Applications of colloidal gas aphrons for pollution remediation

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ABSTRACT:

Colloidal gas aphrons (CGAs), first described by Felix Sebba in his book "Foams and Biliquid Foams - Aphrons" in 1987, consist of a system of spherical microbubbles with diameter mostly above 25 μm and classified as kugelschaums (ball foam). They possess some colloidal properties and can be pumped at uniform rate through pipes and channels, much like liquids. Also, they have high stability due to very small size and thick surfactant shells. Research works published over the period of the past two decades indicate effective applications of CGAs for clarification of particles and microorganisms, protein separation, gas and nutrient transfer and pollutant separation from water and soil matrices. In this review paper, the generation techniques of CGAs and their application for pollution abatement have been discussed. Some mineral separation processes by CGAs flotation have also been reviewed because of their relevance to the contaminant removal processes. The CGAs were found to function on the principles of bubble entrained floc flotation, electrostatic and ionic interaction, diffusion of entrapped gas and hydrophobicity of the pollutant particles. Two tables have also been provided to present a comparative overview of the generation technologies and the effectiveness of the pollution remediation techniques.

Keywords: Colloidal Gas Aphrons, CGA, microbubble, contaminant, separation, pollution remediation technology
2 Contents

1. Introduction

2. Property of CGAs
   2.1 Surface structure and shell thickness
   2.2 Physical phenomena
   2.3 Stability and foam drainage
   2.4 CGA rheology

3. Generation of CGAs

4. Application of CGAs
   4.1 Pollutant removal from soil
      4.1.1 Removal of organic pesticide from soil
      4.1.2 Removal of oily waste from soil matrix
      4.1.3 Naphthalene and hexachlorobenzene (HCB) removal
      4.1.4 Removal of other non-aqueous phase liquid (NAPL) from soil
   4.2 Pollutant removal from fluid phase
      4.2.1 Particle and fiber separation from water
         4.2.1.1 Recovery of fibres and oils from industrial wastewater
         4.2.1.2 Removal of suspensions of fine particles from water
      4.2.2 Separation of dye and chemical reagents from liquid mixtures
         4.2.2.1 Solvent purification and removal of dye from water
         4.2.2.2 Recovery of astaxanthin from aqueous solutions
         4.2.2.3 Recovery of gallic acid from aqueous solution
         4.2.2.4 Removal of particulate matter from air
   4.3 Particle separation by flotation process
      4.3.1 Clarification of wastewater by CGAs
      4.3.2 Flotation of fine pyrites
      4.3.3 Flotation of Cu(II)
      4.3.4 Separation of fine particles of CuO from silica
      4.3.4 Froth flotation of minerals by nanobubbles
   4.4 CGAs as carrier
      4.4.1 Carrier of microorganism, nutrient and oxygen
      4.4.2 Mass transfer by CGAs

4.5 Soil flushing system

5. Conclusion

References
INTRODUCTION

Colloidal gas aphrons (CGAs) is a system of microfoam, having some colloidal properties and consisting of spherical microbubbles, mostly above 25 μm diameter and classified as kugelschaums or "ball foams". They were first described by Sebba\(^1\). The schematic diagram of CGAs is illustrated in Figure 1. The CGA system entraps 65% of air by volume and has a specific gravity of only around 0.35. CGA bubbles retain same charge as the surfactant solution from which it is generated. CGAs were primarily produced by stirring an aqueous surfactant solution contained in a fully baffled beaker via a spinning disk driven at high speed (6000 rpm) by an electric motor. Later, it was produced by various other methods such as dispersed air flotation, homogenization, sonication, electroflotation, etc. In nature, microbubbles have been reported in the form of geogas microbubbles and were found to be responsible for transport of pollutants in aquifer\(^2-3\).

![Schematic diagram of structure of CGAs according to Sebba](image)

**Figure 1**: Schematic diagram of structure of CGAs according to Sebba

CGAs are highly suitable as the separation and mass transfer agents. They have shown promising results in the fields of contaminant separation from liquid and soil matrices, fine particle flotation, mineral separation, gas transfer for bioremediation and protein separation\(^4-10\) but have not been practically utilized to its full potential. Our objective behind this review is to expose the reader to the
full spectrum of the research conducted on contamination separation and pollution abatement by CGAs over the past two decades, primarily for demonstrating new research possibilities in this discipline.

2. PROPERTY OF CGAs

2.1 Surface structure and shell thickness

CGAs and regular foams differ in terms of bubble morphology. Sebba\(^1\) speculated that in CGAs, the bubbles were encapsulated in a multilayered shell consisting of surfactant and liquid. However, CGAs microfoams were found to consist of gas bubbles covered by a monolayer of surfactant molecules immersed in the solution containing micelles. The repulsion amongst likely charged surfaces of microbubbles prevent their coalescence. Amiri and Woodburn\(^{11}\) estimated the shell thickness of CGAs prepared from cationic surfactant CTAB to be 750 nm while Bredwell and Worden\(^{12}\) determined the shell thickness for non-ionic surfactant Tween 20 to be 200–300 nm, based on the study of gas diffusion from the CGA bubble to the liquid bulk. Jauregi et al.\(^{13}\) used TEM and X-ray diffraction and measured the thickness of a surfactant shell to be 96 nm. According to this study, the shell did not provide room for finite inner water phase as proposed by Sebba\(^1\) and the soapy shell consisted of multiple layers of surfactant molecules although the exact number could not be determined. Extremely large interfacial area is an important characteristic of CGAs. It was calculated that 1 L of CGAs containing 60% of air, in bubbles 24 µm in diameter will expose an area of 150 m\(^2\) of interface to the water and 10\(^{14}\) such microbubbles.\(^{14-15}\)

