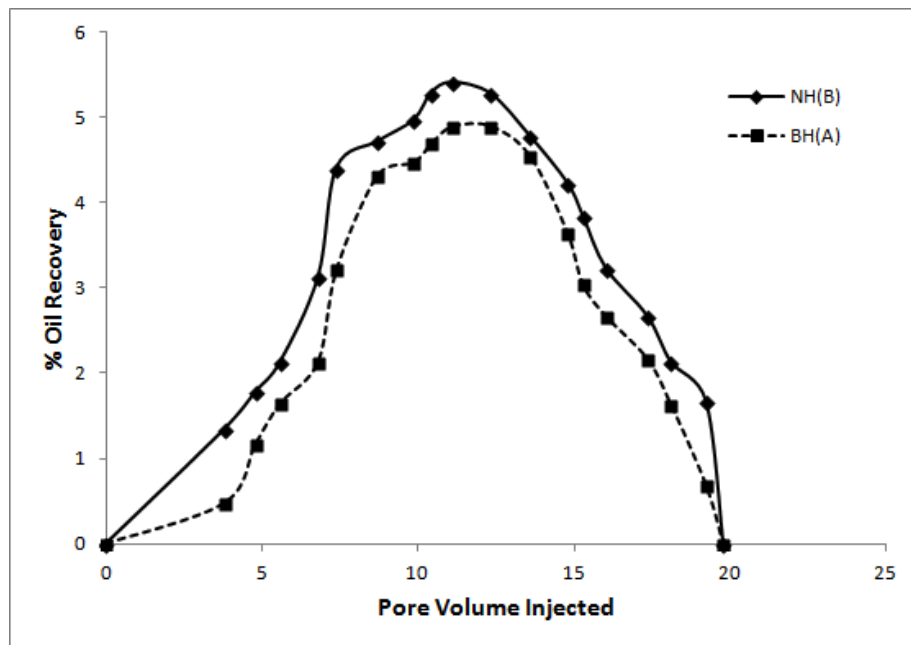


Figure 03: Oil recovery by Surfactant Flooding for BH(A) & NH(B)

The figure shows a comparison of oil recovery from Bhogpara & Nahorkatiya porous media. The oil recovery from NH(B) core sample is found to be 55% whereas from BH(A) core sample is 49%. This shows that oil recovery from NH(B) porous media was better than BH(A) porous media because NH(B) core sample was coarse grained and BH(A) core sample which was fine grained. Coarser grained samples efforts better permeability and porosity than fined grained samples.

The figure also shows that in both the cases, as the pore volume injected increases, the oil recovery slowly decreases to almost zero. Several mechanisms may be responsible for this decrease. One of the reasons may be reduction in the quantity of surfactant in flooding solution because of its adsorption over rock layers.

Adsorption

The absorbance of BL in DW and in varying salinity and pH solutions on porous media are shown in Figure 4, 5 & 6. Figure 4 shows that the amount of BL in mg adsorbed in g on the solid phase (i.e. the adsorbent or porous media) was more on NH(B) than for BH(A), this indicates that adsorption was more for coarse grain than for fine grain porous media. Increase of salinity in the adsorbate increase the solid phase concentration, which means that adsorption increased as NaCl concentration increased, while adsorption of BL on porous media decreased with increased in pH and temperature as shown in figure 5 & 6.

