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# Surfactants-based remediation as an effective approach for removal of environmental pollutants—a review

Tahir Rasheed<sup>\*a</sup>, Sameera Shafi<sup>a</sup>, Muhammad Bilal<sup>b</sup>, Tariq Hussain<sup>c</sup>, Farooq Sher<sup>d</sup>, Komal Rizwan<sup>\*c</sup>

<sup>a</sup>School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

<sup>b</sup>School of Life Science and Food Engineering, Huaiyin Institute of Technology, Huaian, China

<sup>c</sup>Key Lab of Ocean Engineering, School of Naval Architecture Civil and Ocean Engineering Shanghai Jiao Tong University, 200240, China

<sup>d</sup>School of Mechanical, Aerospace and Automotive Engineering, Faculty of Engineering, environmental and computing, Coventry University, Coventry CV1 5FB, United Kingdom.

<sup>e</sup>Department of Chemistry, University of Sahiwal, Sahiwal 57000, Pakistan

\*Corresponding authors:

Emails: [masil@sjtu.edu.cn](mailto:masil@sjtu.edu.cn) (T. Rasheed); [Komal.rizwan45@yahoo.com](mailto:Komal.rizwan45@yahoo.com) (K. Rizwan)

## Abstract

Deterioration of environmental quality and equilibrium by rampant industrial expansion, accelerated urbanization and unchecked population growth has become a high-priority concern. The release of an alarming number of toxic polluting agents such as volatile organic compounds, dyes, heavy metals, pharmaceuticals, pesticides, industrial wastes, and personal care products due to natural or anthropogenic activities pose direct adverse effects on human health and living entities. This issue is inescapably increased because of the lack of efficient technologies for the proper disposal, management, and recycling of waste. It is of paramount importance to track alternative solutions to address these pollution problems for an eco-sustainable environment. Conventional remediation

techniques are either inefficient, cumbersome or restricted due to certain techno-economic limitations. Environmental compatibility and high pollutant-removal efficacy make surfactants valuable for removal of organic pollutants and toxic heavy metal ions from different mediums. In this review, we present recent and up-to-date information on micelles/surfactants-assisted abatement of a vast number of toxic agents of emerging concern from water/wastewater including volatile organic compounds, personal care products, pharmaceutically active residues, toxic metals, dye pollutants, pesticides, and petroleum hydrocarbons. Based on the literature survey, it can be concluded that micelles-assisted water and soil treatment technology can have a better future on large-scale decontamination of wastewater. Though bio-surfactants are environmentally friendlier matrices and have successfully been employed for environmental decontamination; their large-scale applicability is challenging owing to high costs. Additional research efforts on the development and employment of novel bio-surfactants might render wastewater treatment technology greener, smarter and economical.

**Keywords:** Pollutants; Environmental impact; Removal strategies; Micelles; Biosurfactants; Volatile organic compounds; Pesticides; Petroleum hydrocarbons

## **1. Introduction**

Although the industrialization is inextricably linked with the progress of any country, these are often criticized as the major source of releasing hazardous wastes into the aquatic ecosystems. The controlled and/or uncontrolled discharge of industrially polluted wastewater results in assimilating toxic contaminating agents to the groundwater, surface water, and subsurface soils. The presence of dye pollutants, pharmaceuticals and

personal care products, toxic metals, volatile organic compounds, pesticides, and petroleum hydrocarbons in industrial wastewater undesirably compromise the quality of water and manifests a serious menace to human beings and aquatic creatures [1-5]. A range of conventional techniques including adsorption, precipitation, membrane separation, solvent extraction, reverse osmosis, adsorptive ultrafiltration (UF), electrochemical, and ion exchange are being employed for the treatment of wastewater [6-9]. Environmentally compatible surfactant based approaches have received great attention for removal of pollutants from different mediums because of their eco-sustainability, high pollutant-removal efficiency, versatility, and work based on “green chemistry” principles [10-13].

Micellar enhanced ultrafiltration (MEUF) integrates the enhanced processing efficiency of ultrafiltration and higher selectivity of reverse osmosis [14]. In the process of MEUF, the addition of surfactants into the polluted water samples above their critical micelle concentration (CMC) result in the formation of micelles, an aggregate of large amphiphilic surfactants. Organic contaminants are solubilized in the micelles hydrophobic core using hydrophobic interfaces, whereas the metals tend to adsorb on the oppositely charged surface through electrostatic attractions [15-17]. Surfactants are a unique class of amphiphilic molecules comprising of head and tail, which exhibit a robust attraction for polar and non-polar species. They operate in solvents by reducing their surface tension as they accumulate on the surface and play a role of a bridge between the air and liquid. In water-based solutions, the surfactants tend to accumulate at critical micelles concentration [18, 19], and such aggregates are composed of 50-100 monomers [20]. Recently, the application of biosurfactants has achieved a lot of attention from

environmental scientists and researchers. They have gained priority than synthetic surfactants owing to their high effectivity, non-toxicity, biodegradability, renewability, and wide environmental acceptability [21]. An array of various contaminants of emerging concern including pharmaceutically active residues, VOCs, personal-care products, toxic metals, organic contaminants, dyes, pesticides, and petroleum hydrocarbons can be removed by the use of (bio) surfactants [22-25]. The pollutants-coupled micelles are then separated by ultrafiltration owing to their larger size than the actual pores of the filter. In this review, we have presented the literature survey related to micelles/surfactants-assisted abatement of an array of toxic agents of emerging concern from water/wastewater.

## **2. Literature survey and selection criteria**

The multi-purpose/multifunctional wastewater treatment should be represented as a shift from one to more than pollutant control in wastewater according to the environmental protection strategies and global sustainable development approaches [26]. Greater interest should be devoted to technologies and new materials for treating a wide range of wastewaters such as dyeing and printing manure, domestic sewage, industrial waste effluent and pharmaceutical wastewater via real-time elimination of co-existing contaminants including organic moieties, pathogens, and inorganic compounds. At contemporary, an accelerated interest has been shown by researchers, around the globe, to deal with the environmental pollutants accompanied by the development of sophisticated technologies/materials in removing these contaminants. These developments are being carried out through synergism and multi-functional nanotechnology techniques/tools/agents used for wastewater treatment [27, 28].

A detailed bibliographic study was carried out by using different keywords. Several databases (Science Direct, Francis & Taylor, PubMed, Scopus, Google Scholar, Web of Science, SciELO, SciFinder, Wiley, Springer, Google) were explored for collecting information. Various concerned books, full text manuscripts and abstracts were consulted and details were collected for this review article.

### **3. Wastewater; pollutants sources and health hazard effects**

Various pollutants including volatile organic compounds (VOCs), natural organic matter (NOM) commonly known as dissolved organic matter (DOM), nutrient ions (phosphate and nitrate) personal care products, pharmaceuticals products, petroleum hydrocarbons, pesticides, dyes and heavy metal ions *etc* are responsible to contaminate the water. These toxic substances destroy the water quality and make it unsuitable for irrigation and domestic purposes. This review focused on potential role of micelles and surfactants for wastewater treatment. The ground and surface water from reservoirs and rivers is available as drinking water. Therefore, geographical divisions through which water flows may contain organic and inorganic pollutants. Similarly, the water can also be contaminated by manmade chemicals or the presence of microorganisms. Up till now, several human activities have increased the water pollution; these actions may be categorized as sewage treatment, industries, and agricultural runoff. The NOM involves the materials generated after the transformation and decomposition of dead animals and plants due to microbial activity. These contaminants may be present in the form of undissolved and dissolved organic matter (DOM) that can be distinguished on the basis of separation techniques. The organic materials that easily pass through 0.45  $\mu\text{m}$  filtration membrane are known as DOM. Whereas the material left behind on the membrane is

termed as particulate organic matter (POM). Generally, the DOM is originated from terrestrial and soil-based materials, synthetic organic substances and surface water derived phytoplankton/algal materials *etc.* Likewise, the presence of DOM in groundwater reduces the optical clarity of water due to enhancement in turbidity. On the other hand, inorganic pollutants such as phosphate, nitrates and heavy metal ions are also present to a significant concentration in wastewater. Only a small amount of these pollutants can be removed by existing wastewater treatment processes. Intrinsically, the amount of these chief nutrients are still on the higher side in treated sewage compared with the irrigation water from other sources. In agriculture areas pesticides are responsible for water contaminations and they also pose serious health issues.

Similarly, hydrocarbons and petrochemicals are also present as pollutants in wastewater causing severe health risks to aquatic and human health. There is another class of pollutants, which also plays an important role in water pollution known as “emerging pollutants” (EPs) EPs occur naturally or synthetically during the preparation of various chemicals which are not monitored on regular basis in the environment. Preparation and disposal of new and existing chemicals can generate new sources of EPs respectively. The main reasons for these contaminants are wastewater treatment plants, verbose sources of atmospheric deposition, crop or animal dumps, and their production services. The main classes of these may include disinfection byproducts, pharmaceuticals, industrial chemicals, pesticides, dyes, etc. Nevertheless, their existence is supposed to exert substantial adverse effects on the environment and humans.

More than 700 toxic constituents have been listed by WHO in marine environments that can be characterized as EPs, including their transformation and metabolite products.

