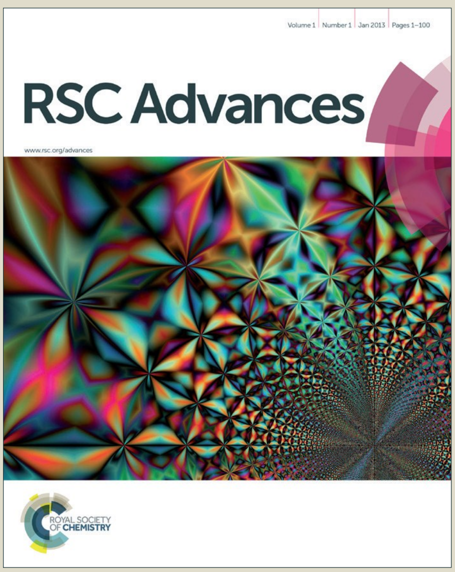
RSC Advances



Modernization of surfactant chemistry in the age of Gemini and bio-surfactants: A Review

Monohar Hossain Mondal[a,c], Susanta Malik[c], Ankit Roy[c], Rumpa Saha[b] and Bidyut Saha*[,c].

[a]Chemical Sciences Laboratory, Government General degree College at Kalna-I, Burdwan 713405, WB, India

[b]Department of Chemistry, TDB College Raniganj, Raniganj, West Bengal 713383, India

[c]Homogeneous Catalysis Laboratory, Department of Chemistry, The University of Burdwan, Burdwan 713104, WB, India

*Corresponding author, E-mail Id: b_saha31@rediffmail.com (B. Saha) Mobile +91 9476341691, Tel: +91-342-2533913 (O), Fax: +91-342-2530452 (O)

Abstract:

The modern surfactant science demands chemistry which is benign by design. Efficient green chemicals like Gemini surfactants along with natural resources derived bio-surfactants are thus most dependable in this case. In the venture of less pollutant, ecologically beneficiary solvents, more and more environmentally accepted trends are coming every day in market, species related to properties like less toxicity, biodegradability, chemical stability, environmental safety, efficient solubilization and of course, ease of recycling, can be the tool of talisman. Bio surfactants along with the geminis are of greater interest for their very efficient working ability, lower CMC and other up to date features that modern science desire for the betterment of mother nature. This review contains elaborated discussions on the efficiencies of Gemini and Bio-surfactants as modern generation green chemicals in varied fields *viz.* the laboratory based kinetic experiments, electron transfer reactions, emulsification, solubilization, agro-industrial and bio-medicinal fields which enlights the hope of an amazing future prospect of this type of green chemicals.

Keywords:

Bio-surfactants, Gemini surfactants, green chemistry, agro-industry, future prospect.

1. Introduction:

Surface chemistry is immensely effected by the presence of surface-active substances i.e. the surfactants. Their presence on a liquid interface not only changes its physicochemical properties like surface tension, viscosity but also affects a lot to the solvent nature of the liquid and chemical reactions that take place in the solvent; due to this reasons surfactants are used as catalysts in numerous reactions worldwide.

The present write up is an attempt to summarize the recent advancements in synthesis, physical characterization and utilization of novel surfactants of different kinds investigated globally which includes Bio- Surfactants from recyclable resources and more recent Gemini-Surfactants. Since synthesis and catalysis together cover substantial part of the laboratory based researches, it is the supreme desire of recent era to elicit a "Renaissance" in those fields by choosing more green ways of science to put aside the planet Earth from getting sicker further. There are twelve principles, if obeyed; a chemical reaction can earn the esteemed "green" title before its name [1]. Harmless solvent assortment, inferior expenditure of energy, high atom economy of the yields is the major issue that ought to be followed. In a predictable chemical reaction it is established that if product and reagents are excluded, the rest part, the solvent alone is over 80% of the total mass of the system. More amusingly, 70% of total energy consumed by the reaction mixture is only a caution deposition kept to the banker solvent [2]. The essential diversity of conventional chemistry thus requires simple but well-behaved prototypes as chemical building blocks and synthetic strategies that best go with environment to accommodate varied range of physicochemical properties. Who else can meet these requirements other than the Mother Nature herself? In the venture of less pollutant, ecologically beneficiary solvents, more and more environmentally accepted trends are coming every day in market, species related to properties like less toxicity, biodegradability, chemical stability, environmental safety, efficient solubilization and of course, ease of recycling, can be the tool of talisman. In this framework if substitute is asked then the proposal would be more use of aqueous media or application of solvent free chemical reactions. Although water is an eco-friendly solvent for reaction medium, due to the solubility problem of the organic substrate, researchers have selected aggregated surfactant media which have two different parts: one is hydrophobic which easily solubilize the organic moieties and another is hydrophilic to solubilize inorganic substrates with ease. Aggregated surfactant medium composed of different nano aggregates, such as, micelle, vesicle, large uni-lamellar vesicle, etc. above its critical micelle concentration (CMC) in aqueous medium. Surfactant in miceller aggregated form catalyses several reactions such as redox transformation, hydroformylation, Diels Alder reaction, several organic syntheses, remediation treatment etc. [3]. There are several commercially available surfactants such as CPC, SDS, SDBS, TX-100 etc. are hugely used worldwide.

On the other hand the introduction of "Gemini surfactant" in surface chemistry is a testimonial to man's eternal quest of modification of presently available humdrum materials to supreme active glamorous one. The cultivated mind of Menger and Keiper has drawn a mass attentive judgment by giving the superfluous terminology "Gemini surfactant" to this newly established super active second generation surfactants [4]. The Gemini or dimeric surfactants posses two or more hydrophilic with two or more hydrophobic head groups chemically bonded with a spacer group. As far as the unique properties are concerned this new class of surfactants with double physical ability is also very much efficient in their surface active chemistry with respect to the traditional single chained fellows. The incredible property they posses is the lower CMC values and can produce significantly lower tension with respect to the same molar mass concentration of monomeric surfactants. The first debut report of such class of surfactants is a bisquaternary ammonium dihalide surfactants [5]. The use of Gemini surfactants covers the substantial homogeneous catalytic reactions along with solubilisation, emulsification, and many more technical applications in industries like electro-decoating, stabilization of adhesive polymer latex, anti-friction agent, mining, paper manufacturing, preparation of surfactant including softener, cosmetics, and most importantly recent advancement in drug designing, synthesis and application in medicinal field [6-13]. The recent day's demands of our civilization and endless advancement in industries are triggering the research of enormously potential substitution of the traditional monomeric surfactants. The justified response by scientists to this demand is the designing and synthesis of novel chemically bonded twin geminis with polar heads as a gift to our mankind.

Although those above said surfactants are effective in every respect, much more green in nature and friendly for our environment; but these should not be the end, the growing environmental concerns and bio-eco-mimetic approaches shown by contemporary scientific community, surfactant science has also changed its direction to synthesis, apply and judge surfactant activities in terms of renewable feed stocks [14]. The beginning of the 21st century has witnessed some of the deeds, never done before, as far as the next generation surfactants are considered [15]. Use of renewable feedstock can significantly reduce the emission of green house gases associated with the production and use of surfactants. The petroleum industry is ranked as the most surfactant users in terms of oil removal applications since surfactants increase solubility of petroleum components [16]. Majority of surfactants produced today are of petrochemical origin beside from renewable resources like fats and oils. Though it is of most desire that we replace petrochemical surfactants by bio-surfactants to reduce environmental degradation by agro-industrial use, low cost and high performance surfactants are the most significant in surfactant industry. Careful attenuation of biocompatible raw materials is thus always welcome. Bio surfactants in this regard are evaluated as the best as far as surfactant performance is concerned: due to the simple yet versatile structural features and effectively low toxicity, these molecular architectures readily get away from the environment, which prevents the problem of accumulation of bio-surfactants such as shown by chemical surfactants. Therefore, terms such as ‘green chemicals’ [1,17], ‘renewable surfactants’ [18] are appropriate for their environment helped behavior. The biological origin these surfactants have, grants them the most inherent characteristic of eco-compatibility also; production from cheaper and safer biological materials such as bacteria, yeast, fungi help to use them more. Different carbon resources ranging from hydrocarbons, carbohydrates to lipids and nitrogen resources like ammonium salts can be used separately or in combination to produce them biologically. In addition, bioremediation of land and water can be favored with the use of bio-surfactants. There are reports on biosurfactant use in hydrocarbon degradation and bioremediation of soil and oil-spill. Bio-surfactants can be used as encapsulating ligands for heavy metal remediation, their amphiphilic behavior in terms of traditional properties like softness, hardness, macro cyclization, effectiveness at the extremes of temperature, and good surfactant properties like low CMC, foaming power, detergency, solubility, emulsifying properties, salinity have far lying consequences in detoxification of specific pollutants, de-emulsification of industrial emulsions and food applications. Science has gone today too far synthetically tailored molecular machines crafted by some ever wondered technology have made possible the re-embodiment of the chemical community, yet approaches to greener vision by re-discovering the environment seems to be increasing only in recent years. Derivation and synthesis of surfactants should incorporate the pollution-free bio-organisms to build a greener world. However, large-scale production of these molecules has not been realized because of low yields in production processes and high recovery and purification costs, our aim should be focused in this direction to make them more cost effective and market friendly.