2.2 Physical phenomena

CGAs display the same physical phenomena as those taking place in foams including (i) liquid drainage, (ii) interbubble gas diffusion, and (iii) Gibbs–Marangoni effects.\(^{16}\) However, due to spherical shapes of the microbubbles, capillary drainage or Plateau border suction effect occurring in polyhedral foams does not take place in CGAs. Moreover, due to the small size of the CGAs microbubbles acting as colloidal
particles, the buoyancy caused by the density difference between the gas and the liquid phases is relatively limited. Most applications of CGAs take advantage of their large interfacial area, the adsorption of particles at the microbubble interfaces and their stability for enhanced mass transfer.  

2.3 Stability and foam drainage

Stability of foam is a major concern for its practical application since it is a thermodynamically metastable system. Two basic phenomena, viz. coarsening or disproportionation and film rupture usually cause foam collapse. Jacobi et al. theoretically derived an equation for foam drainage and correlated it with liquid viscosity. Although CGAs is different from normal foam and are more stable, with passage of time and in course of transportation, the microbubbles' shape may distort from sphere to spheroid, even polyhedron.

Sebba deduced that the collapse of microbubbles was owing to gas transfer out of bubbles, the driving force being inversely proportional to the radius. Therefore smaller the bubble is, slower will be the rate of transfer of the gas out of the bubble. However, Sebba neglected the volume of the gas bubble. According to Dai and Deng, the escape rate per unit volume, considering the volume factor, is 1/r².

\[
\frac{\text{Rate of escape}}{\text{Volume}} \propto \frac{1}{r^2}
\]  

Therefore, from this relationship, it is obvious that smaller the bubble is, quicker it diminishes. So, microbubbles below diameter of 25 m is not very common. Nevertheless, Dai and Deng stabilized bubbles below 25 m by preventing the diffusion of the gas through encapsulation of the bubbles at room temperature with silicic solution. The suitable concentration of silicic sol was found to be between 0.15 and 0.25 mol dm⁻³ and the proper pH scale was about 7 to 10.

CGAs stability can be measured directly from the rate of liquid drainage. Amiri and Woodburn proposed a predictive model for liquid drainage rate of CGAs while Save and Pangarkar found that CGAs drainage pattern follows an existing mathematical model. Yan et al. proposed a kinetic model to
describe the liquid drainage profiles of CGAs. The discussion included the effect of the system
temperature and the concentration of surfactant on the kinetic stability of CGAs. Drainage behavior was
fitted by the empirical Equation 2.

\[ V_t = V_{\text{max}} \frac{t^n}{K^n + t^n} \]  

where \( V_t \) refers to the volume of drained liquid at time \( t \), \( V_{\text{max}} \) refers to the maximum volume of drained
liquid, describing the sigmoidal character of the curve and \( K \) is equal to the half-life (\( t_{1/2} \)) of drainage.
This kinetic model was successfully tested by using the Arrhenius equation. From the analysis of the
liquid drainage rate as a function of time, two distinct stages of drainage of CGAs were identified.\(^{23}\)

Luo et al.\(^ {24}\) measured drainage rates of CGAs prepared from different surfactants under different
concentrations and system temperatures to find a satisfactory mathematical model. The whole drainage
process was divided into two stages. The first stage was dominated by gravity driven liquid drainage due
to higher density of liquid phase than that of gas phase, which accounted for more than 90% of the total
liquid. In the second stage, if the liquid membrane could be regarded as the capillary, the rate of liquid
drainage was proportional to the film thickness of quartic equation according to Poiseuille’s equation.
Thus, the rate of liquid drainage decreased drastically to zero with the thinning of films. Also, they
proposed that increasing temperature could reduce the viscosity of liquid and make the liquid film thin,
resulting in an increase in the rate of liquid drainage.

Moshkelani and Amiri\(^ {19}\) performed CGAs characterization based on the stability. Variation of integrated
and differentiated electrical conductivity (EC) of CGAs dispersion with surfactant concentration was
found to be a good indicator for probing and characterizing the CGAs dispersion. It resulted in
differentiating three separate stages of CGAs stability compared with two stages in the conventional
aphron drainage method. A study by Feng et al.\(^ {20}\) fitted the three stage drainage of CGAs in a modified
mathematical model. In the first stage, the drainage rate increased with time due to a combination of
upflow migration of bubbles and downward liquid drainage under gravity. Then at the second stage, the
drainage rate decreased with time and was dominated by liquid flow under gravity. Eventually at the third stage, the foam became water deficient and behaved like dry foam. The drainage rate was small due to slow liquid release from films under capillarity suction. With passage of time, the mean size of the microbubbles increased from 69 µm at 0 sec to 92 µm at 360 sec, 239 µm at 1080 sec and 410 µm at 1620 sec due to disproportionation as shown in Figure 2. Expansion of the larger polyhedron bubbles and the disappearance of smaller spherical microbubbles occurred simultaneously. The microbubble stability increased at higher surfactant concentrations, but decreased with alkalinity.²⁰

Figure 2: Photomicrographs of the microbubble dispersion at different times. Photo A represents T = 0 s; B represents T = 360 s; C represents T = 1080 s; and D represents T = 1620 s.²⁰