Furthermore, the presence of heavy metals and dyes posture a serious concern for the quality of water. Waterborne mercury (Hg), copper (Cu), arsenic (As) and chromium (Cr) are major contaminants as their existence in drinking water is described to cause various types of diseases such as peripheral vascular disease, hyperkeratosis and human cancers (lung, skin, liver and probably bladder), etc [29-41]. The occurrence of manganese and iron at greater concentrations also causes significant turbidity and discoloration in water [42]. Figure 1 illustrate the life cycle distribution of various contaminants.

#### **4. Removal of organic pollutants by using surfactant**

##### **4.1. General facts and removal strategies**

A class of amphiphilic molecules comprising of head and tail amphiphilic are known as surfactants. These molecules have a robust attraction for polar and non-polar species. They operate in solvents by reducing their surface tension as they gather on the surface and play a role of a bridge between the air and liquid. The micellar aggregates have different sizes and shapes above CMC while no micellar structure exists below CMC (Figure 2). The removal of various contaminants of emerging concern including, volatile organic compounds (VOCs), pharmaceuticals and personal care products, toxic metals, organic contaminants, dyes, pesticides and petroleum hydrocarbons can be carried out by the use of surfactants as eliminating moieties. Many surfactants have already been reported for the removal of these contaminants. For example, Rodríguez-Escales et al. (2013) [43] utilizes the non-ionic surfactants (Tween Crew, BS-400, and 80Gold) for the removal of a mixture of pyrene phenanthrene, fluorene, and anthracene. The group explored a removal range of 57 to 99% for the soils with <15% fine materials, while the



soil having 20% of fine materials has less eliminating ability. It was observed that the surfactant can only interact with certain PAHs in the mixture. In consequence, increasing the concentration of surfactant may not certainly increase the removal of PAH. On the other hand, synergically using biodegradation and desorption ensures improved PAH removal equated to approaches like “pump and treat”, which separate remediation and desorption. Likewise, the same surfactants were used for pyrene desorption in soils having different grain sizes. The amount of materials and surfactants to be added should closely relate with one another. The results obtained by Tween 80 show the highest desorption compared with Gold crew and BS-400 [44]. In another approach, Hussein and Ismail (2013) [45] investigated the role of TX-100 and Tween 80 for the enhanced removal of pyrene, anthracene, and fluorine, where the desorption capacity of TX-100 was higher than that of Tween 80. Therefore, it can be concluded that the hydrophobicity of PAHs plays a vital role in controlling the desorption of soil. Synthetic surfactants including SDS, Brij 35, and Tween 80 have been meticulously assessed for their character in the remediation of contaminated soils. These surfactants successfully carried out the elimination process of PAHs. The only concern was their toxicity and non-biodegradability. Therefore, more emphasis is being retained on bio-surfactants.

#### **4.2. Removal of volatile organic compounds by surfactants**

Plants, microbes, animals, industrial and environmental activities are producing volatile organic compounds (VOCs) (ethyl-benzene, benzene, xylene, toluene, poly-chloroethylenes, poly-chloromethanes, and poly-chloroethanes) which are well-known pollutants responsible for causing infertility, respiratory diseases and mutagenicity. These are also responsible for the formation of smog by triggering various photochemical

reactions [46]. Despite known damaging effects of VOCs on the environment and health of living organisms, many industries are still using and producing them. Therefore, it is important to remove VOCs from contaminated soil and wastewater before their evaporation in air. Different methods including biological, physical and chemical are in practice for making sure the VOC-free environment [47]. Among all methods, the most efficient removal process under consideration is the surfactant-based absorption process for VOCs.

#### **4.2.1. Removal of Chlorinated VOCs**

By using three different surfactants; sodium dodecyl-benzenesulfonate (SDBS), Turkey red oil sodium salt (TROS) and polyoxyethylene sorbitan monolaurate (Tween 20), a composite adsorbent was synthesized for the removal of chlorinated VOCs from gases exhausts. Comparatively, TROS has low surface tension so they showed 85% elimination of chloro-benzene in comparison to SDBS and Tween 20 [48]. For removal of 2,4,6-trichlorophenol (TCP) from waste materials of petroleum refineries, a batch-adsorption method was introduced by using surfactant modified bentonite (SMB). SMB showed improved adsorption potential for TCP by 2.3 times. From an initial concentration of 10 mmol/L, the synthesized adsorbent showed the high potential of TCP removal (>99.0%). The monolayer potential of prepared adsorbent found to be 70.42 mmol/g, which was higher than commercially activated carbon (52.63 mmol/g) [49]. For effective removal of VOCs and carbon tetrachloride, the iron-based nanoparticle suspended carbon micro/nanofibers have been synthesized. Iron ions were found segregated and mono-dispersed by surfactants [50]. By spreading the silica-nanoparticles within the active layer of composite-membranes by a surfactant (Tween 40); an active hybrid membrane was

developed. High-penetration flux and maximum selectivity were observed by the membrane with 2 wt% concentration of surfactant [51].

For the removal of pentachlorophenol (PCP), the zerovalent iron composite with magnetic-biochar (ZVI-MBC) has been used. This composite material was found effective for efficient adsorption and dechlorination of PCP in discharge, which led to complete removal of PCP. Different tests (aging and leaching) endorsed the stability and durability of ZVI-MBC [52]. Saponins were employed for n-hexane remediation in a biotrickling filter (BTF). When the n-hexane loading rate was decreased ( $120.0$  to  $47.80 \text{ g}^{-3} \text{ h}^{-1}$ ), the removal potential was increased from 56.8-62.8% and 83.3-91.3% for BTF2 (without saponins) and BTF1 (with saponins), respectively. The removal efficiency increased (38.3-61.4% for BTF2 and 64.5-88.4% for BTF1) after increase of gas-empty bed contact times (7.5-30.0 s) [53]. In a small-bubble column, the absorption mechanism of benzene has been investigated [54].

#### **4.2.2. Removal of phenyl ring based VOCs**

Different methods have been used for the removal of aniline from the wastewater [55]. By using poly(ether sulfone) membrane and an anionic surfactant SDS, an efficient and cost-effective methodology (MEUF) was developed for the remediation of low-molecular-weight organic contaminants (aniline). Because of lower CMC values, the anionic and non-ionic mixed surfactants (SDS and Brij 35) showed maximum (~80%) removal of aniline as compared to individual surfactants [56]. The same group of scientists also employed the MEUF method for simultaneous removal of the aniline and nickel from wastewater by employing the synthesized polysulfone-membrane and also commercially accessible NP010 and UFX5 membranes for highlighting the importance of micellar-size.

High elimination of nickel (97%) and aniline (70%) was obtained by small pore size NP010 membrane as compared to UFX5 and polysulfone membranes. Results described that the aniline is encapsulated into the micellar core and interaction of cations with negative charged-exterior of DS micelle as portrayed in Figure 3. It is interesting to note that togetherness of nickel and aniline causes high removal of both of them as compared to their independent existence in solution [57]. MEUF methodology showed promising results for the removal of aniline from the wastewater matrix despite that complete removal of aniline was not obtained.

Different industries are releasing toluene-based contaminants that are highly toxic and can damage the nervous system, liver, kidney. Surfactants play an excellent role in bio-removal of toluene because they can solubilize hydrocarbons (HOCs) in aqueous systems [58,59]. Surfactants-enhanced remediation (SER) is also a potent method for the abatement of VOCs from contaminated soil and wastewater. This technique increases the VOCs solubility because reversible-surfactants have two active redox groups (Fc14 and Fc12) above and below their CMC under both reducing ( $I^+$ ) and oxidizing ( $I^{2+}$ ) conditions [60]. By ferrocenyl surfactants, the solubilization of toluene, benzene, and ethyl-benzene have been reported. The toluene solubilization was surfactant ferrocenyl in  $I^+$  was found 30% greater as compared to achieved in  $I^{2+}$  as well as by CTAB, SDS and Triton X-114 [61].