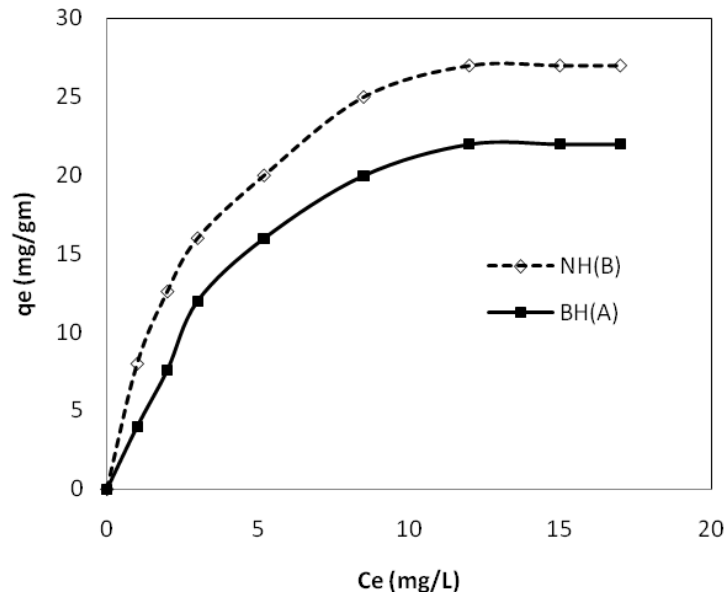


Figure 04: Langmuir isotherms obtained for the adsorption of BL in

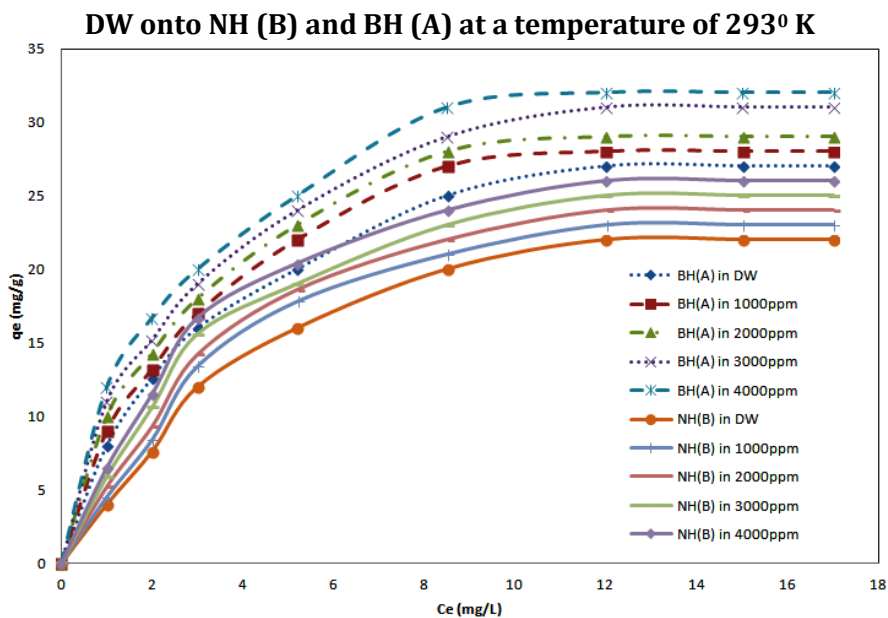


Figure 05: Langmuir isotherms obtained for the adsorption of BL in different salinity adsorbate onto NH (B) and BH (A) at a temperature of 293^o K

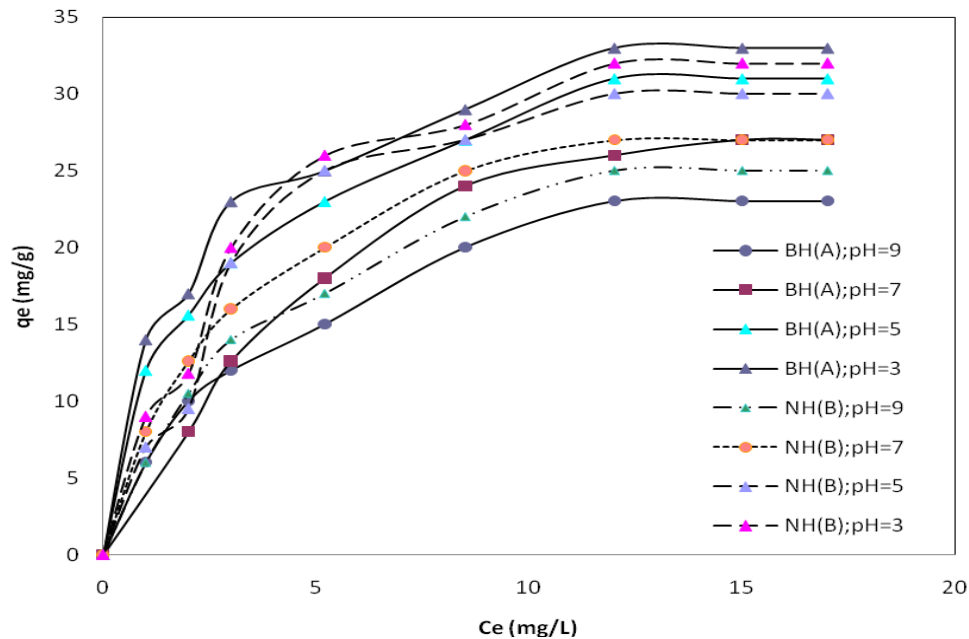


Figure 06: Langmuir isotherms obtained for the adsorption of BL in different pH adsorbate onto NH (B) and BH (A) at a temperature of 293 K

This adsorption of BL onto the porous media leads to decrease in amount of surfactant which is most efficient in lowering the IFT and thereby leads to decrease in oil recovery with further pore volume injection of the surfactant solution.