2.4 CGA Rheology

Rheology can be defined as the study of flow of matter, mainly non-Newtonian fluids such as foams. All the researchers experimenting with the CGAs rheology have concluded that CGAs actually behave as a shear thinning fluid under different conditions of flow rate and surfactant concentrations. Tseng et al. ²⁵ observed that CGAs behaved as a shear thinning fluid while flowing in rectangular mini-channels with hydraulic diameter of 1.03 mm. Its effective viscosity (µₑ) varied with the apparent shear rate (γₘₐₓ) according to the Equation 2:
\[ \mu_e = 122 \gamma \alpha^{0.44} \]  
(for shear rates varying from 1000 to 7000 s\(^{-1}\) \hspace{1cm} (2)

The friction factor \((f)\) for CGAs in laminar flow followed the same law as single phase, i.e. Equation 3.

\[ f = \frac{\lambda b b}{K_g} \] \hspace{1cm} (3)

The Reynolds number \((R_e)\) can be computed from the effective viscosity \((\mu_e)\) of CGAs. The Nusselt numbers and the local heat transfer coefficients for CGAs under imposed heat flux and laminar flow conditions were found to be independent of the mass flow rate and heat flux.\(^{25}\) Larmignat et al.\(^{26}\) stated that under adiabatic laminar flow conditions, CGAs rheology was not affected by the pipe shape or hydraulic diameter and that CGAs could be treated as a shear-thinning fluid in terms of volume equalized apparent shear rate and shear stress with empirical constants. Increasing the surfactant concentration caused the shear stress to increase for a given apparent shear rate. This could be attributed either to the decrease in the maximum packing due to narrower size distribution or to the possible increase in the thickness of the surfactant shell surrounding the CGA bubbles, making them less deformable and behave as solid spheres. The friction factor \((f)\) can be calculated as before as in Equations 3 and 2.\(^{26}\)

Zhao et al.\(^{27}\) studied microfoam rheology made from Tween 20, SDS, and CTAB at various concentrations. The CGAs porosity ranged from 0.54 to 0.72, and Sauter mean radius between 26.4 and 47.6 μm under fully developed laminar flow conditions and also adiabatic conditions. Microfoams behaved as a shear thinning fluid. The results suggest that the dimensionless wall shear stress is proportional to volume equalized Capillary number \((Ca^*)\) defined in Equation 4 as:

\[ Ca^* = \frac{\text{\(\tau_w\)} \gamma \alpha}{\sigma} \]  
\hspace{1cm} (4)

where \(\tau_w\) is the wall shear stress, \(\gamma\) is the shear rate, \(\sigma\) is the surface tension, \(\mu_l\) is the liquid velocity, and \(\varepsilon = \frac{1}{(1-\phi)}\) is the specific expansion ratio. The average value of the power–law index was found to be 0.64±0.04 with 95% confidence interval. Increasing the surfactant concentration causes the shear stress to
increase for a given apparent shear rate. This is likely due to the associated reduction in polydispersity of the bubbles.27

3. GENERATION OF CGAs AND MICROBUBBLES

Sebba1 first described the production of microbubbles and CGAs by a CGAs generator in a baffled beaker. Beside this classical method of production of microbubble and CGAs, many other methods were investigated over years to obtain bubbles less than mm in size including the usage of fine nozzles, orifices and/or pores28-30, pressurizing dissolution methods,31 multiphase flowing methods,32-33 use of a special powerful shear rotating pump.34 In many cases, bubble generation required highly pressurized gas (>400 kPa), powerful pumps and/or special pumps. It has been reported that the properties of microbubbles gets affected by the generation technique employed35-36 thus leading to application in different fields having different requirements such as size, monodispersity, surface properties and stability.37

Few methods for CGAs and microbubble generation are discussed In Table 1.

Table 1: Methods of CGAs and microbubble generation (see at the end)
4. APPLICATION OF CGAs

CGAs have found numerous applications in (1) biological separation, (2) soil remediation, remediation of contaminated water, (4) fermentation and bioreactors, and (5) material synthesis. These applications make good use of (i) the large interfacial area of the CGAs, (ii) the adsorption of particles at the microbubble interfaces, and (iii) the stability of CGAs for enhanced mass transfer. They could also be used in oil recovery and fire fighting. CGAs can be pumped through pipes, columns and fittings, making their application easier.

Microbubble system has been intensely investigated as a potential agent for water purification and sewage treatment. Organic pollutants can be degraded by the process of oxidation by strong oxidizing agent such as ozone. Ozone microbubbles were not only found to effectively degrade persistent organic chemicals but also they reduced the amount of sludge and destroyed bacteria at ambient temperature. Again, when microbubbles were collapsed by ultrasound, localized high temperature and pressure along with large amount of free radicals were produced, which could easily break down organic chemicals and destroyed microorganisms. Thus, the synergistic effects produced by the combination of microbubble technology and ultrasound technology were expected to provide a novel approach to wastewater treatment along with washing and cleaning.

4.1 Pollutant removal from soil

4.1.1 Removal of organic pesticide from soil

Roy et al. was the first to utilize CGAs for augmenting the removal and mobilization of 2,4-dichlorophenoxy acetic acid (2,4-D), a synthetic auxin hormone used widely as herbicide, from contaminated soil. The performance of CGAs were compared with conventional surfactant flushing. No significant difference was observed in the performance of the two processes. Nevertheless, the
CGAs flushing required much lower volume of surfactant per gram of 2,4-D recovered from the soil than with conventional washing. CGAs flushing was found to be advantageous over surfactant solutions due to low flow rates and lower pressure drops across the soil column.