PCB can be removed from soil by mutual use of bio-surfactant and chemical-biological treatment phenomena. Application of microbial-surfactant (PS-17) and synergistic chemical-biological treatment by using  $H_2O_2$  and natural-group of microorganisms devastator polluted soil with PCB and insulating-oil have been studied. This treatment

resulted in a 47-50% removal of PCB. Combined application of bio-surfactant, oxidizing molecules and micro-organisms resulted in improved respiration of soil and activity of dehydrogenase (shown in Figure 4) as compared to the alone application of microorganisms [62]. An electro-dialytic-remediation methodology has been developed by using iron-based nanoparticles, saponins and Tween-80 surfactants for dechlorination of PCB-polluted soil [63]. A group of scientists developed a potential method for remediating the soil polluted with PCBs. In this method, by using polyoxyethylene lauryl ether (Brij35) and hydroxypropyl- $\beta$ -cyclodextrin (HPBCD) first PCBs were extracted from soil by washing method and then degradation was carried out with titanium dioxide photocatalysis. According to the results of studies, the extraction percentage can be potentially increased by PCB chlorination and following HPBCD provides effective photocatalytic degradation of PCBs [64]. Similarly, another interesting electrokinetic technology linked with engineered-nanoparticles has been developed for the treatment of PCB-polluted soil. Three different surfactants, anionic (SDBS), non-ionic (Brij35) and a biosurfactant (rhamnolipid) were incorporated independently with nano-Pd/Fe stabilized by xanthan-gum for improving the solubilization of soil PCBs. With new stabilized nanoparticles, the maximum removal potential was obtained as compared to SDBS and rhamnolipid [65]. S, S-ethylenediamine succinic acid (EDDS) and saponin as combined surfactants were employed for PCBs extraction from polluted soil. Due to the synergistic performance of these surfactants, high removal efficacy was obtained. Enhanced solubility of PCB in saponin-micelle was attributed to EDDS [66]. By using the micro-emulsion technique, a composite material lecithin nano Ni/Fe was synthesized and tested on PCB-77 pollutant. Lecithin proved environment-friendly- biosurfactant and operated as

a vital part of micro-emulsion, which proved efficient for agglomeration of organic pollutants. Removal of PCB-77 occurred at a higher rate as compared to blank-carrier because composite material has characteristics of lecithin and bimetal [67]. Another soil remediation method was developed, which is called foam flushing, in which washings mobility is controlled by the foam. The solubilization phenomenon is involved in the removal of PCB by foam flushing. The combined usage of flushing, foam, water, and surfactant solution showed that this method potentially integrates the solution solubilization characteristics and foam's mobility control. From coarse sand, almost 94.7% of PCB was eliminated [68]. Scientists determined the effect of foam-mobility upon elimination of PCBs along with various concentrations of the Triton X-100 (surfactant) and also contents of gas by two different sand samples. Foam flushing enhanced the PCB removal by flushing through grainy (79.4-85.1%) and fine (64.2-79.1%) sand. Presence of foam responsible for decrease the mobility and enhancement of sweep-efficacy results in increased removal of PCBs [69].

#### **4.2.3. Removal of Phthalates**

Phthalates are volatile organic contaminants that destroy the environment and have adverse effects on human and animal health [70]. Mixed hemi-micelles solid phase extraction (MHSPE) had great potential for pre-concentration, extraction and determination of phthalates even at minor concentrations. The MHSPE method was developed with nanoparticles-capped mesoporous silica ( $\text{Fe}_3\text{O}_4/\text{meso-SiO}_2$  NPs) that worked as an excellent adsorbent for phthalates removal from polluted water. This method proved efficient for extraction and removal of phthalates (di-n-butyl phthalate, butyl benzyl phthalate, di-n-octyl phthalate, and di(2-Ethylhexyl phthalate). This may be

attributed to unique characteristics of adsorbent like large surface-area (570 m<sup>2</sup>/g), uniform mesopore size (2.8 nm) and superparamagnetism [71]. From the wastewater, the effective adsorption of diethyl-phthalate was obtained on SDS covered nano-sized alumina as compared to SDS-covered microsized alumina. This is attributed to a smaller size and increased surface binding energy. Adsorption phenomena were further facilitated due to the hydrophobic nature of mixed-hemimicelles [72].

#### **4.2.4. Degradation of residual surfactants used for elimination of VOCs**

The micellar solution of surfactants play great role in removal of VOCs. Usage of surface-active agents as detergents and soaps cause damage to aquatic life and human health and disturb the ecosystem [73]. So it is important to protect the environment from hazardous effects of residual surfactants. So removal of residual surfactants is important phenomena. Colomer and his colleagues [74] determined the cytotoxicity and environmental-fate of lysine-based surfactant. This surfactant was pH sensitive and the sensitivity was found adjustable by changing their chemical structures using erythrocyte and fibroblast cells. By increasing the hydrophobicity and charge density of surfactant, the toxicity for erythrocytes was increased and *vice versa* results were observed in the case of fibroblasts.

Effective biodegradation of these surfactants occurred under aerobic conditions through the CO<sub>2</sub> headspace test (biodegradability test). On zebrafish larvae, the effects of cationic (1227), anionic (SDS) and non-ionic (AEO) were determined. Non-ionic and cationic surfactants were found toxic (1 µg/mL) to the locomotive activity of larvae, while anionic surfactant showed no effects. Exposure to nonionic AEO surfactant led to stunted height, smaller head size, and reduced eye size as compared to 1227 and SDS. Less expression

of *krox20* because of inhibited cell growth is responsible for the shorter size of the head [75]. Toxicity of three pre-manufactured and three commercially available detergents was assessed through different degradation tests as biodegradability (OECD301F), mutagenicity, *Vibrio fischeri*, and *Daphnia magna* toxicity tests. No mutation was observed in bacteria by detergents. Furthermore, little increase of micronucleus frequency was induced in the root cells of *A. cepa* by commercially available detergent (eco-labeled). The destruction of DNA was also noted by all tested pre-manufactured surfactants and also one commercial in human leukocytes. Further studies and testing are required for evaluating the mutagenic and toxic characteristics and degradation of detergents [76]. Biodegradation of surfactants is the safest method for the removal from marine and land environments [77]. Surfactants-based biological degradation may be carried out through microorganisms that consume these molecules and use them as carbon and energy sources. Two different steps are involved in the biodegradation of surfactants. During the first step, structural variations occur, which involves the breakdown of the hydrocarbon chain. During the second step, the primarily degraded products are converted into minerals, water and carbon dioxide [78]. Studies suggest that degradation capacity of biosurfactants and their stability in soil was higher as compared to synthetic surfactants [79]. The oxidation of surfactant nonylphenol-decaethoxylate (NP-10) by two different methods (photo-Fenton and H<sub>2</sub>O<sub>2</sub>/UV-C methods) was studied. Also, degradation products and toxicity levels were investigated. Less toxicity was found in the photo-Fenton method (12% inhibition) as compared to H<sub>2</sub>O<sub>2</sub>/UV-C, which showed 27% inhibition. This was determined based on photoluminescence inhibition tests [80]. Anionic surfactants mainly linear alkyl-



benzenesulfonates (LAS) are very important in detergents and as well as in cosmetic products, however, their bioremediation to manage the pollution in the environment by conservative activated sludge methodology proved not so productive due to little production of foam and less degradation potential of microorganisms. Twenty different bacteria were isolated for degradation of LAS from the soil, which was surfactant polluted by taking the help of enrichment culture technique. Two bacterial strains; *Pseudomonas aeruginosa* (L12) ( $81.81\pm 0.8\%$ ) and *Pseudomonas nitroreducens* (L9) ( $81.33\pm 0.7\%$ ) showed high degradation efficacy. At pH 7-7.5, these bacteria showed degradation of LAS concentration up to 0.05 g/L [81]. Researchers conducted a study to determine the degree of biodegradation of nonionic and anionic surfactants by a combination of ozonation and biodegradation method for excluding the surfactants especially linear alkylbenzene sulfonates (LAS) and alkylpolyglucosides. Benzene ring containing anionic surfactant was earlier oxidized as compared to non-ionic surfactant. Both surfactants showed reduced mineralization due to primary attack of ozone on CO<sub>2</sub> during the ozonation process. This phenomenon corroborated the efficacy of combined implication of biodegradation and ozonation for surfactant remediation [82]. Tehrani-Bagha investigated the degradation of synthetic surfactants as sodium dodecylbenzene sulfonate and a nonylphenol ethoxylate having 40 oxyethylene units by employing UV and ozonation method. Total organic carbon and chemical oxygen demand (COD) decreased 2-times *via* UV treatment and ozonation vs each process separately. This indicates partial oxidation and reduction of mineralization of surfactant solutions [83]. A series of four cationic surfactants (dicephalic) having different alkyl chain length ( $n\text{C}_9\text{H}_{19}$  to  $n\text{-C}_{15}\text{H}_{31}$ ) along with various counterions as bromide, methylsulfate, and chlorides were

used to investigate their toxicity and bio-degradability. Below 1 mg mL<sup>-1</sup> concentration, the tested cationic surfactants showed no antimicrobial activity against *Pseudomonas putida*, *Escherichia coli* (Gram-negative bacteria), *Rhodotorula glutinis*, and *Saccharomyces cerevisiae* (yeasts). Moderate activity was observed against *Bacillus subtilis* and *Staphylococcus aureus* (Gram-positive bacteria). The chain length of the alkanoyl group in surfactants was responsible for variation in toxicity against *Vibrio fischeri* and EC<sub>50</sub> values in the range of 2.6-980 mg/L [84]. The degradation of LAE (non-ionic linear alcohol-ethoxylate) surfactant was studied under anaerobic conditions by adding 4.7-107.4 mg/L LAE to 535-882 mg/L synthetic organic substrate. Almost 98.5% of degradation of LAE was obtained [85]. Enhancement of solubility of fatty acid-based surfactants can be done by incorporating counter-ion choline as compared to sodium, and potassium soaps. It also enabled the long-chain derivatives to perform at ambient-temperature. The choline-based fatty acid soaps are highly biocompatible due to degradability of choline, but choline is prohibited in the cosmetic industry because they are classified as quaternary ammonium ion [86].