2. Critical Micelle Concentration:

CMC is defined as a particular concentration of a surfactant which dictates the start of aggregation of surfactants to micelle, vesicle, large uni-lamellar vesicle, (Fig.1, 2) etc. in a particular state of reaction condition [4]. As already discussed all types of surfactants are amphiphiles with both hydrophilic and hydrophobic moieties. This feature renders surfactants capable of reducing surface and interfacial tension and forming emulsions. Interest in research and application on bio-surfactants is progressively increasing due to their environmental friendly nature and lower toxicity comparing with synthetic surfactant [19]. Diverse functional properties of Gemini surfactants, such as emulsification, foaming, wetting, cleansing, surface activity, phase separation and reduction in viscosity of crude oil, makes it some of the most versatile processed chemicals [20]. The activities of surfactants depend on their concentration until the critical micelle concentration (CMC) is obtained. The CMC is usually used to measure surfactant efficiency. More efficient surfactants have lower CMC, i.e. less amount of surfactant is needed to decrease the surface tension [4]. Hydrophilic-Lipophilic Balance (HLB) value is a measure to indicate the type of emulsion (e.g. oil in water or water in oil). Emulsifiers with low HLB stabilize water-in-oil emulsion, whereas emulsifiers with high HLB do the opposite. According to some investigations, the surface activity of bio-surfactants is analogous to that of synthetic surfactants, where the Gemini surfactants are of much more efficiency regarding this parameter.

To acquire the information on different physicochemical properties of surfactants like micelle formation and structure, surface activity, adsorption, solubilization, foaming property, wetting, phase behavior etc. a chemist must investigate a few experiments like light scattering, spectrophotometry, conductometry, calorimetry, NMR, ESR spectroscopy and many other associated experiments for characterization. However, critical micelle concentration (CMC) is like a finger print evidence, always trusted as the pivotal character of a particular micelle in every surface research that includes micellization. CMC is defined as the concentration above which surfactant molecules abruptly forms aggregation called a micelle [4, 21]. There is a list of 19 surfactants in **Table 1** where it is evident that CMC sharply decreases for a gemini when compared with a traditional one.

Surfactants	CMC
1. $C_{12}H_{25}N^+(CH_3)_3Br^-$	16
2. $C_{12}H_{25}N^+(CH_3)_3Cl^-$	22
3. $C_{16}H_{33}N^+(CH_3)_3Br^-$	1
4. $C_{12}H_{25}N^+(CH_3)_2(CH_2)_n\ C_{12}H_{25}N^+(CH_3)_2\ .2Br^-$	1
5. $C_{12}H_{25}N^+(CH_3)_2(CH_2)_{16}\ C_{12}H_{25}N^+(CH_3)_2\ .2Br^-$	0.12
6. $C_{16}H_{33}N^+(CH_3)_2(CH_2)_2\ C_{16}H_{33}N^+(CH_3)_2\ .2Br^-$	0.003
7. $C_{16}H_{33}N^+(CH_3)_2(CH_2)_5\ C_{16}H_{33}N^+(CH_3)_2\ .2Br^-$	0.009
8. $C_8H_{17}N^+(CH_3)_2(CH_2)_3\ C_{16}H_{33}N^+(CH_3)_2\ .2Br^-$	55
9. $C_{12}H_{25}N^+(CH_3)_2(CH_2)_2O(CH_2)_2N^+(CH_3)_2C_{12}H_{25}\ .2Cl^-$	0.5
10. $C_{12}H_{25}N^+(CH_3)_2(CH_2)_2O(CH_2)_2N^+(CH_3)_2C_{12}H_{25}\ .2Br^-$	0.004
11. $C_{16}H_{33}N^+(CH_3)_2CH_2(CH_2OCH_2)_3CH_2N^+(CH_3)_2C_{16}H_{33}\ .2Br^-$	0.002
12. $C_{12}H_{25}N^+(CH_3)_2CH_2CHOHCH_2N^+(CH_3)_2C_{12}H_{25}\ 2Br^-$	0.8
13. $C_{12}H_{25}N^+(CH_3)_2CH_2CHOHCHOHCH_2N^+(CH_3)_2C_{12}H_{25}.2Br^-$	0.7
14. $C_{12}H_{25}N^+(CH_3)_2CH_2CHOH\ CH_2\ N^+(CH_3)_2CH_2CHOHCH_2N^+(CH_3)_2C_{12}H_{25}.3Cl^-$	0.5
15. NOGl C_8Di	0.45
16. NOGl C_9Di	0.55
17. NOGl C_{12}Di	0.12
18. NDoGl C_{10}Di	0.125
19. NDoGl C_8Di	0.03

Table 1. A list of surfactants with their respective CMC values from both traditional and gemini classes.

It is evident from the above Table 1 that Gemini surfactants are much more efficient regarding their CMC values with respect to the monomeric traditional type analogue. The reason for this is the presence of higher degree of hydrophobic tail which indeed is more efficient than twice that of the monomeric ones. The strong repulsion towards water they exert drives them to get agglomerated forming the micelle at much lower concentration. This may also be interpreted as the cooperative interaction of the two chains knotted with an aromatic and/or aliphatic spacer group. The gross enmity of the tail group along with the spacer towards the solvent water is thus the main reason why they form micelle at that much lower concentration. On the other hand the natural surfactants are made up of giant organic frameworks which inherently are strong water repellant. Conversely it may also be presented as the affection of the hydrophilic polar heads which drag themselves towards water to get knotted as soon as they get in the vicinity of one another. It is also interesting that geminis possess twin heads in a single molecule which also influence the same. For bio-surfactants there is every possibility to have several polar heads in a single giant architecture of the organic moiety to enhance micellization in lower concentration.

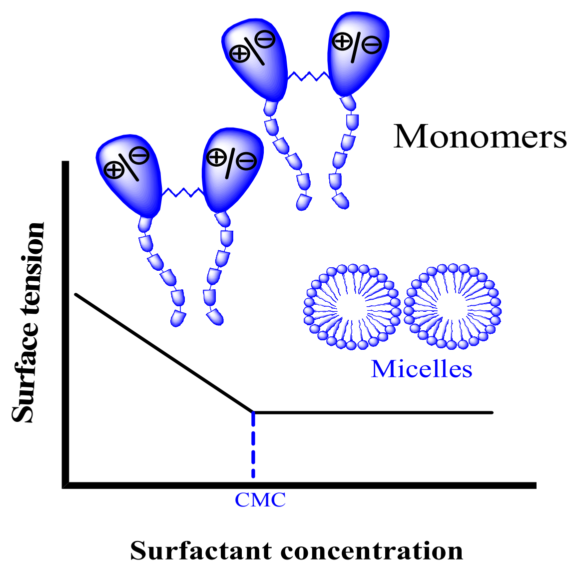


Fig.1. The variation of surface tension with surfactant concentration.

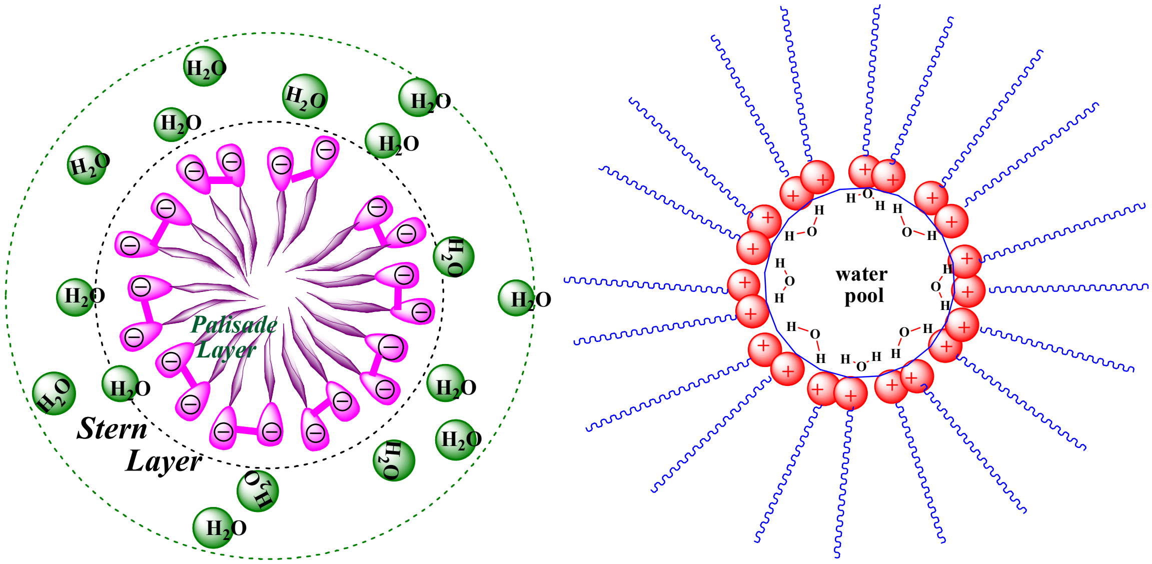


Fig. 2. Representation of gemini based micelle in aqueous solvent media.

a. Reverse micelle in aqueous

b. Micelle in aqueous media

3. Structure and Classification:

3.1. Gemini Surfactants:

The structure of Gemini surfactants can be simply described as the kind of surfactants composed of two ionic head which are affectionate to water groups with two hydrophobic parts (generally organic moieties like aliphatic chain or aromatic group) connected covalently with a rigid or non-rigid spacer group (which connects the two individual amphiphilic bodies) which indeed may be aromatic or aliphatic shown in **Fig. 3**.