4.1.2 Removal of oily waste from soil matrix

Roy et al.\textsuperscript{9} were one of the very first to apply CGAs for in-situ flushing of subsurface soil to remove oily waste from soil. They compared the efficiency of CGA suspensions prepared from sodium dodecylsulfate (SDS) with conventional surfactant solutions and water floods under different flow regimes. Their performances have been shown in Table 2. The CGA suspensions demonstrated best soil flushing ability.

The higher removal rate of oily wastes by the CGA suspension was thought to be due to phase separation between liquid and gas phases. The microbubbles collapsed after travelling to a short depth releasing the gas which in turn escaped to the atmosphere, possibly carrying away some volatile portion of the oily waste. Separate gas and liquid fronts moving at different velocities were observed in the column. Increasing the surfactant concentration from 8 to 30mM did not enhance the removal efficiency for either CGA suspensions or conventional surfactant solutions.\textsuperscript{9}

Roy et al.\textsuperscript{61} again used CGAs prepared from SDS to flush residual levels of automatic transmission fluid (ATF), a light non-aqueous phase liquid (LNAPL) from the soil of a Superfund site in USA. CGA suspension and surfactant solution of 8mM concentration prepared from the same surfactant were compared for their removal efficiency against water in downflow and upflow modes. In both modes they performed much better than water. CGAs acted better in downflow mode. It was proposed that the ATF removal by CGAs and SDS solutions involved displacement, solubilization, dispersion of ATF and electric repulsion mechanisms at the surface of the soil particles. In upflow mode, water performed better than in downflow mode, due to the fact that water being heavier than ATF, pushed it upwards. Table 2 can be referred for detailed comparison. With passage of CGAs through soil, channels were observed to open up, relieving the pressure inside the column. The pressure drop was at
around 4-12 psig. No channel was formed for SDS solution and water and the pressure in their cases remained higher at around 25-50 psig and 8-17 psig, respectively. Increasing the SDS concentration to 30 mM did not improve the percentage of ATF removal. Liu and Roy\textsuperscript{62} suggested that this phenomenon occurred due to formation of precipitates of calcium dodecyl sulfate which eventually blocked the soil pores, resulting in poor conductivity. Finally, it was concluded that CGA suspension at any concentration was more effective in removing ATF than the conventional surfactant solution of the same concentration or conventional water floods.\textsuperscript{61}

Couto et al.\textsuperscript{63} investigated the remediation of sandy soils contaminated with diesel oil by surfactant solution, regular foams and colloidal gas aphrons. CGA suspension was found to remove the contaminants most effectively. The higher efficiency of CGAs were attributed to its closer contact and larger interfacial area with the contaminant. Neither the CGAs structure collapsed nor the gas hold up decreased after it passed through the soil. Unlike the experiment done by Roy et al.,\textsuperscript{61} the pressure drop was least for surfactant solution, more for CGAs and maximum for regular foam. Regular foam received greater resistance due to larger size. In this experiment using sandy soil, channeling was observed for surfactant solution. The process of oil removal by surfactant solution was favoured by higher initial oil concentration and particle diameter and lower surfactant flow-rate. The CGAs or foam remediation efficiency had no relation with surfactant concentration. CGAs showed high efficacy for remediation of sandy soils contaminated with diesel oil.

### 4.1.3 Naphthalene and Hexachlorobenzene (HCB) removal

Roy et al.\textsuperscript{47} once again experimented with CGAs, this time to evaluate its effectiveness in removing naphthalene from soil. The objectives were primarily to assess the relative suitability of nonionic (Tergitol), anionic (SDS) and cationic (HTAB) surfactants to remove naphthalene from a contaminated soil matrix. Among them, non-ionic Tergitol was most effective. Cationic HTAB was strongly adsorbed on negatively charged soils while SDS precipitated as Ca(DS)\textsubscript{2} by exchanging its Na\textsuperscript{+} with Ca\textsuperscript{2+} of clayey soil, thus both of them were ineffective. Hence, solutions and CGAs of
Tergitol were used to flush the soil. Tergitol solution of concentration 0.15, 20 and 50 mM removed 13%, 30% and 66% of naphthalene, respectively while CGA suspension of those solutions correspondingly removed 1%, 11% and 51% naphthalene. Thus, higher surfactant concentration resulted in higher removal of naphthalene from the soil matrix. CGAs showed less efficiency, perhaps due to channeling and soil pore clogging and there was a decrease in the hydraulic conductivity of the soil matrix, reducing the removal of naphthalene. Naphthalene is actually hydrophobic in nature and its solubility increases in presence of the surfactant micelles having an affinity towards the hydrophobic interior of the micelle, which is increasingly formed at higher surfactant concentration, facilitating the easy naphthalene removal from the soil matrix. In case of CGAs, the pressure drop across the column was around 15 psi, while the solution had pressure drop of around 25 psi. So, the lower pressure drop made CGAs favorable to use in field condition.\textsuperscript{47}