#### **4.3. Elimination of personal care products and pharmaceuticals by surfactants**

Pharmaceuticals and personal care products (PPCPs) are a vast group of emerging pollutants [87]. These products are important because of their extensive presence in the environment and large production and consumption. Their improper removal from wastewater may diffuse into the soil and move to water reservoirs [88,89]. PPCPs are biologically active compounds that can persist and accumulate in organisms and posing serious health issues and cause ecological-toxicity. They are also called endocrine-disrupting chemicals as they cause estrogenic effects [90]. Pharmaceuticals include

veterinary and human-beings drugs used for illness treatment and these drugs consist of 3000 various active ingredients [88]. Pharmaceuticals are released in the environment either as parent molecules or as transformed secondary metabolites. Personal-care products also consist of a broad range of compounds e.g. parabens, triclosan, benzophenones, and bisphenols, etc. These are used in many household products including detergents, plastics, disinfectants, toothpaste, sunscreens, shampoos, conditioners, lotions, preservatives, and some other products that are released in the unaltered condition in the environment [90]. Advanced technologies are required to remove PPCPs from sewage as conventional treatment plants failed to remove them efficiently because of their slow degradation [89,91]. The role of surfactants have been found promising for the removal of PPCPs. Emulsion-liquid membrane (ELM) integrating surfactants is gaining importance to eliminate PPCPs from wastewater. Selective permeability of solutes through membranes is based on this methodology. It comprised of emulsion globules consisting of internal phase trapped inside the membrane phase that only allows selective solutes from the external phase, which is the aqueous phase. In ELM, surfactants play a role to enhance the stability of emulsion to avoid the issue of rupture of membrane. Surfactants also inhibit leakage of emulsion [92,93]. Daas and his colleague reported the removal of ketoprofen and ibuprofen (>90%) from mineral, pure and sea-water medium with the help of emulsion-liquid membrane by using SPAN 80 as a surfactant, hexane (diluent) and Na<sub>2</sub>CO<sub>3</sub> (internal phase). Another study reported the removal of paracetamol with ELM using surfactant Span 80 and an inner aqueous solution of potassium chloride [94]. Different studies were conducted [95-98], which showed that SPAN 80 (sorbitan monooleate) is the most efficient surfactant for removal of PPCPs by

using ELM system. Kerosene and hexane played the best role as membrane-phase or diluents mixed with surfactants. Sodium carbonate and sodium hydroxide were found preferable as internal phases at different concentrations. The role of extractants/carriers has also been studied to enhance the solute transfer to the internal phase [98]. For better selectivity and multiplicity, this ELM method is beneficial. Activated granular-carbon is a common choice for adsorption phenomena as it can potentially remove organic pollutants [99]. Different synthetic and natural adsorbents modified with the addition of surfactants to increase the adsorption of PPCPs have been reported especially with kaolinite, vermiculite, bentonite clays [100,101]. Clays are hydrophilic in their natural form, and are not effective for adsorbing non-polar organic and anionic pollutants [102]. Surfactants modify the surface-properties of such materials to boost up the adsorption of organic contaminants [103]. Hari and coworkers [2005] [104] reported the adsorption of different pharmaceutical drugs as norfloxacin, acetaminophen, nalidixic acid and carbamazepine in a natural subsurface material. Surfactants such as cetylpyridinium chloride (cationic) and Tergitol NP9 (ethoxylated nonionic) were employed. Surfactants enhanced the adsorption capacity of carbamazepine and acetaminophen. The adsorption of nalidixic acid was increased at a high pH level with the help of a cationic surfactant. Surfactant-assisted elevated removal of sulfonamide and tetracycline have also been inspected by using benzyldimethylhexadecylammonium (BDMHDA) micelles (cationic surfactants), which were pre-adsorbed on montmorillonite clay [105]. These have been reported as efficient candidates for organic contaminants removal [106]. Sodium dodecyl sulfate (SDS) surfactant (anionic surfactant) has been documented for adsorptive removal of amoxicillin (antibiotic drug) from aqueous solution. An effective removal of 87.7% was recorded at

the optimal surfactant-concentration (10 mg/mL) for amoxicillin (4 mg/mL) in 40 min at pH 4 and 50 °C [107]. Removal of PPCPs from complex matrices has been reported with surfactant-modified synthetic adsorbents. Cabrera- Lafaurie, and coworkers (2014) [108] incorporated the cetylpyridinium (cationic surfactant) together with transition metal ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ) into a Y-zeolite by controlling its hydrophilic character for better selectivity and uptake of carbamazepine and salicylic acid in wastewater. The adsorptive capacity of zeolite was increased from 0.03 to 3.9 mg/g after modification. Dong and coworkers [2010] synthesized zeolites from coal-fly ash and HDTMA and maximum adsorption potential for bisphenol (114.9 mg/g) was obtained as compared to zeolite fly-ash. For the removal of PPCPs, the surfactants have also been used in electro-coagulation flotation (ECF) [109]. Cetyltrimethylammonium bromide (cationic surfactant) has been employed for the removal of ketoprofen, ibuprofen, and diclofenac from wastewater. Without the addition of surfactant, the removal efficiency of ECF was found lower for ibuprofen, diclofenac, and ketoprofen (44%, 14%, and 10%), respectively. While surfactant addition significantly enhanced the removal capacity from 12% to 97%, 12% to 88%, and 6% to 82% for diclofenac, ibuprofen, and ketoprofen, respectively [110].

#### **4.4. Removal of toxic metals by surfactants**

The presence of heavy metals in aqueous system poses long-lasting dangerous effects for plants, aquatic life, humans, micro-organisms and animals. Metallurgy, pharmaceutical, leather, pesticide, fertilizer industries are the main cause of heavy metal contaminations. Weathering, erosion and fuel-burning also play the role of heavy metal adulterations [111,112]. Thirteen different metals Pb, Cu, Zn, As, Cr, Ni, Cd, and Hg are the most persistent pollutants listed by the United States Environmental Protection

Agency (USEPA) [113-115]. The free or bound form of these heavy metals has high water-solubility and mobility along with high toxicity and mutagenicity. Biodegradation of organic contaminants is reduced by metal contamination and it affects the ecology and physiology of microbes and responsible for reducing soil fertility [115]. Application of surfactants in the removal of heavy metals has been studied by using different methodologies as soil-washing/extraction/desorption and phytoremediation, etc. Surfactants also showed capacity in ultra-filtration method, which can be increased by membrane pretreatment with surfactants/biosurfactants for metal ion removal. Similarly, the surfactant modified activated carbon showed 2-4 times higher potential for removal of metal ions as compared to plain carbon [116]. Biosurfactant's scope for the removal of metals is emerging because of their superior characteristics such as low toxicity, good biocompatibility, better degradation, and excellent stability in a wide range of pH and temperature with enhanced foaming quality (Figure 5).

#### **4.5. Remediation of metal-contaminated soil by surfactants**

The role of surfactants for soil washing for the removal of metals is well known. Toxic metals can be removed by washing soil with pure-water along with various chelating agents, chemical additives and solvents. However, the treatment duration and low-availability because of interaction with particles of soil are the major limitations. For this concern, surfactants proved to minimize the time requirement and increase the effectiveness of the followed methodology. *Ex-situ* or *in situ* treatments may be included for the washing of soil with surfactants (Figure 6). In *Ex-situ* treatment, the soil is dug out and placed in a proper place, then the process is followed by washing with the help of a solution of surfactant/biosurfactant. While in the *in situ* treatment, firstly soil is treated with

surfactant followed by its relatively stable complexation with oppositely charged metal ions and then the movement of the resultant complex due to reduced interfacial tension. An ion exchange mechanism is used by charged surfactants, and micelles use electrostatic interaction [117]. Metals can be permanently eliminated, and recycled with less consumption of time [118]. Surfactant-enhanced soil washing for treatment of soil polluted with a high concentration of different metals (Cd, Ni, Cu, As, Zn and Pb) from industrial wastes by using 11 various kinds of surfactants has been studied [119]. Anionic surfactant Texapon N-40 showed higher removal of Zn (86.6%), Cu (83.2%) and Ni (82.8%). Tween 80 removed a high amount of Cd (85.9%), Zn (85.4%) and Cu (81.5%) and Polafix CAPB potentially removed the Zn (83.2 %), Ni (79%) and As (49.7%). By using additives as complexing agents or by varying the pH, the metals desorptions with surfactants can be supplemented. Wen and Marshall [120] reported that the use of ethylene-diaminedisuccinic acid (EDDS) (as an additive) with surfactant can mobilize Cd, Ni, As, Cr and Zn as well as organic pollutants during the washing process, whereas Ca, Fe, Cu, and Mn were found in residual-fraction. Washing treatment aided with ultrasonication can increase the removal of metals from soil. When EDDS was used at higher pH values, the removal of Zn and Pb was less efficient because of the formation of anionic hydroxide complex, while Cu and As were not lowered because of their association with iron oxides. Similarly, different surfactants as Triton X-100, SDS (anionic) and cetyltrimethylammonium bromide (cationic) were studied for their potential to remove metal ions in the presence of diphenylthiocarbazon (DPC), EDTA and at increasing pH level [121]. Under acidic conditions, the cationic surfactants showed excellent efficacy. Anionic and non-ionic type surfactants showed high desorption of Pb, Cd, and Zn. The

addition of EDTA increased the metal desorption efficacy while DPC inclusion lowered (2-4 times) the capacity. An increase in pH also decreased the metal removal capacity of surfactants [121]. Slizovskiy and coworkers reported the effect of pH on the removal of heavy metals by using 1-dodecyl pyridinium chloride (DPC) (cationic), oleyl dimethyl benzyl ammonium chloride, ammonyx KP (nonionic), and rhamnolipid surfactants. Up to 95% of metals (Pb, Zn, Cd, and Cu) removal capacity was enhanced by acidification with EDTA or citric acid buffer [122]. Shin and Barrington [123] reported a combination of SDS and Triton X-100 with iodide ligand for the desorption of cadmium from polluted soil. Cadmium removal was augmented by an increase in the concentration of iodide ligand and surfactant, but no effect was detected on other metals (Pb, Cu, and Zn).