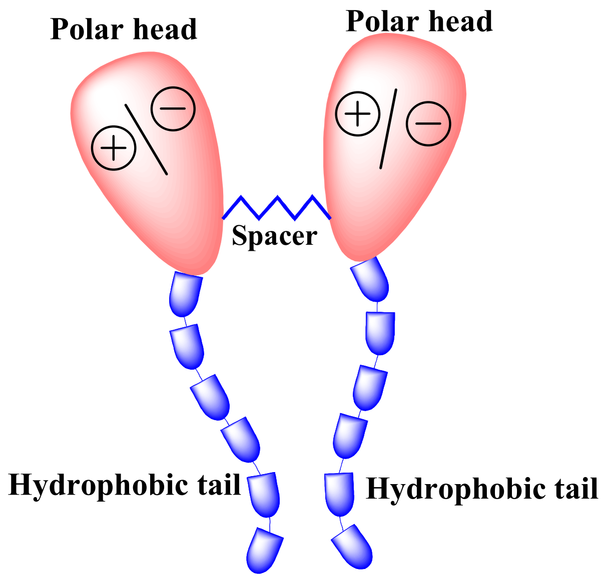


Fig. 3. Simplified schematic representation of physical structure of a gemini surfactant.

The several common properties that gemini surfactants always carry include the following:

i) All Gemini surfactants posses at least two hydrophobic chains and two cationic or two anionic or even mixed polar head groups.

ii) The spacer group that covalently binds the two segments of these kinds of surfactants can be greatly varied from short chain of two methylene groups to a long chain of twelve methylene groups; from rigid stilbene type to non-rigid flexible methylene chain type; from polar polyether to non-polar aliphatic type; even aliphatic methylene to aromatic type.

iii) Geminis with more than three or more polar heads with three or more hydrophobic chains can be synthesized.

The classification of ionic Gemini surfactants can be done into several types based on different physicochemical features of the hydrophobic tail group and the spacer group.

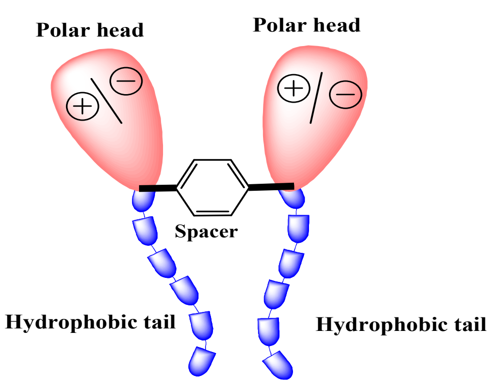
a) **Rigidity of Spacer:** depending upon this feature of the spacer group Gemini surfactants are classified into two different sub categories: surfactants with rigid spacer and surfactant with non-rigid flexible spacer with significantly different physicochemical properties.

b) **length of the spacer:** the length of the spacer group i.e. the number of carbon atoms enhances the surface activity of the surfactant appreciably, in addition to that, physical properties of surfactants too alter, thus the classification of Gemini surfactants into two sub-categories:(i) Gemini surfactant with short chain spacer and (ii) Gemini surfactant with long chain spacer based on the length of the spacer is justified.

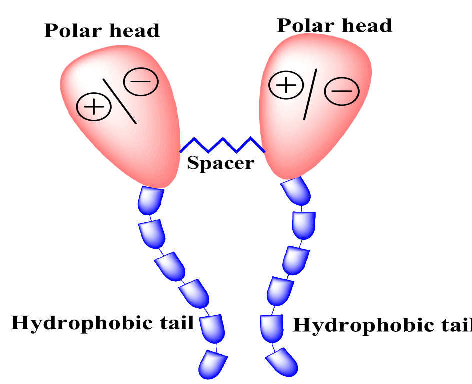
c) **Polarity of spacer:** the polarity of the spacer group of a Gemini surfactant greatly affects their CMC value; based on it geminis are further sub-divided into two categories: (i) Gemini with a polar spacer and (ii) Gemini with a non-polar spacer.

d) **Degree of symmetry of hydrophobic tail:** the two segments of a Gemini are not always identical; rather surfactants with even two different hydrophobic tails are available: (i) Gemini with two identical hydrophobic tail and (ii) Gemini with two non-identical hydrophobic chain.

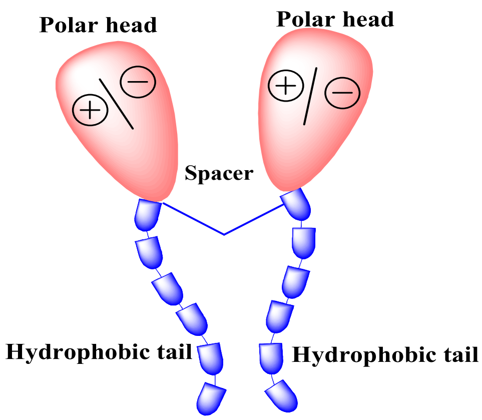
The relevant structural features of the different classes of Gemini surfactants can be illustrated by the below mentioned **Scheme 1**.



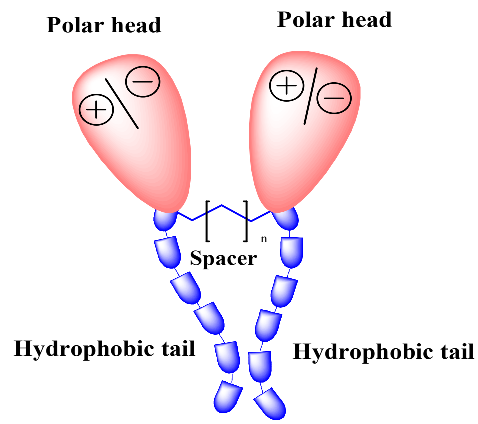
a(i)



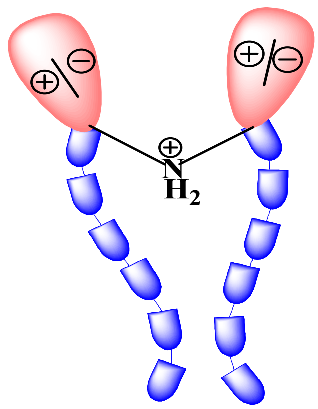
a(ii)



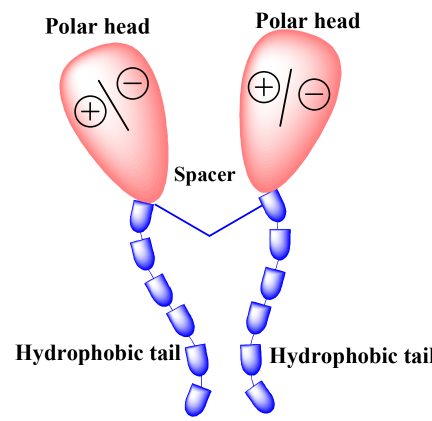
b(i)



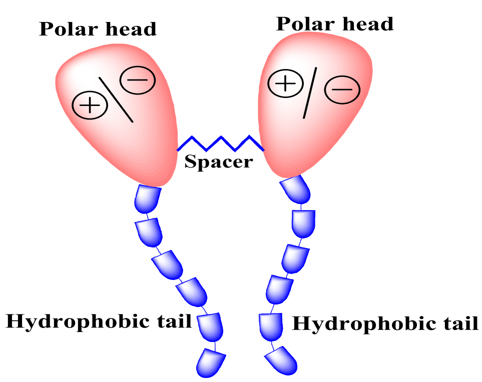
b(ii)



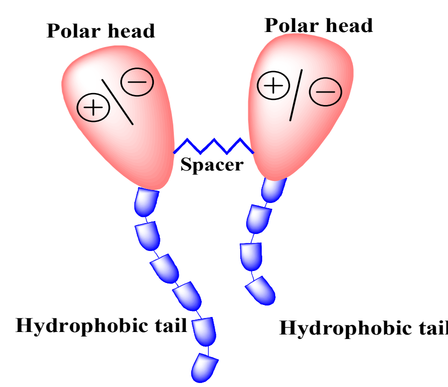
c(i)



c(ii)



d(i)



d(ii)

Scheme 1. a (i) Gemini surfactants with rigid spacer. a (ii) Gemini surfactant with non-rigid flexible spacer. b (i) Gemini surfactant with short chain spacer. b (ii) Gemini surfactant with long chain spacer. c (i) Gemini with a polar spacer. c (ii) Gemini with a non-polar spacer. d (i) Gemini with two identical hydrophobic tail and d (ii) Gemini with two non-identical hydrophobic chain.

3.2. Bio-surfactants:

Unlike the chemically synthesized surfactants, which are usually classified according to the nature of their polar groups (cationic, anionic, zwitterionic and non-ionic), biosurfactants are usually categorized mainly by their chemical structure and microbial origin. Structurally, they are no anomalous to the other members of surfactant family. They are also amphiphilic containing a hydrophilic moiety (comprising an acid,alcohol, peptide cations, or anions, mono-, di- or polysaccharides) and a hydrophobic moiety (made up of unsaturated or saturated hydrocarbon chains or fatty acids). The hydrophilic part of biosurfactants is responsible for their rate of solubility in water. The lipophilic part is responsible for capillary activity. These two parts are joined by ester linkage (including lactones) with organic and inorganic acids or amide linkage (single and peptide) or glycosidic linkage (sugar-sugar and sugar-hydroxy fatty acids). Rosenberg and Ron classified biosurfactants in two categories according to molecular mass [22].

i. **Low-molecular weight surface active agents:** having efficiently lower surface and interfacial tension. Major classes include glycolipids, lipopeptides and phospholipids.
ii. **High-molecular weight surface active agents:** effective as emulsion-stabilizing agents. Major classes include polymeric and particulate surfactants.

The major types of biosurfactants and their producer are presented in **Table 2**. (*adapted from* [23])

Biosurfactant			Microorganism
Group	**Sub-group**	**Class**	
		Rhamnolipids	*P. aeruginosa, Pseudomonas* sp.