The adsorption equilibria were interpreted from Langmuir, Freundlich and Redlich-Peterson isotherms. The parameters were estimated by a nonlinear regression analysis using Revenberg-Marquardt's method (Thanh ND, 2002) and the computation was carried out in a Pentium PC (Digital) by using NUMERICAL RECIPES in C+ at IIT-Madras. It was found that squared regression coefficient, r^2 was close to unity. So, the best fit model in this case was Langmuir model. In Langmuir adsorption model the molecules do not interact and adsorption occurs through the same mechanism. At the maximum adsorption, only a monolayer is formed i.e., molecules of adsorbate do not deposit on already adsorbed molecules of adsorbate (Dacie and Lewis, 1998). It is also seen in Table 4.3 that with the increase in temperature the adsorption decreases. The parameters were estimated by a nonlinear regression analysis using Revenberg-Marquardt's method for different salinities and pH solutions for both NH(B) and BH(A) porous media and the results predicts that Langmuir model fits the better fit of pH and brine data.

Table 02: The parameters were estimated by a nonlinear regression analysis using Revenberg-Marquardt's method

Isotherm ↓	T(K) →	283 ^o	293 ^o	303 ^o	313 ^o
q_e (mg/gm)[input given] →		29.3	28.0	27.9	26.7
Langmuir	K_a (L/mg)	0.432	0.410	0.378	0.297
	r²	0.987	0.998	0.994	0.989
Freundlich	1/n	0.342	0.365	0.386	0.423
	K_F (mg/gm)(L/mg)^{1/n}	9.43	9.54	9.33	9.52
	r²	0.965	0.923	0.904	0.894
Redlich-Peterson	g	0.876	0.768	0.912	0.732
	B (L/mg)^g	1.309	1.89	0.657	1.69
	A(L/gm)	21.0	23.5	13.8	24.8
	r²	0.966	0.876	0.876	0.804

Conclusion:

Systematic investigation of adsorption of a natural product from paper and pulp mills, BL on porous media obtained from oil producing horizons of Upper Assam Basin was made in order to access the effect of EOR efficiency. Adsorption of BL on porous media leads to decrease in the amount of surfactant required for flooding mechanism. This decrease in surfactant leads to loss of high equivalent-weight fraction that is most efficient in lowering the IFT and thereby leads to decrease in oil recovery with further pore volume injection of the surfactant solution.

The datas were interpreted from the well known models of Langmuir, Freundlich and Redlich-Peterson and it was found that the Langmuir model fits the better fit of pH, salinity and temperature data over the entire range of variables studied in this work. An increase in ionic strength due to the addition of NaCl increased the adsorption. With the increase of pH the adsorption of anionic BL on the porous media have decreased because clays were negatively charged (Winsor PA, 1948, Danielsson, I.; Lindman, B. 1981) and as the pH of the BL increased the negativity of the sulfonate also increased and so it was assumed that there was no attraction between the clays and the sulfonate molecules. The adsorption was more for coarse grained sand core sample of NH(B) than for fine grained sand core sample of BH(A). This suggested that an increase in the number of sites in the coarse grain NH(B) core sample lead to an increase in adsorption of the sulfonate on the surface. The increase in adsorption may be due to an increase in the surface area of the sample and possibly increased surface contamination of the harder quartz particles with softer minor constituents such as clay, carbonate or possibly alumina. The lower adsorption capacity of BH(A) sand was attributed to the fact that it contained mainly silica and less of clay and carbonate minerals.

Acknowledgement:

The authors gratefully acknowledge the financial support provided to this project (SB/S3/CE/057/2013) from Department of Science and Technology, Government of India.