#### **4.6. Removal of dye pollutants by surfactants**

There is number of dyes being used up in the textile industry during the dyeing and bleaching process of fiber [124]. It has been estimated that 10-20% of the dyes after being used find their way to wastewater while 50% of that reach the ecosystem after passing through different treatment steps [125]. All types of available dyes have different chemical structures with many stable aromatic functionalities that resist their degradation during the typical treatments [126]. Even a small quantity of these waste dyes cause serious toxicity for the water bodies. The process of photosynthesis in water is being affected and slowed down by the wastewater with some dye concentrations of even less than 1 ppm [127,128]. Furthermore, this exposure of dyes to the anaerobic reductive bacteria generate many carcinogenic compounds. Therefore, the effective removal of these dye pollutants is very meaningful. There are different methods for the removal of dyes, in which adsorption methods have been proved to be useful [126,128]. A very common dye



named Congo red (CR) was studied under different experimental conditions in a batch-mode sorption process. Different solutions of 20, 40 and 100 mg/L were made at pH 6.8 at 30 °C and the effect of concentration on dye sorption was observed. Dye sorption per unit of soil mass was observed with respect to time, and equilibrium reached in 40 min. The results showed that the sorption process was rapid during the first 2 min and removal efficiency was about 63%, but it increases up to 91% after 10 min, by keeping the pH, temperature, and concentration of dye constant while the dose of sorbent between 0.1 to 10 g. It shows that by increasing sorbent, the removal of dye increases because of the existence of more sorption sites and increased surface area of micropores [128]. A 2.5 g sorbent dose showed the best possible efficiency of dye removal up to 94% while further increase did not exhibit any difference [127]. The results showed the appropriateness of the sorption procedure for the deletion of dyes. By using surfactants, an increased dye removal efficiency was achieved. For this purpose, a surfactant named sawdust (SD) modified with cetyltrimethylammonium bromide (CTAB) was used to absorb the abstraction of CR. The effect contact time, solution pH, dose amount and starting concentration of the dye on the CR removal efficiency of CTAB. SD with CTAB modification at pH 6-8 removed maximum CR (around 98-99 %). Adsorption of CR dye molecule with negative charge increase due to enhanced positive sites by modified sawdust surface [129], Further study reveals that an adsorption system of three parameters sips was developed to make a model of adsorption data of two selected dyes (yellow and red dye), against a mesoporous alkoxy silane silica gel with sodium dodecylbenzene sulfonate (DBS) at 25-55 °C. The presence of attractive forces among dye and surfactant results in micellar aggregates of different sizes and stability levels,

they offer a mechanism about the attractive force between dye and fiber and also smoothens the dye adsorption onto the fiber surface [130,131]. CSL is a lipopeptide biosurfactant, which is extracted from a corn steep liquor [132]. It can form a sphere around the adsorbent, was added as enclosed beads of calcium alginate into the biocomposites based on biowastes. Several kinetic models were used to calculate the bio adsorption capacity of several biocomposites (modified by surfactants). These calculation results revealed that the adsorption capacity of the dye for a hydrogel consists of the hydrolyzed vineyard pruning waste and it can be increased by using natural detergents modified with biosurfactants. Due to the formation of a sphere of the surfactant around biocomposite, the rejection of a dye compound enhances up to 10%. The phenomenon of bioadsorption usually follows the model of pseudo-second-order kinetics in which the bioadsorption process involved the diffusion of both intraparticle and liquid film. Therefore, the biosurfactants are the most trustworthy candidates for the production of eco-friendly adsorbents for pollutant adsorption, specifically dyes. Evidence of sorption is an increase of the area of bio-surfactant modified biopolymer up to 26% was observed. Hence, we can conclude that adsorption causes biocomposites to grow in size as larger ones and to regulate the shape as well [133].

Ionic dyes with a high solubility level in wastewater make them a huge threat to the aqueous system [134-136]. Many types of dyes have been reported as a danger for human beings, flora and fauna [137-140]. Therefore, the proper treatment of some dyes (cationic Methylorange or MO, and anionic methylene blue or MB) is considered to be a must dealt issue before their release. Hence, the property of reverse micelles for the solvation of MO and MB dyes in the sodium dodecyl benzenesulfonate (SDBS)

hexadecyltrimethylammonium bromide (HTAB) in amyl alcohol medium were studied. Different concentrations of surfactants and dyes were studied for the removal of dyes from wastewater. Studies reveal that the elimination of dyes from the water phase to the organic phase majorly depends on the electrostatic force of attractions among ionic head groups of surfactant clusters and the oppositely charged dye molecules. The elimination of dye efficiency enhances by the enhancement of surfactant concentration. Encapsulation of more dye molecules takes place due to the increasing numbers of reverse micelles [141,142]. An increase in the surfactant amount along with 3% CaCl<sub>2</sub> as compared to 1% CaCl<sub>2</sub> enhances the removal efficiency of MO [143]. This behavior is constant with the salting-out effect, which causes the lower down of the CMC of surfactant. The complex formation of rhamnolipid with methylene blue and CTAB was analyzed to make a quantitative model for the study of all the rhamnolipid molecules in liquid samples [144]. Different molar ratios of rhamnolipid to combined methylene blue and CTAB was studied. Higher absorbance was observed with molar ratios of 1:1 and 1:2, while a constant step increases all between the 200-800 nm wavelength range. Mostly, the absorbance increase recommends the colloidal nature of ion-paired complexes. Higher molar ratio 3.15:1 did not show any step increase of absorbance and a further increase of the ratios decrease the absorbance and cause a shift of 664 nm absorbance peaks to slightly shorter wavelengths.

A hybrid named as rhamnolipid-functionalized graphene oxide (RL-GO) was used for the elimination of MB from artificial as well as real wastewaters. The effect of the RL-GO quantity on the adsorption of MB can be observed in Figure 7. The MB removal percentage gradually enhanced by improving the quantity of RL-GO up to a specific limit,

but further increase in adsorbent amount caused a little increase in removal percentage. This is certainly because of the higher adsorbent amount, which is followed by a huge excess of the active sites, hence continuing to the lower use of the sites with a selective amount of MB solution [145,146]. It has been also investigated that the RL-GO is better than GO due to the sorption of MB under the specific experimental conditions because of bigger layer spacing and excessive oxygen-containing functional groups present in RL-GO as compared to GO. Spontaneity and endothermicity affiliated to the physisorption and chemisorption processes with respect to MB adsorption can be associated with the electrostatic attraction,  $\pi$ - $\pi$  interaction, and hydrogen bonding between RL-GO and MB. The RL-GO is useful and potentially efficient adsorbent due to its recycling and higher capability for the removal of MB from wastewaters [147].

Oakes et al. studied the interaction of surfactant models and the azo dye at molecular level and briefly described the surfactant-dye interaction chemistry [148]. Different types of azo-dye interactions were investigated by changing the chain length and main functional head group of nonionic and ionic surfactants. A chain of prepared azo dye model was set to acquire the tautomeric types of the aqueous systems. The dyes possess a single pKa value, which was affected due to the presence of surfactant micelles [149]. For the detection of the changes in tautomeric forms, the UV-vis spectroscopic technique was found to be very sensitive and it measures the pKa values of the dyes [150]. In this study, the nonionic surfactant C12EO5 was used primarily along with SDS as the anionic surfactant.

A UV-vis spectrum of 1-aryl azo-2-naphthol in water system with 10 pH and 25 °C showed a  $\lambda_{max}$  at 484 nm confirmed the presence of this dye in the hydrazine tautomeric form

[150]. One more dye named as N-methylated orange 1 has structural similarity with 1-aryl azo-2-naphthol, depicts the decrease in the absorbance capacity of the main band by showing the appearance of an absorption peak at 420 nm that indicates the presence of equilibrium among the bulk dye in solution and it is solubilized in the micelles. By increasing the micelles concentrations, the equilibrium moves towards solubilized dye. The concentration of the nonionic surfactant was calculated by keeping the CMC value  $6.5 \times 10^{-5}$  M and micelle aggregation number 100. This calculation helped with the complete solubilization and incorporation of a single dye molecule per micelle. No spectral changes were taking place by introducing a nonionic surfactant beyond CMC, which shows that it is unlikely that micelles contain more than one dye. Solubilization of the dye micelles and its spectral shifts towards a shorter wavelength shows a rich azo character. Further studies showed that the dye has an attraction for the nonionic micelles and it increases with the p-substituent in the order of p-CH(CH<sub>3</sub>)<sub>2</sub> > p-CH<sub>3</sub> ≈ p-Cl > H > p-OCH<sub>3</sub>. While it decreases when negatively charged substituents were introduced, such as p-SO<sub>3</sub><sup>-</sup> and p-CO<sub>2</sub><sup>-</sup>. Due to the electrostatic repulsion among sulfonate groups and micelles of SDS with a negative charge, the dye has less attraction for SDS micelles. For nonionic and anionic micelles, the pKa values increased above the CMC, which suggests that micelles possess a higher level of attraction for the undissociated dye. Several substituents are reluctant towards the dye with a more hydrophilic environment of polyoxymethylene shell of nonionic micelles with hydrazine tautomeric form. Contrariwise, a dye with a polar substituent make some way to penetrate the hydrocarbon center of nonionic micelles and undertake the azo tautomeric form. Some specific dyes

with azo tautomeric form in nonionic micelles represent a typical spectrum of the hydrazine tautomeric form in SDS micelles [150].