Kommalapati et al.\textsuperscript{64} characterized CGAs generated from a biosurfactant prepared from the fruit pericarp of the soapnut or \textit{Sapindus mukurossi}, a tree generally grown in tropical regions of Asia. Roy et al.\textsuperscript{65} compared the HCB and naphthalene removal ability of various surfactant solutions with the soapnut solution. Compared to water flooding, 0.5% and 1% soapnut solutions were 20 and 100 times more efficient respectively in recovering HCB. Also, Kommalapati et al.\textsuperscript{66} used the soapnut solution to desorb HCB from soil column. The HCB recovery was up to 90% of the total HCB for soils contaminated with lower levels. Later, Kommalapati et al.\textsuperscript{8} studied the CGAs produced from the \textit{Sapindus mukurossi} at 0.5% and 1.0% concentrations to flush HCB contaminated soils. For soil contaminated with low amount of HCB (2 mg Kg\textsuperscript{-1}) CGA suspensions generated with 1.0% and 0.5% soapnut performed better than conventional solution. At 92–110 mg Kg\textsuperscript{-1} contamination level, CGA suspension of 1% strength removed about 670 µg of HCB while soapnut solution recovered about 890 µg of HCB under identical conditions of experiment. The detailed percentage of HCB recovery has been calculated and given in the Table 2. The recovery of HCB was lower for low-contaminated soils and it increased with increasing contamination. The pressure buildup for both surfactant solution and
CGAs were identical. This finding was different from earlier observation by Roy et al. who found that CGAs pressure drop was less than that of solution.

4.1.4 Removal of other non-aqueous phase liquid (NAPL) from soil

N-Pentadecane is a hydrophobic non-aqueous-phase organic compound which enters the soil matrix in liquid phase, moving under gravitational and capillary forces. It has low solubility in water and it remains as a persistent pollutant in soil. Huang and Chang tried to remove this n-Pentadecane from a contaminated glass bead column by Triton SP-190 solutions of different concentrations and foams of those solutions having different gas to liquid ratio. It was observed that higher the concentration of the surfactant, higher is the rate of n-Pentadecane removal. In case of foams, higher efficiency was observed with higher gas content. Surfactant solutions of concentration 2000 ppm removed 38% while 400 ppm solution removed only 19% n-Pentadecane. Foam prepared from 400 ppm solution removed 36% contaminant at the gas–liquid ratio of 5:1 and slightly over 74% at a higher gas–liquid ratio of 10:1. Huang and Chang deduced that besides reducing the interfacial tensions between n-Pentadecane and flushing liquid, the surfactant solution promoted an emulsification of n-Pentadecane, thereby resulting in its recovery. In case of the foam, the process of pollutant recovery included mechanism of oil-drop emulsification and imbibition into the foam lamellae structure.

Boonamnuayvitaya et al. studied a commercial biodegradable and non-toxic surfactant BioNonex, for its efficiency to remove pyrene, a NAPL, from pumice. Under identical experimental conditions, CGAs produced from different concentrations of BioNonex solution was found to be more efficient than its conventional solution, the higher concentration being more efficient, probably due to higher number of micelle formation and increased solubility of pyrene. BioNonex CGAs and solution at 7% volume concentration removed 78% and 68% pyrene respectively compared to 55% and 47% removal by 3% volume concentration of CGAs and solution of BioNonex. Pure water flood removed only 11% of pyrene. The initial rate of pyrene removal was very fast, possibly due to its easy desorption from outer surface of pumice while it slowed down after 2 hours due to the mass transfer resistance of
pyrene in the inner pores. Another notable fact was that, to flush over same time period, only 50% of surfactant was required while using CGAs in comparison to the treatment with conventional surfactant.

4.2 Pollutant separation from fluid phase

The separation of suspended particles from an aqueous solution by CGAs treatment is observed to be occurring mostly by two mechanisms, viz. “bubble-entrained floc-flotation” and “ion flotation”. In bubble-entrained floc-flotation, relatively large particles are floated up by the buoyant action of a group of small bubbles. Here the small bubble size and high stability of CGAs are principal factors. In case of “ion flotation”, the charged contaminant species form an ion-surfactant complex with the oppositely charged surfactant molecules on the CGAs microbubbles and the ion-surfactant complex are floated up to the surface.68

4.2.1 Particle and fiber separation from water

4.2.1.1 Recovery of fibres and oils from industrial wastewater

Hashim and Sengupta7 used CGAs prepared from SDS solution of concentration 1 gm m⁻³ to separate fine fibres from a lean slurry of cellulosic pulp from paper mill wastewater in a flotation column. The CGAs were introduced from bottom of the column while pulp slurry was introduced from the top in downflow mode. The pulp fibres could be recovered as foamate from the top of the column. Slurry samples were collected from different sampling heights along the 0.35 m long column to measure the efficiency of the process with column height. The efficiency was seen to increase along with height and 70% separation efficiency was reached within 0.3 m and did not increase beyond that. The average sizes of the fibres in the feed, foamate and tailings were 1702.2, 2204.3 and 1412 nm, respectively. So, the largest particles were mostly recovered by CGAs within the foamate. Also, the recovery was better when the CGAs flow rate was slightly higher than that of slurry in counter-current mode. Zeta potential measurement revealing a 17 mV charge difference between SDS CGAs and the
pulp slurry indicated a charge induced particle-bubble attachment mechanism. This technique could be used for recovering fine cellulosic pulp from paper-machine backwater, thereby reducing the oxygen demand of the wastewater.