References:

1. Bae. J.H., and Petrick. C.B., 1977, Adsorption of petroleum sulfonates in Berea cores, *SPE*, 17, pp 353-357.
2. Lawson. J.B., 1978, The Adsorption of Nonionic and Anionic Surfactants on Sandstone and Carbonates, *SPE* 7072 presented at the 1978 Improved Oil Recovery Symposium, Tulsa.
3. Trogus. F.J., Schechter. R.S., Pope. G.A. and Wade. W.H., 1979, Adsorption of mixed surfactant systems. *JPT*, 31, pp 769–778.
4. Langmuir. I., 1916, The constitution and fundamental properties of solids and liquids. *J. Am. Chem. Soc.*, 38, 2221.
5. Freundlich H.M.F., 1906, Über die adsorption in lösungen. *Z. Phys. Chem*, Frankfurt, 57A, 385.
6. Redlich. O. and Peterson. D.L., 1959, A useful adsorption isotherm. *J. Phys. Chem.*, 63, 1024.
7. Borgohain. P., Hazarika. S., Gilfellow. G.B. and Gogoi. M.P., 2011, Petrography and diagenesis of the Upper Palaeocene–Lower Eocene rocks of Nahorkatiya oilfield, Assam. *Current Science*, 101(5), pp 664-669.
8. Shalaby. M.R., Hakim. M.H. and Abdullah. W.H., 2013, Diagenesis in the Middle Jurassic Khatatba Formation sandstones in the Shoushan Basin, northern Western Desert, Egypt, *Geological J.*, Published online in Wiley Online Library (wileyonlinelibrary.com). DOI: 10.1002/gj.2512.
9. Gogarty. W.B., 1977, Oil recovery with surfactants: history and a current appraisal. In *Improved Oil Recovery by Surfactant and Polymer Flooding*, Ed. Shah, D.O. and Schechter RS, Pub. Academic Press. Newyork, pp 34-37.
10. Gogoi. S.B., 2012, Adsorption – desorption of surfactant for Enhanced oil recovery, *Transport in Porous Media*, 90(2), pp 568-604.
11. Krumrine. P.H., Campbell. T.C. and Falconer. J.S., 1982, Surfactant flooding 1 – the effect of alkaline additives on IFT, surfactant adsorption and recovery efficiency. *SPEJ*, 503, Trans. AIME, 273.
12. Paria. S. and Khilar. K.C., 2004, A review on Experimental Studies of Surfactant Adsorption at the Hydrophilic Solid-Water Interface, *Adv. Colloid Interface Sci.*, 110, pp 75-95.
13. Glover. C.J., Puerto. M.C., Maerter. J.M. and Sandvik. E.I., 1979, Surfactant phase behavior and retention in porous media, *SPEJ*, pp183–193.
14. Trogus. F.J., Schechter. R.S., Pope. G.A. and Wade. W.H., 1979, A new interpretation of adsorption of adsorption maxima and minima. *J. Colloid Interface Sc.*, 70, pp 293–305.
15. Anderson. G.A., 2006, Simulation of chemical flood Enhanced Oil Recovery processes including the effect of reservoir wettability, a *PhD thesis to the University of Texas at Austin*, USA.

16. Sharma. V.K., Ramaswamy. K.V., Vaidya. R.R., Hadker. N. and Beukering. P.V., 1998, The Indian Paper Industry, In *Wastepaper Trade and Recycling in India*, Ed. Beukering PV and Sharma VK, Scientific Publishers Jodhpur, India,
17. Bernard. G.W., 1975, Effect of clays, limestone and gypsum on soluble oil flooding. *JPT*, 27, pp 179–180.
18. Gogoi. S.B. and Das. B.M., 2012, "Use of an effluent for enhanced oil recovery,' Indian J. of Chemical Technology, (Scientific & Industrial Research, (ISSN: 0971-457X), 19, pp 366-370.
19. Darcy. H., *Les fontaines publiques de la ville de Dijon*. Paris: Victor Dalmont, 1856.
20. Johnson. E.F., Bossler. D.P., Naumann. V.O., Hydrogen in cold-worked iron-carbon alloys and the mechanism of hydrogen embrittlement. *Trans AIME*. 1959; 216(3), pp 70–2p.
21. Babu. D.R., Hornof. V. and Neale. G., 1984, Use of Spent Sulfite Liquors in Enhanced Oil Recovery Operations, *J. Can. Pet. Tech.*, pp. 48-53.
22. Thanh. N.D., 2002, *New Methods for Protein Analysis Using Ultra Violet / Visible Spectroscopy*, University of Colorado at Boulder, Colorado 80309, 7.
23. Dacie and Lewis, 1998, *Practical Haematology*, in Lewis S.M. Bain B.J. Bates I. (Ed). P 606. Pub. Churchill Livingstone, China, 606.
24. Winsor. P.A., 1948, Hydrotrophy, solubilisation and related emulsification processes, *Trans. Faraday Soc.* 44, pp 376-378.
25. Danielsson, I., Lindman. B., 1981, The definition of a microemulsion, *Colloids Surf. A*, 3, pp 391-392.