#### **4.7. Role of Surfactants for removal of pesticides**

Pests are being controlled/destroyed by the pesticides and a huge number of benefits are linked with the pesticide use. However, they have drawbacks as well, especially toxic pollutants cannot be ignored. There are many common pesticides (pesticides is a common term used for the control or destruction of pests) that are very hard to remove from the contaminated soils due to their low solubility in water. Thus the remediation technique with the addition of a surfactant may prove useful. For this purpose, bentazone is a selective herbicide, because it destroys only plants that cannot metabolize it. In one report, soil polluted with bentazone were studied for the soil cleaning purpose by using three surfactants alkyl polyoxyethylene, with the same hydrophobic chain but different oxyethylene groups [151]. These surfactants showed a better pesticide recovery. Deactivation of the remaining bentazone was made by doing the photocatalytic treatment of the wastes in which the  $\text{TiO}_2$  particles with simulated irradiation of sunlight, which degrade the bentazone in a fixed period. Brij was considered to be the most effective surfactant with a fast reduction time for bentazone removal from the waste materials [151]. Biodegradation of hexachlorocyclohexane (HCH) is restricted due to biopersistence, low absorptivity, and solubility on the soil surface. Therefore, the HCH biodegradation might be improvised by using biosurfactants, in which the effect of surfactant is measured by the solubility, bioavailability and bio-deactivation of the HCH isomers. The effect of different biosurfactants was studied including rhamnolipid, sophorolipid, and trehalose lipid. Results showed that the solubility of the HCH isomers

increases sharply up to 3-9 folds by using sophorolipid and rhamnolipids with maximum HCH isomer yield at a concentration of 40 µg/mL. On the other hand, trehalose-containing lipid yielded maximum solubility at 60 µg/mL. Out of three surfactants, sophorolipid showed the maximum solubility and highest HCH isomer removal in the soil [151]. Tributyltin (TBT, an organotin) is a natural pollutant used in pesticides. Due to its toxic effects, the removal of contamination is necessary [152].

Tributyltin with its metabolites named dibutyltin (DBT) and monobutyltin (MBT), both acted as polar materials in the soil which have a small concentration of organic carbon where ion exchange is the main adsorption mechanism. For the enhanced desorption of butyltins, sodium dihexylsulfosuccinate (SDHS) was found better. More amount of SDHS is needed, while the TBT desorbed gave a synergistic effect, which is harmful to the bacterial life present in the soil. SDHS is less harmful, while below the CMC did not enhance the TBT desorption but increase the bacterial deactivation of TBT. Due to the formation of the complexes between TBT and SDHS monomers, the soil and TBT bacteria involvement was expected to improve. Hence, anionic surfactants at or it's below the level the CMC considered to be useful for the removal of TBT-contaminated soil [152]. As anionic and ionic surfactants have their benefits, so Guo et al. [2009] [153] studied the combined effect of a surfactant by mixing nonionic/anionic surfactant solutions. (i.e., sodium dodecylbenzene sulfonate (SDBS) and Tween 80) for p-nitro chlorobenzene (pNCB) removal of contamination from the soils. Out of many common vital chemical intermediates, pNCB is being used up in many organic synthesis procedures i.e pesticides, pharmaceuticals, dyes, and rubbers. But USEPA and china state environmental protection agency (SEPA) have mentioned pNCB in the hazardous

environmental pollutants list due to its harmful nature and non-degradability. Due to the low vapor pressure and aqueous solubility, pNCB easily gets adsorbed on the soil particle's surface. Research about the removal of pNCB from the polluted soil is limited and very small work has been reported [153], in which surfactant mixture e.g. SDBS/Tween 80 were used for the removal of pNCB from the soil. Results revealed that the amount of surfactant and the mixture SDBS/Tween 80 ratios majorly affects the solubility of water and the distribution constant of soil-water mix matrix, removal of pNCB and the absorption of soil's surfactant. As the mixed micelles form due to the addition of SDBS and it becomes more effective as compared to the Tween 80. Infact, SDBS increases the solubility of water and restricts the surfactant sorption on the soil. The low dosage of surfactant i.e <2 g/L of Tween 80 restricts the removal of pNCB while a greater amount of Tween 80 enhances the desorption of p-NCB from the soil. According to the reported work, the maximum p-NCB removal took place with equal ratios of SDBS/Tween 80 mixture as 1:1 and showed potential for the removal of pNCB and similar chemicals [153].

#### **4.8. Role of Surfactants for removal of petroleum hydrocarbons**

Petroleum hydrocarbons such as PAHs are some natural contaminators that are very problematic to remove. They are carcinogenic, and thus highly important to remove from the soil. We cannot ignore the importance of petroleum products as an energy source but their leakage and accidental spills are the reason behind the soil contamination. To overcome their pollution, temporary solutions are being adopted such as mechanical and burial methods. Surfactants are a good option for the cleaning of soil from petroleum contamination. A study about soil washing of the diesel contamination was made by



Khalladi et al. by using anionic surfactants and SDS [154]. The effect of SDS was found suitable above the 8 mM concentration. Diesel content remained constant even after 4-hour treatment of the soil with a surfactant solution, which shows that a specific time is required for the best interaction of surfactant with soil. Diesel fuel contamination from soil was removed 97% by keeping the rate at 3.2 mL/min. While biodegradability remains with artificial surfactants and SDS. Therefore, the removal ability of SDS was compared with biosurfactants such as rhamnolipid and saponin. The comparison showed that SDS was more competent for the elimination of crude oil from the soil than rhamnolipid and saponin. However, different surfactants have a different level of affiliation with components of crude oil, such as SDS can remove aliphatic hydrocarbons more efficiently, while saponin can interact well with aromatic hydrocarbons [155]. If we compare the cost then SDS is more expensive than biosurfactants but is more efficient. Similarly, Lai et al. (2009) [156] compared two biosurfactants i.e rhamnolipid and surfactin with artificially made surfactants (Tween 80 and Triton X-100) for the complete removal of petroleum hydrocarbons from polluted soils. They used 0.2% mass of biosurfactants i.e. rhamnolipids, surfactin and artificial surfactants i.e Tween 80 and Triton X-100. Results showed that the removal ability of total petroleum hydrocarbons from polluted soil was 23%, 14%, 6%, and 4%, respectively, which proved that biosurfactants are far better than artificial surfactants. Han and co-workers [157] studied the effect of biosurfactants on weathered crude oil-contaminated soils (COCSs) [158]. A new class of nonionic surfactants named alkyl polyglucosides (APGs), which can be synthesized by recyclable sources e.g. sugars and fatty acids. Owing to their high biodegradability and low toxicity, APGs have gained substantial interest [158]. APG1214 with long alkyl chains were

considered to be more active as compared to APG0810 for the removal of crude oil. The crude oil removal efficiency (CORE) of APG1214 was further enhanced by adding the inorganic sodium salts. Investigation about various cleaning parameters e.g. time, temperature, speed and ratio between solution and soil was adjusted by using an orthogonal design, where at appropriate conditions, the CORE value reached up to 97%. GC/MS analysis showed that the amount of smaller n-alkanes (i.e., C16–C23) in the leftover crude oil elevated slowly. Moreover, the interaction of APG1214 with inorganic salts removes the bigger n-alkanes effectively while using them separately, an opposite effect was observed [158]. Natural gums are another option to be used as biosurfactants. They are very common polysaccharides present in woody plants or seed coatings and immensely involved in the industrial processes due to their emulsifying, stabilizing and microencapsulating features. Their use as biosurfactants was found suitable for the cleaning of soil due to diesel contamination by accidental pipeline leakage. The results of these biosurfactants were compared with synthetic ionic and nonionic surfactants [159]. Natural gums were found effective as biodegradation enhancers after carrying out the biodegradation experiments. Especially, the guar gums with a very low concentration of 2-ppm showed extraordinary results by showing 82% TPH diesel cleaning rate. Therefore, guar gums are the cost-effective alternatives for biodegradation-enhancers. The actual target of the surfactant enhancer's cleaning strategy is to remove the hydrophobic contaminant. Surfactant use for soil cleaning processes states about the cleaning ability of the surfactants in terms of their efficiency to form the contaminants concentrates in the liquid phase of effluents. Although the objective of the soil cleaning processes is to recover the original and clean sand, the ability of these pollutant removals