Hashim et al.\textsuperscript{69} again used CGAs prepared from SDS to clarify oily wastewater by flotation technique. Two parameters, namely sparging rate and column height were related with the separation efficiency of palm oil from oily wastewater. A model for calculating mass transfer coefficient was proposed in this work. The recovery rate increased with increasing sparging rate and column height. The model was shown to be validated by the experimental results. The surfactant SDS dissociated to form DS\textsuperscript{−} ions which being hydrophobic, remained outside the surfactant monolayer and inside the continuous phase of the CGAs, which ultimately acquired a net positive charge. Thus the oil globules, carrying negative charge in an aqueous medium, adhered to the outer side of the positively charged gas apheres and floated up. The CGA bubbles, being much larger than the oil droplets, could accommodate many of the droplets on its surface.

4.2.1.2 Removal of suspensions of fine particles from water

Mansur et al.\textsuperscript{70} used CGAs to separate fine particles of the order of a few microns or less from aqueous media. The effects of surfactant concentration, CGAs flow rate, surfactant type and particle concentration on the separation efficiency of polystyrene were studied. The results indicated that CGAs, generated from cationic surfactant of HTAB and anionic surfactant of SDBS, separated around 97\% of polystyrene particles from wastewater. Again, Mansur et al.\textsuperscript{68} used CGAs prepared from Tween 20, SDBS and HTAB to remove magnesium hydroxide with particle size 2.3–9 m and polystyrene, having particle size of 24–300 m, through flotation process. Yields higher than 50\% of magnesium hydroxide and 97\% of polystyrene was obtained at surfactant concentration near critical micelle concentration (CMC). Beyond CMC, due to formation of larger sized foam bubbles, the removal efficiency decreased. Magnesium hydroxide and polystyrene had no charge relationship with surfactants and were floated by bubble-entrained floc-flotation mechanism. Since more stable
dispersion could be obtained with ionic surfactants than with non-ionic surfactants, CGAs generated
with SDBS and HTAB were more efficient for the removal of fine particles than that generated with
the non-ionic surfactant Tween 20. Since the shell of CGAs are very thick due to its small size, fine
particles show very low penetration and they only tend to stick to the shell of the thick shelled bubble
and rise with it to the aqueous surface. For the polystyrene particles of diameter 24–140 µm, removal
rate was the highest, but it decreased for bigger particles of around 300 µm because these were too
large to be floated by CGAs microbubbles of diameter 88 to 125 µm for ionic surfactant and between
29 and 35 µm for non-ionic surfactant. So, an optimum particle and bubble size resulting in high
removal efficiency should be determined.

4.2.2 Separation of dye and chemical reagents from liquid mixtures

4.2.2.1 Solvent purification and removal of dye from water

Caballero et al. applied CGAs prepared from hexadecyl trimethyl ammonium bromide (HTAB) for
purification of methyl orange within 2-octanol. The yield was higher than 95% and was finished
within 6-7 min while in the conventional technique using only air for sparging, 20 min was necessary
to obtain a slightly lower yield. Roy et al. investigated separation of organic dyes from wastewater
by microbubble flotation using CGAs. The mechanism of removal was found to be ion coupling of the
oppositely charged species of the surfactant forming the CGAs and the dye and flotation of the ion-dye
complex on the surface of CGAs microbubbles. Basu and Malpani used CGAs in a flotation column
to remove methyl orange and methylene blue dye from water. When the surfactant and dye had a
similar charge, 40% removal of dye from the water was achieved. On the other hand, oppositely
charged dye and surfactant resulted in 98% removal of dye. Under alkaline conditions, the removal of
methyl orange was higher with CGAs generated from the cationic surfactant, HTAB. The removal of
methylene blue was higher in alkaline condition when generated from the anionic surfactant SDBS.
With increased flow rate, smaller size of CGAs microbubble and increased gas holdup, the percentage
of removal of methyl orange and methylene blue increased. Above CMC, no effects of surfactant
concentration on the percent removal of dye were observed. Later, Huang et al. \(^\text{74}\) observed that the flotation process of organic dyes principally followed four mechanisms, viz. ion coupling between the surfactant forming the CGAs and the organic dye having opposite charges, reactions between CGAs and the organic dye, ion-dye complex adsorbed on the surface of CGAs and hydrophilic or hydrophobic characteristics of the organic dyes.

Fuda et al. \(^\text{75}\) experimented with CGAs of AOT (sodium bis-2-ethylhexyl sulfosuccinate) under different conditions for separating lactoferrin and lactoperoxidase from sweet whey with varying results. A mixture of CGAs and whey was allowed to separate into the top aphron phase and the bottom liquid phase. Expectedly, the main factors influencing the partitioning were pH, ionic strength and the initial volume of whey. At an optimum pH of 4 and ionic strength of 0.1 mol L\(^{-1}\), the recovery was 90\% and the concentration of lactoferrin and lactoperoxidase in the aphron phase was 25 times higher than that in the liquid phase. However, the conditions favoring hydrophobic interactions i.e. pH close to pI as well as high ionic strength led to lower performance and the adsorption of both target proteins and contaminant proteins were favored, resulting in low selectivity. CGAs acted as ion exchangers and the selectivity of the process and the surface properties of microbubbles could be largely manipulated by changing the main operating parameters such as type of surfactant, pH and ionic strength. \(^\text{75,76}\) Similarly, they experimented on the recovery of whey proteins, gallic acid \(^\text{43}\) and norbixin \(^\text{4}\) with CGAs which acted as ion exchanger and interacted preferentially with oppositely charged molecules or particles with their subsequent selective separation in the CGAs phase.