Low-molecular weight surface active agents	Glycolipids	Sophorolipids	*T. bombicola, T. apicola*
		Trehalolipids	*R. erythropolis, Mycobacterium* sp.
		Cellobiolipids	*U. zeae, U. maydis*
	Lipopeptides & lipoproteins	Surfactin	*B. subtilis*
		Viscosin	*P. fluorescens*
		Peptide-lipid	*B. licheniformis*
	Fatty acids, neutral lipids and phospholipids	Fatty acids	*C. lepus*
		Neutral lipids	*N. erythropolis*
		Phospholipids	*T. thiooxidans*
High-molecular weight surface active agents	Polymeric surfactants	Emulsan	*A. calcoaceticus*
		Biodispersan	*A. calcoaceticus*
		Alasan	*A.radioresistens*
		Liposan	*C. lipolytica*
	Particulate surfactants	Vesicles and fimbriae	*A. calcoaceticus*
		Whole cells	Variety of bacteria

Table 2. Classification of biosurfactant and important types of microbial origin.

4. Technologies for production :

4.1. Technologies for production of Bio-surfactants

Bio-surfactants are a heterogeneous group of microbial metabolites and, therefore, exhibit vastly different physic-chemical properties. Especially with respect to foaming properties, reduction of surface-tension, and emulsification capacities, this has consequences for handling bio-surfactant fermentations in bioreactors. For example, the bio-surfactants rhamnolipid, surfactin, and mannosylerythritol lipids can be grouped into high-foaming biosurfactants, whereas sophorolipids are low-foaming bio-surfactants. Owing to this diversity, several bioreactors have been reported for bio-surfactant production reaching from “standard” constructions like stirred tank bioreactor to “exotic” constructions like the rotating disc bioreactor [24].

4.1.1. Batch Cultivation:

Batch cultivations have been reported in many biosurfactant production processes. The production of rhamnolipid with Pseudomonasaeruginosa PAO1 as a model, for instance, is realized by a batch fermentation process [24]. In batch fermentation strategies, no regulation of the amount of substrates in the bio-reactor growth rate over time is possible. However, due to complex regulation in rhamnolipid production coupled with the quorum-sensing system, applied fed-batch strategies in rhamnolipid production are based on heuristic approaches leading to a production comparable to the batch processes. Next to batch fermentation, sequential batch processes are also used in biosurfactant production.

4.1.2. Fed-Batch Cultivation

When using fed-batch strategies, concentrations of substrates and the growth rate can be controlled by feeding. This may lead to effective process strategies achieving high amounts of bio-surfactants by fermentation. One example is the production of using fed-batch cultivation; the production process can be divided into two phases [24]. In the first phase biomass is produced, whereas sophorolipid production is relatively low. Upon nitrate depletion, biomass production stops and an extensive production of sophorolipids start by utilizing the fed substrates glucose and rapeseed ethyl esters. Product inhibition is circumvented by cultivation parameter leading to a low solubility of sophorolipids in the aqueous media. These fermentation procedures lead to a production of 320 g/L sophorolipids with a weight yield of up to 65% with respect to the carbon source. The highest yield of sophorolipids reported in a fed-batch process was 422 g/L utilizing a two-stage process.

4.1.3. Continuous Cultivation

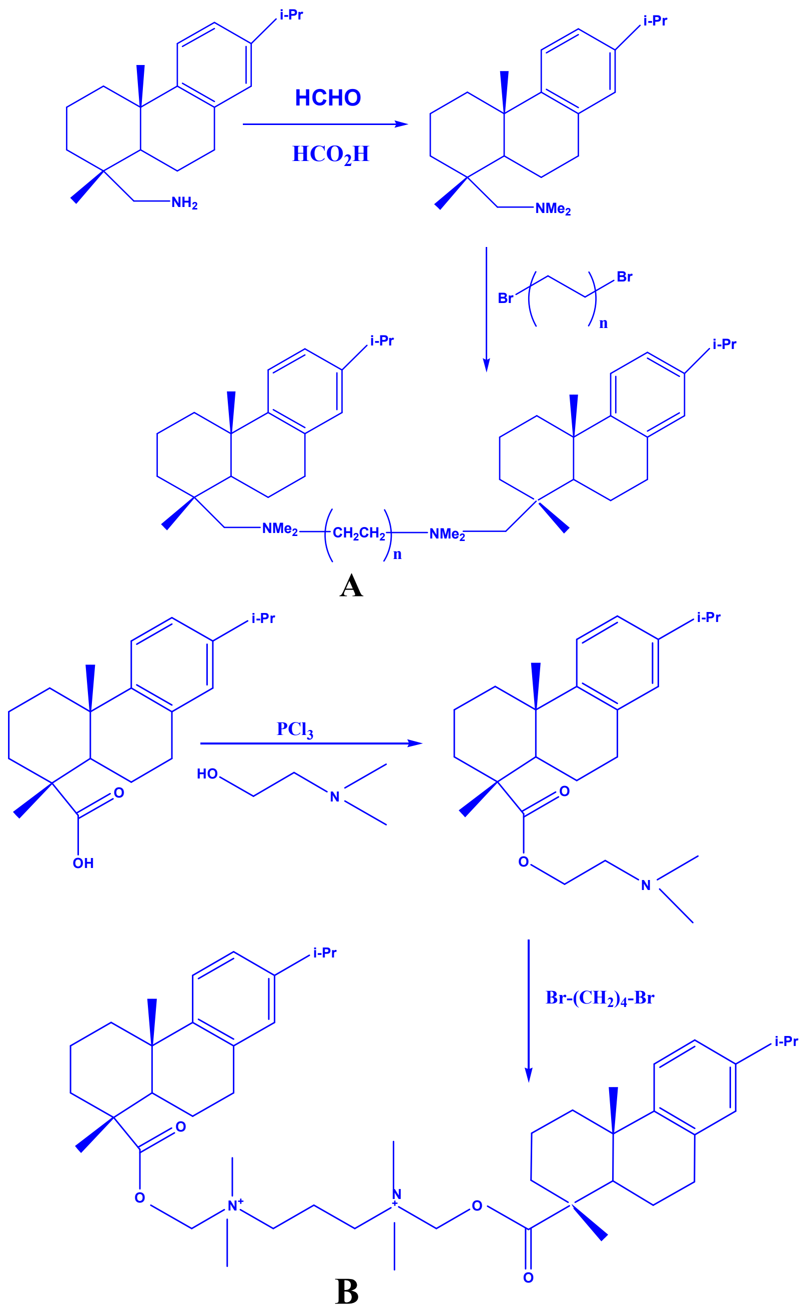
A third fermentation strategy is continuous fermentation. Two examples are the production of surfactin [24] and rhamnolipids [25, 26]. Different systems were established exhibiting quite low dilution rates of 0.065 h^{-1} in the case of rhamnolipids and 0.1–0.2 h^{-1} in the case of surfactin for an optimal bio-surfactant production.

4.2.Technologies for synthesis of Gemini surfactants:

There are several traditional lab based strategies for the synthesis of Gemini surfactants, but we shall look forward for more green approaches which have provided the synthetic chemistry a new horizon.

Initially we refer to green molecular design of a few cationic geminis obtained from naturally occurring rosin based moieties; Rosin acids are a novel source of hydrophobic groups with a tricyclic hydrophenanthrene structure that can be used for the synthesis of surfactants with natural origins.

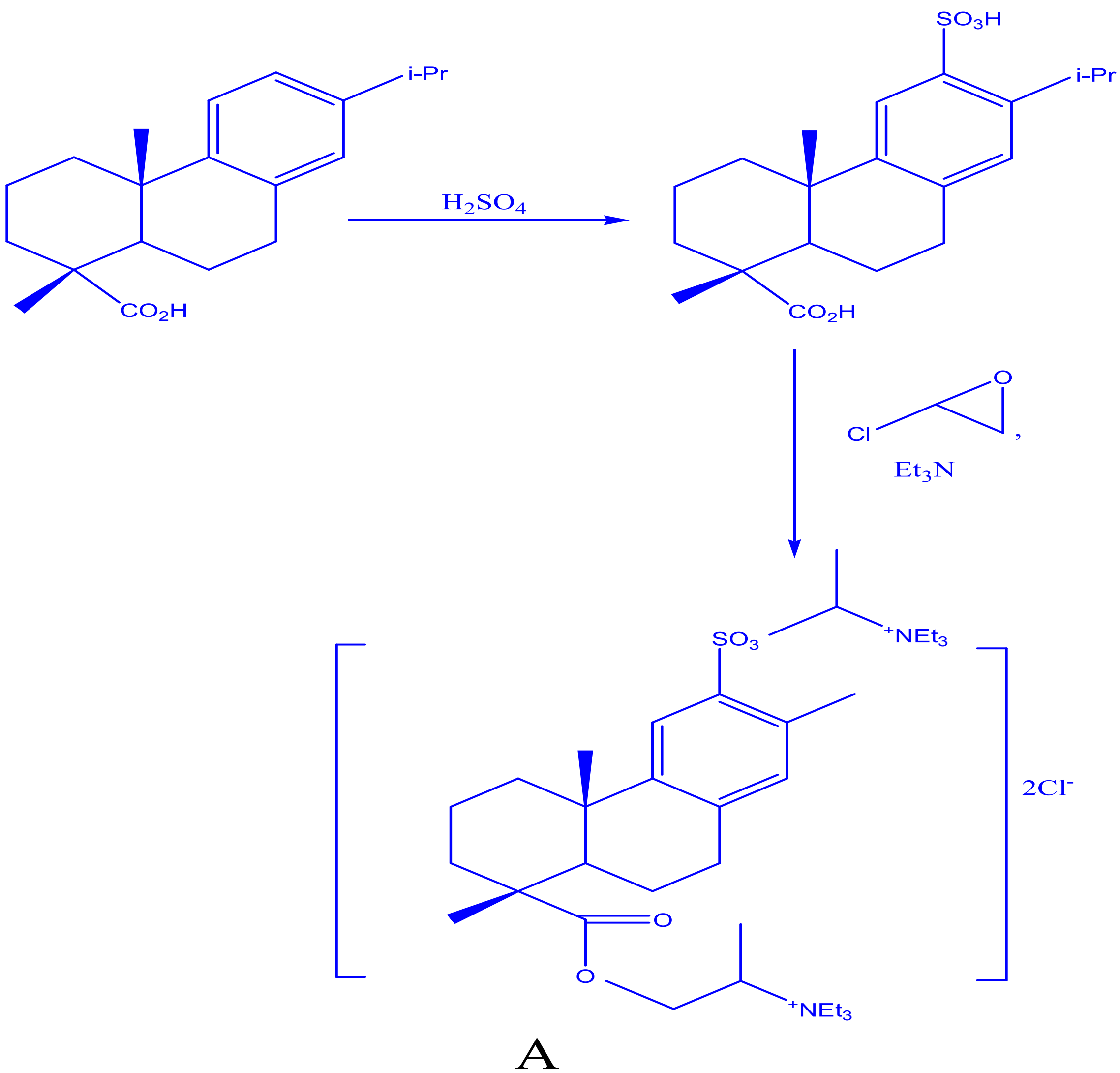
In our previous paper [4] we have presented the novel work of Jia et al. which have reported the synthesis of cationic Gemini surfactants from dehydroabietylamine by reaction with DMDHA and α, ω- bisbromoalkanes; they also have reported the Cationic Gemini surfactant with rosin based hydrophenanthrene structure:

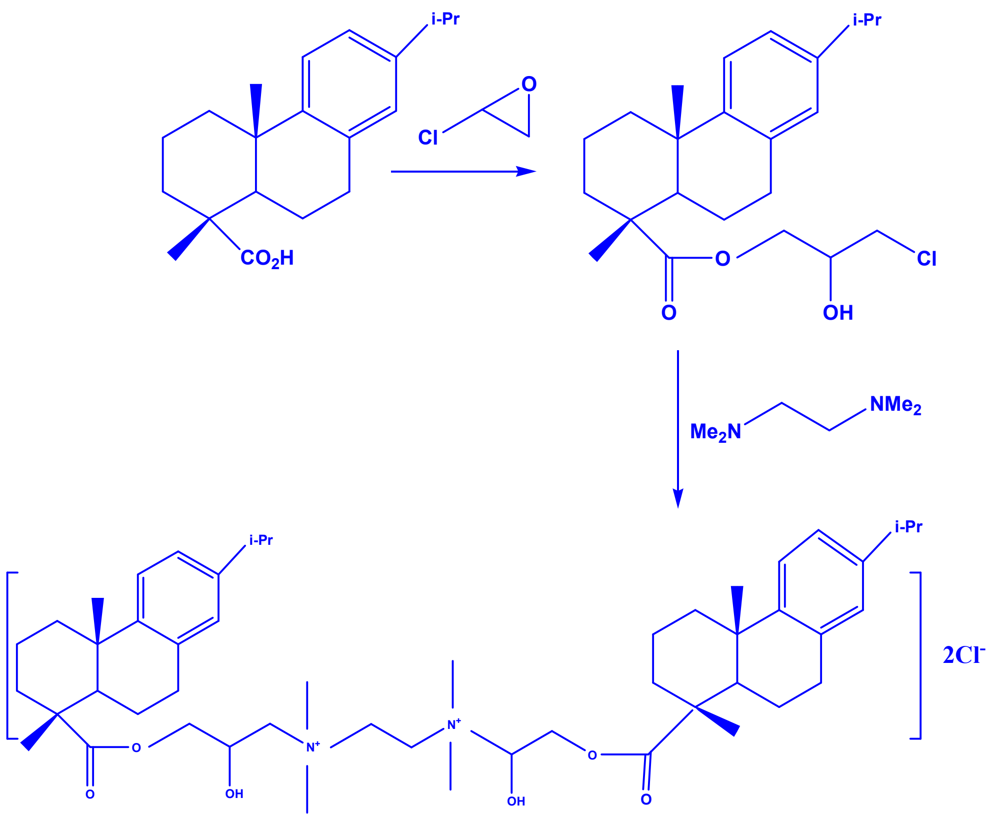


Scheme 2. A) Novel cationic geminis from dehydroabietylamine and DMDHA, (n = 1-4); B) Gemini surfactant with rosin-based hydrophenanthrene unit [4,27].

Chen et al. and Hu et al. [28-29].

A new sulfodehydroabietic acid based on a bis-quaternary ammonium cationic Gemini has been synthesized by Chen and co-workers. The synthetic procedure involves sulfonation of DAA, followed by reaction with epoxy chloropropane and triethylamine; Theeco-friendly synthetic methods that epoxy chloropropaneprovides, can also be mentioned. In this regard, C_sH_{2s}-α, ω-bis-(dehydroabietylhydroxypropyltetra- methylethyldiammonium) chloride surfactant can be synthesized through an epoxy chloropropane intermediate,



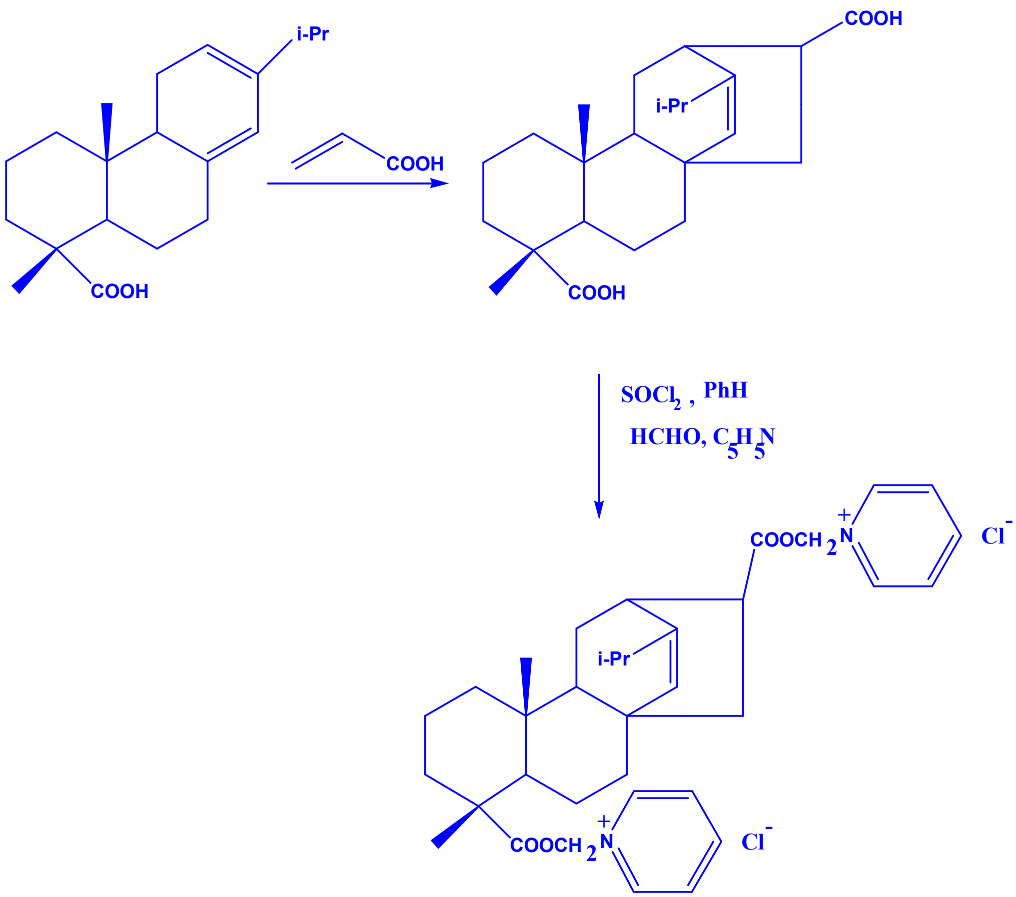


B

Scheme 3. Synthesis of (A) Sulfodehydroabietic acid-based Gemini surfactant (B) Epoxychloropropane based cationic Gemini surfactant [28-29].

Wei. et al. [30].

Connecting two hydrophobic moieties towards the end of their hydrophobic tails in a so called bola-form surfactant and physicochemical properties of such species are different from those of conventional geminis. bis-quaternary ammonium cationic bola geminis have been synthesized using acrylic-modified rosin, thanks to Wei. et al.



Scheme 4. Synthesis of bis-quaternary ammonium cationic bola geminis using acrylic-modified rosin, Wei. et al. [30].

5. Utilization:

5.1. Metal mediated redox kinetics:

The studies on the effect of the organized assemblies on the rate of electron transfer reaction have been receiving considerable attention. The effect of organized assemblies on the rate of reactions can be attributed [3, 21] to hydrophobic and electrostatic interaction in partition of the reactants. For catalytic process micellar solution provides a way for alternative synthetic routes in an aqueous medium. In an aqueous phase surfactant molecules aggregate, at ambient conditions, forming micelles with a hydrophobic core and hydrophilic corona [5] .Many important biochemical redox reactions involve electron transfer reactions occurring in a micro-heterogeneous system, which consists of an aqueous and lipophilic moiety. A number of interfacial electron transfer process have been investigated [3, 21] in the polyelectrolyte, vesicular designs and micellar surfaces. In the model systems, micelles are considered to mimic cellular membranes. Such studies have increased our understanding of electron transfer mechanism in micro heterogeneous system. The studies of kinetics and equilibrium on electron transfer reaction in micellar systems are also important [4] from the standpoint of understanding of different phenomena, such as therapeutic activities of different drugs (e.g.- phenothiazine derivatives) interacting with a cellular membrane , photochemical energy storing systems involving compounds of photo redox properties in a micellar or vesicular designs. The mechanistic aspects of oxidation of different aliphatic and aromatic moieties by different transition metal ions like, Cr, Mn, Fe, Ti, V, Cu etc. in aqueous acid media have been reported [5]. Various chelating agents are known to catalyse in the metal mediated oxidation of different organic substrates. In this regard, bipyridine (bpy), pyridine (py), phenanthroline (phen), edta etc. are quite efficient. Notably it is true that a diversity of selective chromium (VI) oxidizing agents as pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), imidazolium dichromate (IDC) etc have been developed which allow for the oxidation of a large range of compounds [31].