should be specific towards the sand. In addition, fractions of clay and silt are usually highly contaminated and need to be disposed off. The ideal way could be to concentrate these contaminants in these polluted sand fractions as opposed to the liquid effluent. It is found in one specific study that soil cleaning solution was analyzed on soil contaminated due to TPH and the results revealed that the most appropriate surfactant for the cleaning of gravel and sand was Sea Power 101, which were noted 54% and 65% improved over water-only cleaning/washing [160]. Also, Sea Power 101 removed 94% of the contaminants into the salt fractions. On the other hand, Tween 80 moved 95% extra TPH in the effluent phase as compared to the water-only washing, but it did not enhance the TPH cleaning abilities from the sand and gravel fractions. Therefore, if the amounts of contaminants are needed to be in the solid phase, the best and suitable surfactant should be chosen. The contaminant must be disposed off properly after getting removed from the soil. However, the liquid effluent from the surfactant enhanced removal process contains not only the pollutants but also surfactants. That is why for the removal of surfactants from effluents, bacteria may be used. But it is also important to note that surfactants might be harmful to the living microorganisms. Therefore, the surfactants must be treated biologically and their concentrations in the matrix should not increase more than  $1 \text{ g/dm}^3$  because this amount is harmful to the removal of microorganisms and creates extra foam in the aerated bioreactors. Due to this reason, an extra method must be used for the disposal of the surfactants. For this purpose, pretreatments are planned for surfactant removal. One of those pretreatments is the Fenton reaction, which is an advanced oxidation process (AOP), in which an iron (II) salts mixture and hydrogen peroxide are mixed with wastewater. The advantage of this AOP is to form the highly

reactive oxygen species (ROS), which are suitable for the degradation of pollutants in wastewater [158]. Moreover, the Fenton reaction is cost-effective and tells the usefulness of biosurfactants. Although synthetic surfactants are more efficient than the biosurfactants but the overall method can be optimized by selecting the naturally existing biosurfactants. Biosurfactants could be the most appropriate and cost-effective for the removal of the contaminants from the petroleum-contaminated soils without using the additional Fenton reaction processes.

## **5. Conclusions and future recommendations**

Herein, the rigorous efforts are being put forward for the removal of hazardous contaminants from wastewater. Conventional techniques used for the remediation of water/wastewater have certain limitations such as high cost, incompatibility, lack of versatility and their own environmental risks for the real-time elimination of organic, inorganic and metal-based pollutants, which hinder their wide range use in various fields of environmental decontamination. These allegations can easily be addressed by the use of surfactants-based remediation technologies, which can easily encounter the stringent environmental regulations. These remediation technologies have the capacity of sustaining the requirements of integrity and stability of the systems. The wastewater treatment technologies advocate that surfactants can prove the future for treatment of wastewater. Because the micelles architecture can capture hydrophobic organic pollutants in their core and inorganic pollutants in their exterior. A wide number of surfactants have already proved a promising candidate for the decontamination of soil and wastewater from pharmaceuticals, heavy metals, personal care products, and dyes. The removal efficacy of the surfactants is greatly influenced by many factors including

micellar size, pH, soil chemistry, electrolyte content, ion-exchange capacity, concentration and nature of pollutant and aeration state. With the help of micellar structure of ionic and non-ionic surfactants, the production of clean water accompanied by the recovery of valued metals from industrial wastewater can be achieved without harnessing the environment. Based on the extraction percentage and distribution ratio, we can conclude that micelles-assisted water and soil treatment technology can have a better future on large scale decontamination of wastewater. On the contrary, the bio-surfactants are environment friendlier matrices and have successfully been employed for the purpose, however, their large scale applicability is still a challenging task owing to their high costs. Advance research on cost-affordability and development of bio-surfactants can make wastewater treatment technology greener and economical.

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#### **Conflict of interest**

The authors declare that they have no conflict of interest.

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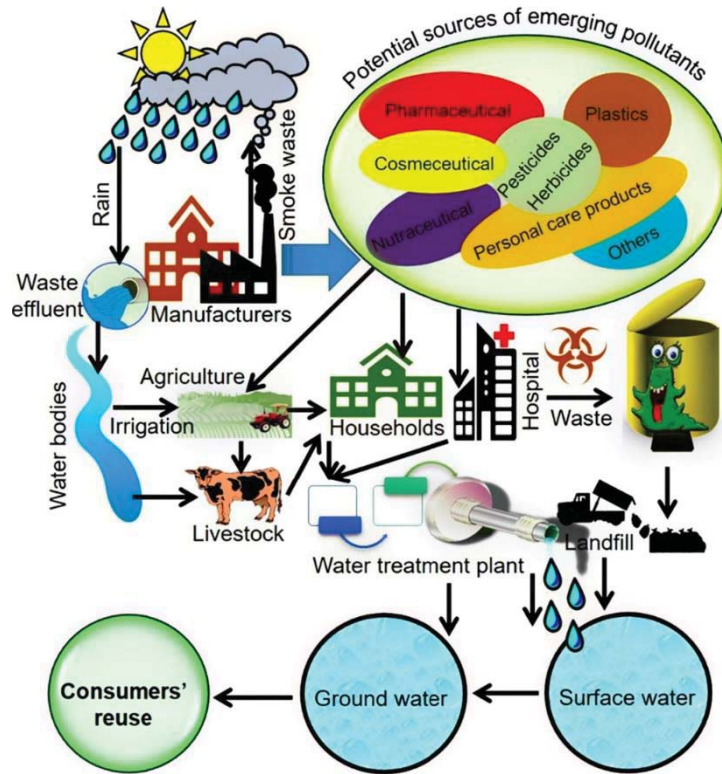
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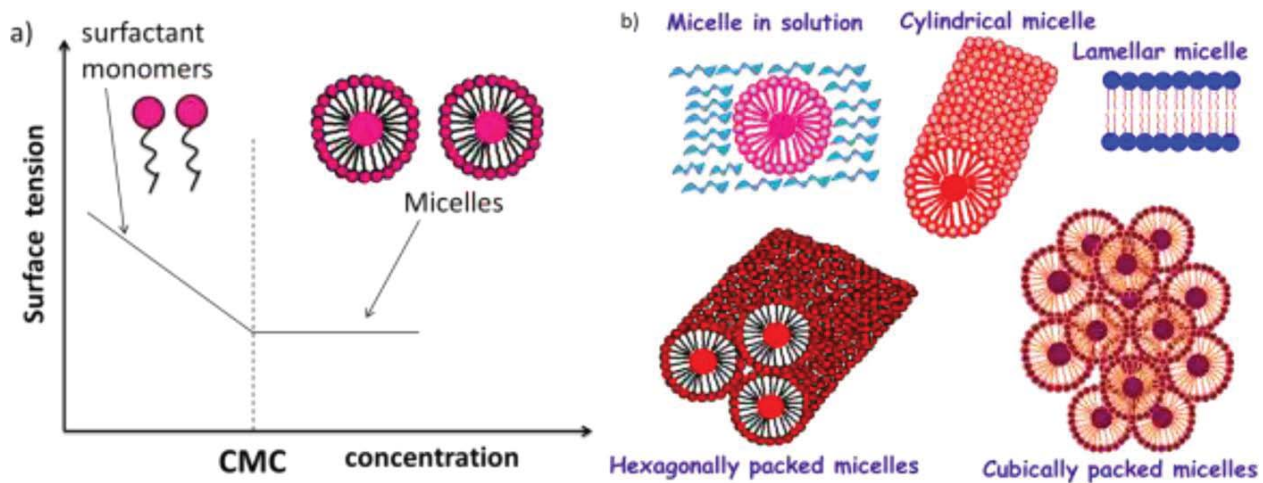
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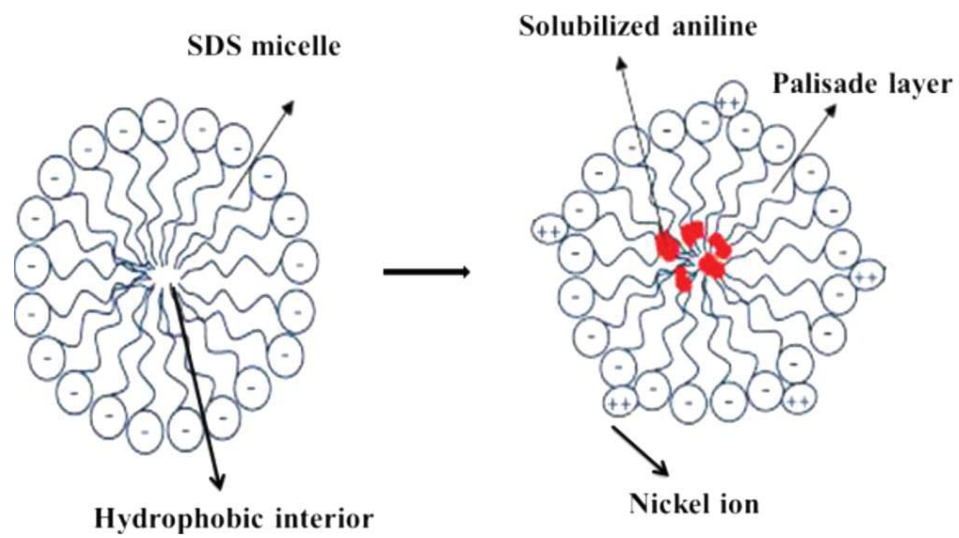
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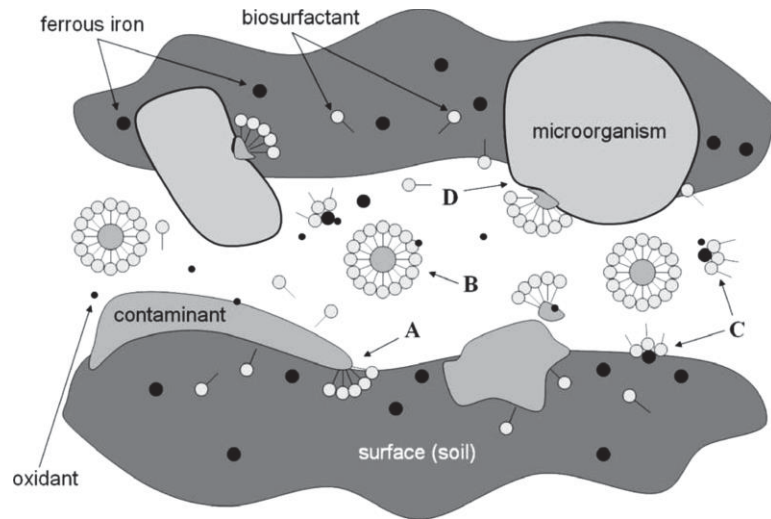