Electrostatic interactions was the primary mechanism for the recovery of these molecules.

Comparative experiments of conventional air bubble flotation and micro-bubble flotation were carried out by Liu et al. \(^\text{79}\) to enhance pretreatment of dye effluent. The total mass transfer coefficient of microbubbles reached 1.1754 min\(^{-1}\) while that of conventional air bubbles was 0.7535 min\(^{-1}\). Under identical conditions, compared with the conventional air bubble flotation, the removal efficiencies of COD, color and oil for the microbubble flotation increased 30\%, 110\% and 40\% respectively.
Furthermore, the wastewater biodegradability was also enhanced after coagulation followed by microbubble flotation.

### 4.2.2.2 Recovery of astaxanthin from aqueous solutions

Dermiki et al.\(^{80}\) recovered astaxanthin, a natural antioxidant belonging to the family of xanthophylls, from the cells of *Phaffia rhodozyma* using CGA suspension as the separation tool. Up to 90% recovery was achieved under pH 11 with NaOH 0.2 mol L\(^{-1}\) with CGAs generated from the cationic surfactant CTAB. Three different approaches were investigated for the separation process of astaxanthin from the complex fermentation broth, such as in the first case, CGAs were applied directly in the broth. In the second case, CGAs were applied to the clarified suspension of cells. Finally, in the in situ approach, CGAs are generated within the clarified suspension of cells. Among all these approaches, the first approach showed the highest recoveries of up to 78%. In addition, up to 97% recovery of total carotenoids could be achieved from the clarified suspension after pretreatment with NaOH. Thus, CGAs were proved to be highly effective for the recovery of bioactive components from complex feedstock.

Dermiki et al.\(^{81}\) investigated the mechanism for the recovery of astaxanthin from aqueous solution using CGAs produced from a cationic (CTAB), an anionic (SDS), a non-ionic (TWEEN 60) and mixtures of TWEEN 60-SPAN 80 surfactants. At low pH, astaxanthin was found to be protonated with a positive or nearly zero value of zeta potential while at pH greater than 3, it developed strong negative charge. So under different pH values, different mechanisms were involved in its removal. The recovery was significantly higher when it was dispersed in a solution of pH 10.8 than at pH 6 and at pH 2.2, as because astaxanthin is more strongly charged at higher pH. At low pH of 2.2, the recovery is the lowest and independent of the CGAs to astaxanthin volumetric ratio \(V_{\text{CGA}}/V_{\text{ast}}\), whilst at pH 10.8 the recovery reaches a maximum at \(V_{\text{CGA}}/V_{\text{ast}}\) of 4 decreasing at higher volumetric ratios, confirming that the recovery was driven by electrostatic interactions. Considering the pH, CGAs to
astaxanthin volumetric ratio and ionic strength of the aqueous solution, the mechanism of recovery of astaxanthin could be explained as a flotation process known as “bubble-entrained floc-flotation”.

### 4.2.2.3 Recovery of Gallic Acid (GA) from aqueous solution

Although GA (3,4,5-trihydroxybenzoic acid) which is widely present in fruits and vegetables is a non-toxic substance, the removal technique presented here can be applied in case of pollutants. Spigno et al. attempted to get a better understanding of the separation mechanism of GA by CGAs prepared from CTAB. Charge characterization of GA and CTAB revealed that at pH> 3.4, GA became negatively charged and at pH>7, it lost its anti-oxidant capability. CTAB being a cationic surfactant, at pH>3.4, there was good electrostatic interaction between CTAB and negatively charged GA. At pH 3, there was very poor recovery of GA by CTAB while at pH 6 and 8, the recoveries significantly increased. Besides pH, the ionic strength of the solution influenced the recovery. In the presence of buffers, the positive charge of the cationic surfactant was reduced resulting in less interactions between the surfactant and GA, thus reducing the recovery rate. Although pH 8 was ideal for the recovery, it was not suitable for antioxidant power of GA. The experimental observations confirmed that electrostatic interactions were the main forces driving the separation as the highest recoveries were achieved at basic pH at which the GA was ionized and negatively charged, and at low ionic strength. Also, optimum contact time was found in the range of 9–12 minutes and the optimum molar ratio of surfactant to GA was > 5. This process could be successfully applied for the recovery of polyphenols from complex feedstocks.

### 4.2.2.4 Removal of particulate matter from air

Jarudilokkul et al. applied CGAs for removing dust comprised of fly ash, wheat flour and powder of polyvinyl chloride from air. They studied the effects of type of surfactant, type of dust and it's concentration, rate of air flow and CGA flow velocity on the efficiency of the process in a separation column. The nonionic surfactant (Triton X-100) performed best with the collection efficiency of 95% while cationic surfactant (CTAB) collected 90% and anionic surfactant (SDS) arrested 92% dust.
mechanism of dust removal by CGA was found to be dominated with aerodynamic capture. Increasing CGA and air flow velocity and larger particle size improved the collection efficiency. However, air flow velocity higher than 6 m s\(^{-1}\) and higher dust concentration had an inverse effect on the efficiency. The density of particle was revealed to affect the collection efficiency more than the wetting ability of dust particle.