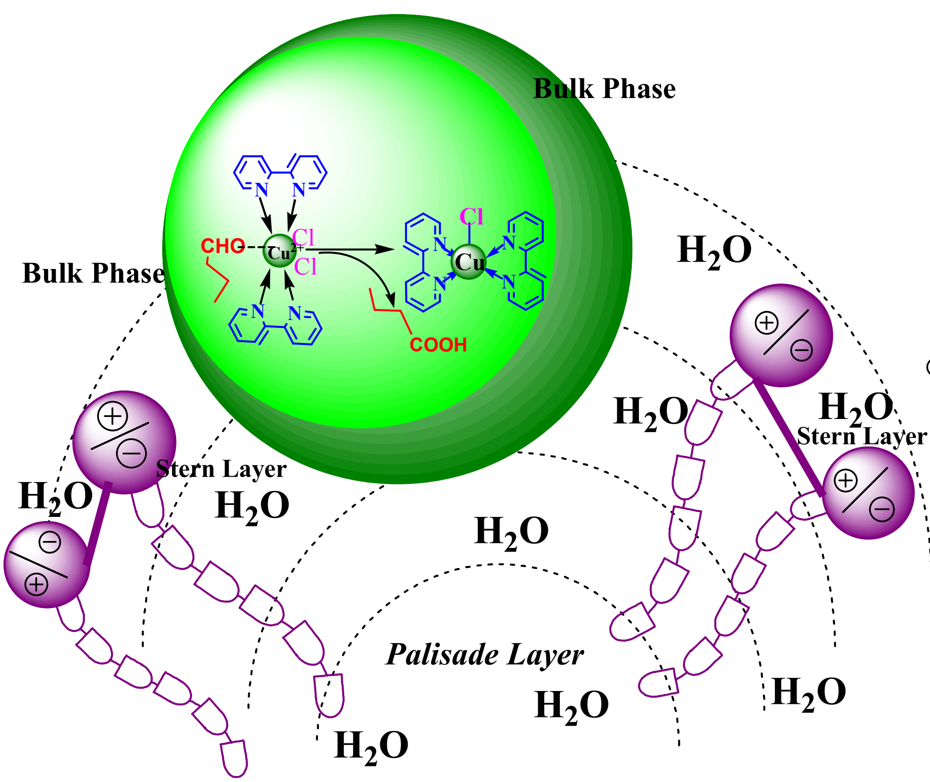


Fig. 4. The simplified diagrammatic presentation of oxidation kinetics in micellar media of Gemini surfactants, where the oxidant is Cu(II), promoter is bipyridine(bpy) and the substrate is butanal

So the combination of metal (as oxidant) and promoters in association with bio surfactant, traditional or more efficiently with Gemini surfactants likely plays a significant role in the growth of value-added chemicals from biomass and precursors. Thousands of scientific journals are found every year on the micellar assisted oxidation of different important chemical substances [32-35a]. The kinetic studies of several organic transformation reactions in gemini micellar media have been reported [35b, 35c]. The supreme efficiency of novel cationic Gemini surfactant on the cleavage of carboxylate ester has been reported by B. Kumar et.al. [35d]. It is thus of greater interest for optimizing the consumption of time and energy and maximizing the yield. In the greenolution [4] of a normal brown kinetics bio-surfactants and geminis are thus act as one of the leading pivot.

5.2. Microbial Enhanced Oil Recovery (MEOR): MEOR is an efficient scientific skill that recovers oil resting in reservoirs with lower permeability or crude oil with high viscosity. It is an obvious technical problem for the oil based industries that after their concerned process that deals with oil a remaining part of oil in the reservoir is often positioned in locations that are hard to access and the oil remains trapped in the pores by capillary pressure [36]. Bio-surfactants as we have already discussed for their efficient ability to minimize the interfacial tension between oil/water and oil/rock diminishes the capillary forces restricting oil from removing. Bio-surfactants also for their affection towards hydrophobic aliphatic/aromatic oily moieties can bind firmly to the oil-water interface thereby forming emulsion. For this formation of emulsion the remaining oil now gets dissolved in the injected water containing the surfactant removes oil as n effluent [37]. It is reported that *Bacillus subtilis* a precursor to bio-surfactant, at 45ºC has good sand-pack oil recovering ability [38, 39].

5.3. Soil Washing Technology and Bioremediation of Crude Oil-Contaminated Environments:

Highly hydrophobic contaminants have ability to bind very tightly with soil, thereby inaccessible to biodegradation. Surfactants potentially have the ability to promote desorption of the contaminants from soil. Biosurfactant like rhamnolipids was effective in removing polycyclic aromatic hydrocarbons (PAHs) and pentachlorophenol from soil with removal efficiency of 60-80% [40,41].Crude oils have very low water solubility, high adsorption onto soil matrix. Oil-contaminated soil is especially difficult for bioremediation as oil excess forms droplets or films on soil particles. It is a powerful obstacle against microbial degradation. Bio-surfactants are produced to reduce the tension at the hydrocarbon-water interface thereby pseudo solubilizing the hydrocarbons and thus increasing mobility, bioavailability and consequent biodegradation [42].That's why bio-surfactants are very useful for applications in the oil industry and this is reflected in the market, where the large majority of bio-surfactants produced are for petroleum-related applications [43]. The BS29 bio-emulsions produced from *Gordonia* sp. are promising washing agents for the bioremediation of hydrocarbon-contaminated soils.

The effects of the hydrocarbon chains and spacer groups of gemini surfactants, salt, temperature, and polymer on the interfacial tension of crude oil–water mixtures were investigated by Han et.al. [44]. The length of the alkyl chain is a major factor affecting the properties of a gemini surfactant, and the spacer group is also an important factor influencing the surfactant properties. The addition of salt results in a great decrease in the CMC and favors the reduction of interfacial tension, which shows that a cationic gemini surfactant has a good synergism with salt. Variation in temperature will affect the dynamic and equilibrium interfacial tension, and increasing the temperature can shorten the time to reach the equilibrium and decrease the equilibrium interfacial tension in the range of experimental temperatures. The surface tension or the interfacial tension of surfactants greatly related to the adsorption of the surfactant at the interface. The surface area occupied by one surfactant at the interface is an important characteristic of a surfactant and is very important in surfactant science. The possibility of a partial binding of a counter ion by a gemini surfactant ion at a concentration C\CMC arose in the analysis of the plots of the surface tension c vs. C for gemini surfactant solutions given by Han et.al.[44].

5.4. Metals Remediation: Contamination of soil and water with heavy metals is very hazardous for human and other living organisms in the ecosystem. The consumption of heavy metal contaminated water directly, causes diseases like black foot for As, Itai-Itai for Cd, Willson for

Cu etc. due to their exceptionally toxic nature,[45] presence of even low concentrations of heavy metals in the soils has been found to have serious danger. Several surfactants have the ability of metal remediation. Rhamnolipids are known to have ability to remove heavy metals [46]. In our bio-remediation laboratory we have witnessed several such experiments which concludes that, the mixing of traditional and bio-surfactant together effects the rate of metal remediation to enhance by several folds [47, 48].

5.5. Biomedical Field: As because of their bio origin, biological surfactants are extensively useful in the biomedical grounds and these are much faster accepted by bio-organism. Several bio-surfactants have strong antibacterial, antifungal and antivirus activity. These surfactants act as anti-adhesive agents to pathogens and so they are useful for treating many diseases. So they can be used as therapeutic and pro-biotic agent. Rhamnolipid produced by *Pseudomonas aeruginosa*, mannosylerythritol lipids from *Candida Antarctica,* lipopeptides produced by *B. subtilis* and *B. licheniformis* have been shown to have antimicrobial activities. Iturin, a lipopeptide produced by *B. subtilis* showed anti-fungal activity against the morphology and membrane structure of yeast cells [49]. A rhamnolipid mixture obtained from *P. aeruginosa* AT10 is found to have inhibitory activity against the bacteria *Escherichia coli*, *Serratia arcescens*, *Micrococcus luteus*, *Alcaligenes faecalis* , *Mycobacterium phlei* and *Staphylococcus epidermidis* and excellent antifungal properties against *Aspergillus niger*, *Enicillium crysogenum ,Chaetonium globosum*, *Aureobasidium pullulans* and the phytopathogenic *Rhizoctonia solani* and *Botrytis cinerea*. Sophorolipids from *C. bombicola* has a virucidal activity against the human semen [49]. Other advantages and applications of bio-surfactant in medicine are Gene delivery, immune-modulation, wound healing, insecticidal, anti-tumoral activities etc.

Now if we look at Gemini surfactants for their contribution to medical field it is too of great importance.