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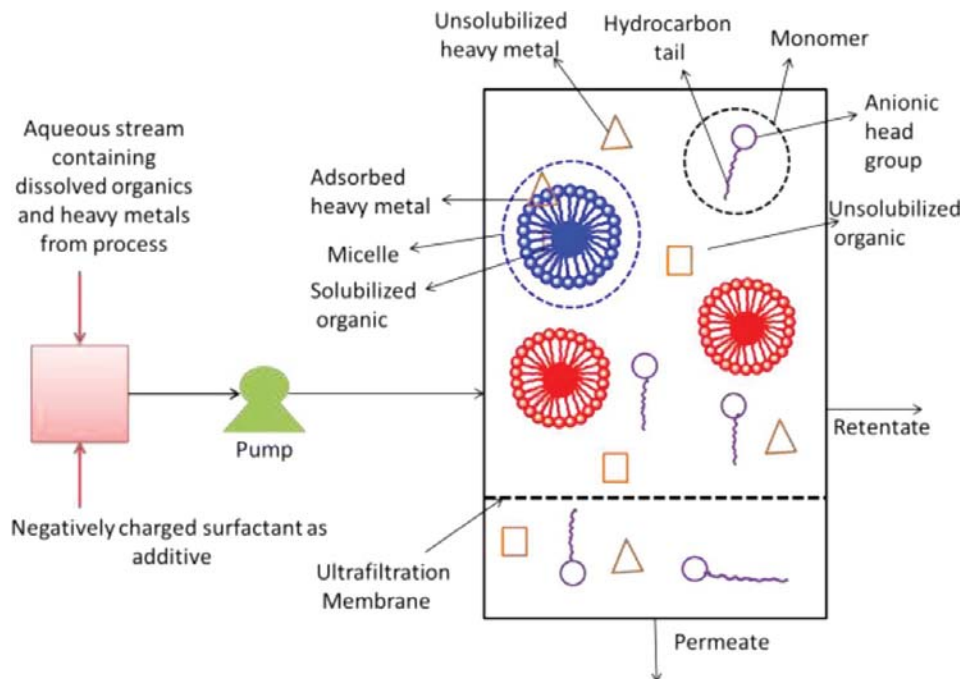


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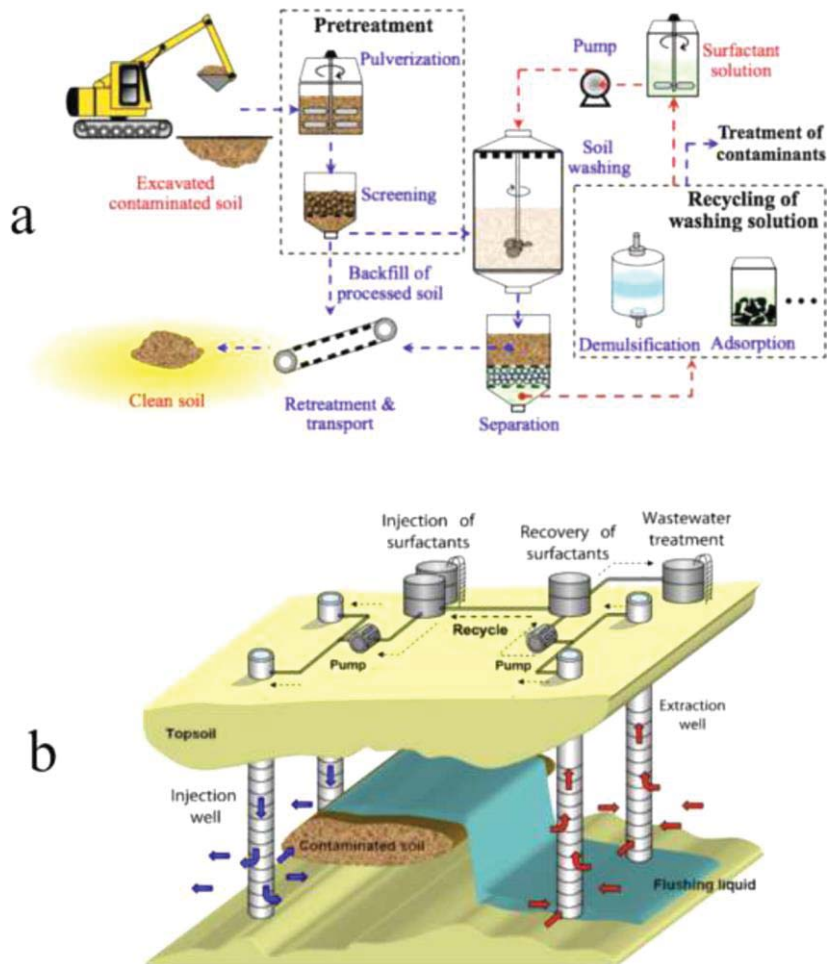




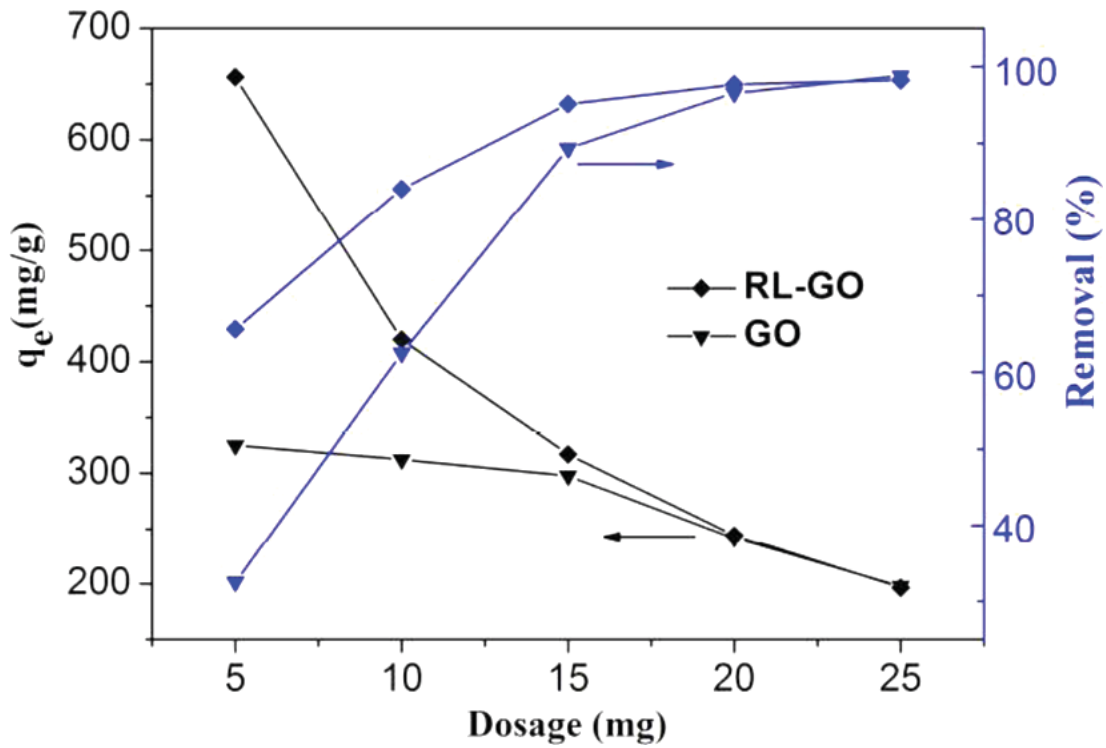
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