Han *et.al.* [44] found that cationic gemini surfactant $C_{12}C_6C_{12}Br_2$ micelles can effectively disassemble mature Aβ(1-40) fibrils in vitro because of their bicharged hydrophilic head groups and strong self-aggregation ability. The synergistic hydrophobic and electrostatic interactions account for the strong ability to disassemble Aβ(1-40) fibrils. As a prototype delivery system, the nano-carriers may simultaneously perform dual functions (i.e., disassembly of Aβ fibrils and transport of therapeutic agents). The investigation of Han et.al. indeed have opened a promising strategy to treat Alzheimer's disease and other amyloidoses. To optimize disassembly and drug delivery efficiency further, new system with much lower cmc and better biocompatible surfactants than those of the present surfactants synthesis is a recent day target in several laboratories working on micellar studies.

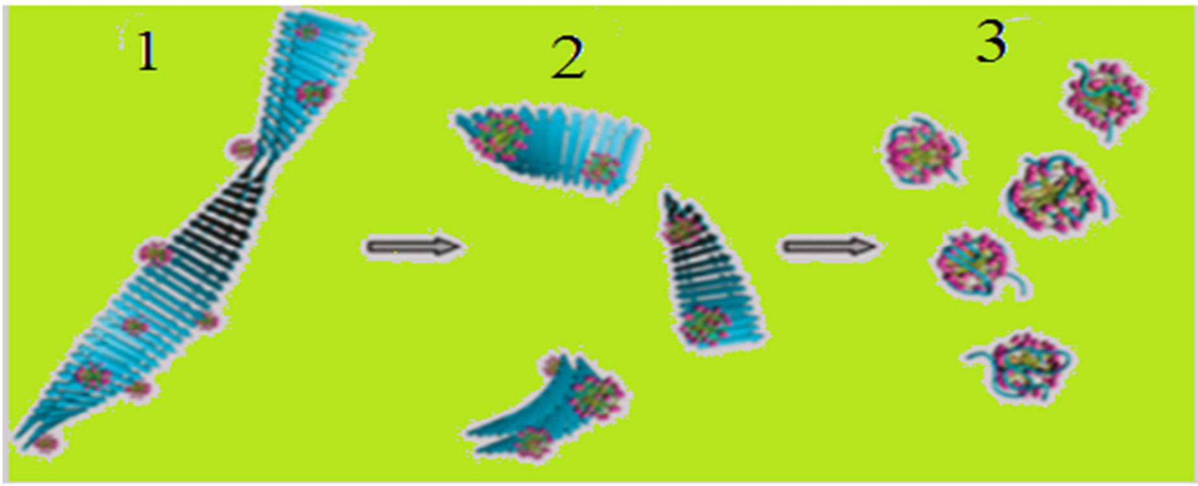


Fig. 5. Proposed mechanism of the$C_{12}C_6C_{12}Br_2$ micelles disassembling the Aβ(1-40) fibril. Binding of the $C_{12}C_6C_{12}Br_2$ micelles on to the fibril surface. (2) Breaking down of a long fibril into short pieces. (3) Complete disassembly of fibrils and the formation of mixed aggregates [44].

M. C. Feiters*et al.* [50] has reported a few tartaric acids based cationic Gemini surfactants with biocompatible palmitoyl tails and head groups, and showed their aggregation in water, monolayer behaviour, DNA binding, and gene transfection activities.

5.6. Agricultural Field: The development of agricultural science which leading to maximization of production of food stuffs inhibiting the use of chemicals and pesticides in agricultural field for arthropod control, which in short time based term may increase the production but often produce undesirable hazards to nature and eco-system in long term. To minimize the devastation bio-surfactants may play dual character primarily these are efficient for the removal of water insoluble organic pesticides and also shows antimicrobial and insecticidal activity itself. Moreover, no adverse effects on the environments or human beings are anticipated from them. The bio-surfactants lipopeptide, produced by several bacteria show insecticidal activity against fruit fly *Drosophila melanogaster* and hence they can be used as bio-pesticide [51]. In addition to this bio-surfactants can also be used to obtain good wettability and to achieve even distribution of fertilizer in the soil. The removal of extra fertilizers from soil to maintain the pH could also be a great achievement by using these kinds of surfactants.

5.7. Laundry Industry: The chemicals that are used for the synthesis of almost all commercially available detergents are very much toxic for the residents of fresh water living organisms. But bio-surfactants, as are very much bio degradable are eco-friendly. Moreover, bio-surfactants like CLP (Cyclic Lipopeptide) are stable over a wide pH range (7.0 to 12.0) and no loss of their surface-active property occurs when they are heated at high temperature [52].Their excellent and their excellent foaming compatibility and affection to bond formation with bio-organic compounds i.e. stabilization favors their inclusion in the formulation of laundry detergents.

5.8. Food Processing Industry: Bio-surfactants are also being used in food industries generally as food additives (emulsifiers). For instance, fatty acid esters containing glycerol, lectin and its derivatives, sorbitan or ethylene glycol and ethoxylated derivatives of monoglycerides along with recently synthesized oligopeptide [53].These emulsifiers improve the taste, flavor and quality of food-products with minimal health hazards. Their potential applications in food industry includes fat stabilization in food oils, defoaming in sugar production, increased solubility in instant drinks and soups, starch complexation in instant potatoes and protective coatings for vegetables, fruits etc.

5.9. Cosmetic Industry: Bio-surfactants have now become the best alternative to chemical personal care products. The demand and use of bios stuffs have found a niche in the health care and cosmetic industry due to their skin friendly and health friendly properties. Sophorolipids can be esterified or blended with ethylene oxide and can be used as skin moisturizers. Kao Corporation (www.kao.com/jp/) in Tokyo, Japan, Himalaya Health Care (www.himalyahealthcare.com) in India and many more such companies are using oils extracted from different plants or vegetables even from in the personal care sector. Bio-surfactants are used as foaming agents, emulsifiers, solubilizers, wetting agents, cleansers, antimicrobial agents, mediators of enzyme action, in insect repellents, acne pads, antacids, bath products, anti-dandruff products, contact lens solutions, baby products, mascara, lipsticks, toothpaste etc. [54].

6. Future prospect of Gemini and Bio-surfactants:

With advancement of science and supreme supervision, it will not be very much difficult to believe the existence of single molecule micelle. If a large number of single surfactants are chemically joined with each other and a macrocyclic giant Gemini is prepared then due to the enhanced cooperative interaction, the CMC for such giant molecular micelle will be so much low that a single molecule of such Gemini surfactant will be sufficient to overcome the desired critical concentration. The synthetic approach of such low CMC giant geminis must be a burning topic for scientist around the world working on surface chemistry, which indeed will have much better impact on the industry of emulsification, paint, cosmetics, medicine and even biology, the best part is that the chemistry of surface study will be more greener than ever before.

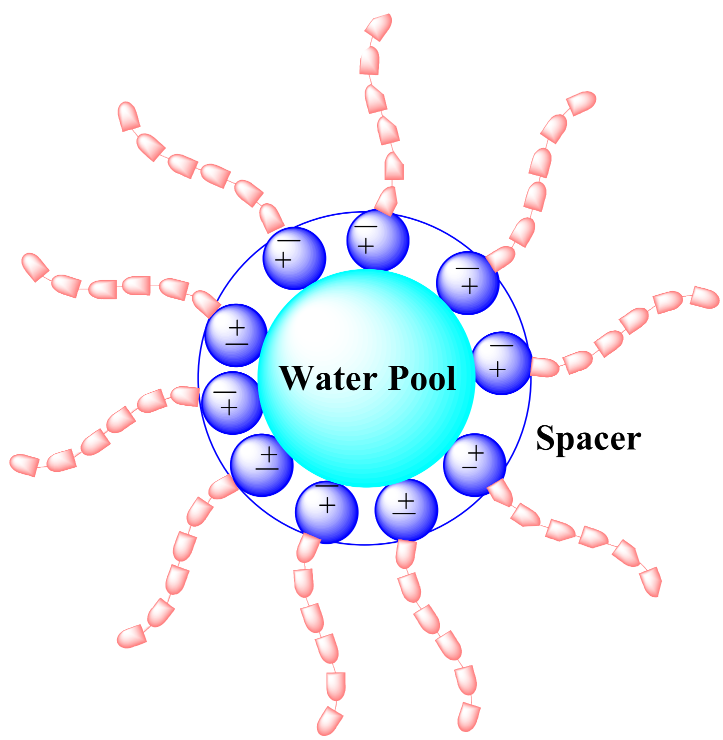


Fig. 6. Schematic representation of proposed single molecule giant gemini surfactant.

Comparing to synthetic surfactants, bio-surfactants possess many industrially attractive properties and advantages as we have already discussed. Yet, their commercialization is on the question mark! The major cause to this could be the relatively high cost for the production, separation and purification of these natural resources. To overcome this, use of pure carbon sources (such as oleic acid) is of relatively economy friendly option. Use of available bio resources as low-cost raw materials can be a possible solution for this obstacle. Different substances such as vegetable oils, animal fat, distillery and dairy wastes, soya molasses, starchy wastes etc. can be used as raw materials. Rhamnolipid production from olive oil mill effluent by *Pseudomonas* spp. is a remarkable development in this field. If it is the question of further development in bio-surfactant field then of course the issue will be the minimization of post production and pre-utilization cost. The remediation can be executed *in situ*, production could also be performed *in situ* .This would be technical & cost effective and less labor & transport would be required. Therefore, the process would be both ecologically and economically favorable. . We expect that in future, super-active microbial strains would be developed using genetic modification for the production of bio-surfactants at industrial level. Invention of modern methods and discovery of more reliable sources for the production of bio-surfactants are also expected in future. So then yields would be increased and production costs would be decreased and new bio-surfactants will continue to be discovered, and then chemistry of these molecules would be better understood.

7. Conclusions:

This comprehensive review summarizes the findings of numerous literatures aiming to improve the basic understanding of overall surfactant enhanced remediation technologies some aspects like surfactant adsorption on soil, micellar solubilization, emulsification, biodegradation, medicine and drug designing and delivery, partitioning of surfactants and contaminants; and different parameters those affecting these phenomena are discussed. The future prospect of this kind of surface science is thus of very high potentiality because of its direct implication in day to day modern life, with significant green prospect. The overall conclusion of this write up is to bring attention of scientists working in the field of industrial chemistry, green chemistry and catalysis towards the highly prospectus future of novel surfactants, having very low CMC will be substantially applicable in the industry of emulsification, drug designing and synthesis. We want to thank in advance to all the leading nations and their chemists for their evolutionary green thoughts that will incorporate the highly efficient geminis and super duper green biosurfactants, that will trigger a “Renaissance” in the very near chemical era.

Acknowledgement:

Authors acknowledge The University of Burdwan for providing the infrastructural facilities and CSIR, India for providing fund.

References:

[1] G. L. Sorella, G. Strukul, A. Scarso, *Green Chem*. 2015, **17**, 644-683.

[2] G. Bianchini, A. Cavarzan, A. Scarso, G. Strukul, *Green Chem*. 2009, **11**, 1517-1520.

[3] A. Ghosh, R. Saha, K. Mukherjee, S. K. Ghosh, P. Sar, S. Malik, B. Saha, *Res. Chem. Intermed* 2015, **41**, 3057-30.

[4] M. H. Mondal, A. Roy, S. Malik, A. Ghosh, B. Saha, *Res. Chem. Intermed* 2015, DOI: 10.1007/s11164-015-2125-z.

[5] F. M. Menger, J. S. Keiper, V. Azov, *Langmuir*, 2000, **16**, 2062-2067.

[6] A. Ghosh, R. Saha, K. Mukherjee, P. Sar, S. K. Ghosh, S. Malik, S. S. Bhattacharyya, B. Saha, *J. Mol. Liq*. 2014, **190**, 81-93.

[7] M. J. Rosen, D. J. Tracy, *J. Surf. Det*.1998, **1**, 547-554.

[8] Y. X. Ding, M. Zha , J. Zhang , S.S. Wang, *Colloids Surf A*, 2007, **298**, 201-205.

[9] X. Huang, Y. C. Han, Y. X. Wang, Y. Wang, *J. Phys. Chem. B*. 2007, **111,** 12439-12446.

[10] D. Danino, Y. Talmon, R. Zana, *Langmuir* 1998, **14**, 5412-5418.

[11] L. Han, H .Chen, P .Luo ,*Surf. Sci. series*, 2004, **564**, 141-148.

[12] H. Chen, L. Han, P. Xu, *Acta Phys Chim Sin*, 2003, **19**, 1020-1024.

[13] Z. Ye, F. Zhang, L. Han, *Colloids Surf A*, 2008, **322,** 138-141.

[14] F. Siñeriz, R. K. Hommel, H. P.Kleber, *Production of biosurfactants. In: Encyclopedia of Life Support Systems. Eolls Publishers, Oxford* 2001.

[15] A. Singh, J. D. Van Hanne, O. P. Ward, *Biotechnol. Adv*. 2007, **25**, 99-121.

[16] M. Robert, M. E. Mercadé, M. P. Bosch, J. L. Parra, M. J. Espiny, M. A. Manresa, J. Guinea, *Biotechnol. Lett*.1989, **11**, 871-874.

[17] S. K. Ritter, *Chem. Eng. News*, 2004, **82**, 25-29.

[18] N. Krieger, C. N. Doumit, A. M. David, *Adv. Exp. Medic. Bio*. 2010, **672**, 203-210.

[19] I. M. Shete, G. Wadhawa, I. M. Banat, B. A. Chopade, *J.Sci. Ind. Res*. 2006, **65**, 91-115.

[20] M. Mishra, P. Muthuprasanna, P. S. Rani, I. A. S. Babu, I. S. Chandiran, G. Arunachalam, S. Shalini, *Int. J. PharmTech Res.* 2009, **1**, 1354-1356.

[21] S. Malik, A. Ghosh, K. Mukherjee, B. Saha, *Tenside Surf. Det*. 2014, **51,** 325-332.

[22] E. Rosenberg, E. Z. Ron, Appl. Microbiol. *Biotechnol*.1999, 52, 154-162.

[23] J. D. Desai, I. M. Banat, *Microbiol. Mol. Biol. Rev*. 1997, **61**, 47-64.

[24] M. M. Müller, J. H. Kügler, M. Henkel, M. Gerlitzki, B. Hörmann, M. Pöhnlein, C. Syldatk, Hausmann, *J. Biotechnol*. 2012,**162**, 366-380.

[25] M. Garcia-junco, C. Gomez-lahoz, J. L. Niqui-arroyo, J. J. Ortega-calvo, *Environ. Sci. Technol*. 2003, **37**, 2988-2996.

[26] L. H. Guerra-Santos, O. Käppeli, A. Fiechter, *Appl. Microbiol. Biotechnol*. 1986**, 24**, 443-448.

[27] W.H. Jia, X.P. Rao, Z.Q. Song, S. B. Shang, *J. Surf. Det*. 2009, **12**, 261-267.

[28] L.Y. Chen, G.Z. Fang, K. Liu, X. Hu, *Chemistry and Industry of Forest Products*, 2007, **27**, 66-85.

[29] X. Hu, H.C. Li, L.Y. Chen, *Chin. J. of Appl. Chem.* 2007, **24**, 1439-1442.

[30] X. H. Wei, D.R. Cao, S.F. Dong, *Guangzhou Chemistry*, 2003, **3**, 22-27.

[31] A. Ghosh, R. Saha, B. Saha, *J. Ind. Eng. Chem*. 2014, **20**, 345-355.

[32] S. De, S. Malik, A. Ghosh, R. Saha, B. Saha, *RSC Advances*. 2015, **5**, 65757-65767.

[33] K. Mukherjee, D. Ghosh, B. Saha. *Tenside Surf. Det*. 2014, **51**, 521-527.

[34] R. Saha, A. Ghosh, B. Saha, *Spectrochim. Acta Part A*, 2014, **124,** 130-137.

[35a] A. Ghosh, R. Saha, K. Mukherjee, S. K. Ghosh, P. Sar, S. Malik, B. Saha. *Res. Chem. Intermed,* 2015, **41**, 3057-3078.

[35b] B. Gupta, R. Sharma, N. Singh, Y. Karpichev, M. L. Satnami, K. K. Ghosh, *J. Phys. Org. Chem*. 2013, **26**, 632-642.

[35c] B. Kumar, D. Tikariha, K. K. Ghosh, *J. Mol. Liq*. 2014, **193**, 243-248.

[35d] B. Kumar, K. K. Ghosh, D. Tikariha, N. Barbero, P. Quagliotto, *J. Phys. Org. Chem*. DOI: 10.1002/poc.3141.

[36] R. Sen, *Prog. Energ. Combust.* 2008**, 34**, 714-724.

[37] H. Suthar, K. Hingurao, A. Desai, A. Nerurkar, *J. Microbiol. Methods*, 2008**, 75**, 225-230.

[38] I. M.Banat, *Biores Tech*. 1995, **51**, 1-12.

[39] R. S. Makkar, S. S.Cameotra, *J. Ind. Microbiol. Biotechnol*. 1997, **18**, 37-42.

[40] M. Garcia-junco, C. Gomez-lahoz, J. L. Niqui-arroyo, J. J. Ortega-calvo, *Environ. Sci. Technol*. 2003, **37**, 2988- 2996.

[41] C. N. Mulligan, F. Eftekhari, *Eng. Geol*. 2003, **70**, 269-279.

[42] R. Rosen, E. Z. Ron, *Mass Spectrom Rev.* 2002, **21**, 244-265.

[43] G. Bognolo, *Colloids Surf., A*, 1999**, 152**, 41- 52.

[44] L, Han, Z. Ye, H. Chen, P. Luo, *J. Surf. Det.* 2009, **12**, 185-190.

[45] A. K. Das, *Books and allied(P) Ltd. India*. Bio-inorganic chemistry, 2008, 341, 350.

[46] S. Wang, C. N. Mulligan, *Water, Air, Soil Pollut.* 2004, **157**, 315-330.

[47] K. Mukherjee, R. Nandi, D. Saha, B. Saha, *Des.Wat. Treat*. 2015, **54**, 525-532.

[48] K. Mukherjee, R. Nandi, D. Saha, B. Saha*, Des. Wat. Treat*. 2015, **53**, 746-751.

[49] L. Thimon, F. Peypoux, G. Michel, *Biotechnol. Lett*, 1992, **14**, 713-717.

[50] M. Damen, J. Aarbiou, S.F.M. van Dongen, R.M. Buijs-Offerman, P.P. Spijkers, M. van den Heuvel, K. K. vashnina, R.J.M. Nolte, B.J. Scholte, M.C. Feiters, *J.Controlled. Release*, 2010, **145**, 33-39.

[51] A. Abalos, A. Pinazo, M. R. Infante, M. Casals, F. Garcýa, A. Manresa, *Langmuir*. 2001, **17**, 1367-1371.

[52] M. Krishnaswamy, G. Subbuchettiar, T. K. Ravi, S. Panchaksharam, *Curr. Sci*. 2008, **94**, 736-744.

[53] C. N. Mulligan, *Environ. Pollut*. 2005, **133**, 183-198.

[54] E. Gharaei-Fathabad, *Am. J. Drug Discov. Dev.* 2010, **23**, 1-11.