### 4.3 Particle separation by flotation process

Use of microbubbles for flotation of copper, chromium, nickel, lead and zinc particles from aqueous medium is a very old practice. Metal removals of up to 100% were obtained from aqueous medium ranging in concentration from 2 to 20 ppm.\(^{49}\) CGAs, due to their very small sizes, were used to overcome two main problems in the flotation of fine particles. Firstly, the decreased probability of collision between particles and bubbles and secondly, the difficulty of smaller particles having lower momentum to break through the liquid barrier surrounding a bubble \(^{84}\). Finally, the selectivity of a separation always depends on bubble–particle interactions such as electrostatic and hydrophobic forces.

Particle separation by froth flotation depends on the efficiency of collision, adhesion, and detachment processes as shown in Figure 3. Studies showed that tiny bubbles generated by hydrodynamic cavitation were found to change the surface characters of minerals, increasing the contact angle of solids and hence attachment force, bridge fine particles to form aggregates, minimize slime coating, remove oxidation layers on particle surfaces, and in consequence reduce reagents consumption.\(^{85-91}\)
Figure 3: Schematic of three successive steps of in froth floatation: bubble-particle collision, attachment and detachment, adopted from Fan et al.\textsuperscript{92}

Figure 4 schematically shows that nanobubbles on particle surface activate flotation by promoting the attachment of larger bubbles since attachment between nanobubbles or gas nuclei and large bubbles is more favored than bubble/solid attachment.\textsuperscript{92}

Figure 4: Effect of nanobubble on coarse particle froth flotation, adopted from Fan et al.\textsuperscript{92}

Entrainment of fine particles in the channels between bubbles or in the turbulent region surrounding a bubble inside the froth due to their lower mass and momentum plays a major role in their separation.\textsuperscript{93}

Also, at a given gas holdup, using finer bubbles can reduce frother consumption.\textsuperscript{94-95}

These are mainly two mechanisms for separation of minerals i.e. hydrophobic interaction between the bubbles and surfactant-adsorbed particles and the electrostatic interactions.
4.3.1 Clarification of wastewater by CGAs

Subramaniam et al.\textsuperscript{46} was one of the pioneers in using CGAs for clarifying industrial effluent. They used CGAs to clarify suspensions of microalgae, palm oil mill effluent (POME) and a suspension of three inorganic minerals. For the former two, the CGAs were found to be most effective at a pH value close to the pK value of the surfactant concerned. However, no conclusion could be drawn for the inorganic suspensions. The clarification rate increased with the efficiency of air utilization in forming CGAs while the shedding of collected material from the foam layer was directly related with concentration of solid in the suspension. CGAs offered obvious advantage over other systems of air-assisted flotation for clarification.

CGAs were utilized by Hashim et al.\textsuperscript{96} to recover yeast from aqueous solutions in a flotation column. The efficiency of the process was governed by the CGA sparging rate. The separation efficiency increased exponentially from 30% up to 90% when sparging rate was increased from 1.3 ml sec\(^{-1}\) to 2.4 ml sec\(^{-1}\). The initial feed concentration and the maximum achievable efficiency were found to be inversely proportional. The separation efficiency decreased at low pH. In a study involving CGAs prepared from a cationic surfactant benzyl-dimethyl-hexadecyl-ammonium chloride to float baker's yeast suspension, Hashim et al.\textsuperscript{97} obtained a separation efficiency of 95% at the optimum conditions of air flow rate and feed concentration. They derived a simple model for the monolayer adsorption of yeast cells on the bubble surface.

4.3.2 Flotation of fine pyrites

Cilliers and Bradshaw\textsuperscript{98} used CGAs generated by impeller to float fine pyrite below 38 µm diameter and compared this system with a conventional batch flotation cell at pH 4 and 8 in presence and absence of copper sulphate. The collector was sodium n-propyl xanthate and the frother was Dow 400. Earlier, Amiri\textsuperscript{99} successfully separated ultra-fine sulphur particles from nitrilotriacetate (NTA) dispersion by aphron flotation. The rate of recovery of pyrite was slower for the CGAs impeller under all conditions although the ultimate recoveries remained unaffected. The lower rate was due to lower
buoyancy and smaller contact time with pyrite particles for the CGAs. The size of the CGA bubbles were estimated to be of the order of 50 µm\textsuperscript{11} and the critical bubble diameter required for 38 µm pyrite flotation was calculated to be 478 µm.\textsuperscript{100} So, coalescence or multiple bubbles were required for the necessary buoyancy when using the CGAs impeller. In the case of standard bubbles, the diameter was estimated to be 500 µm\textsuperscript{101} and this helped in the mineral removal from the pulp. The contact time between the mineral particle and bubble was much shorter for the smaller CGA bubbles than for the standard bubbles, reducing the collision efficiency and the rate of flotation.\textsuperscript{102} However, in presence of copper sulphate, at pH 4 and 8, the stability of CGAs increased and so the rate of pyrite, gangue and water recovery increased to a great extent. For the standard impeller, an increase in grade was observed when froth stability increased. Hence, flotation by CGAs was found to be useful for selective separation of very fine minerals.\textsuperscript{98}

4.3.3 Flotation of Cu(II)

Caballero et al.\textsuperscript{73} applied CGAs prepared from HTAB for the coflotation of Cu with Fe(OH)\textsubscript{3}, the separation percentage was higher than 95% in less than a minute in the absence of an induction time, which amounted to 25 min in the conventional technique of air flotation. Guan et al.\textsuperscript{103} studied adsorption flotation technique for the removal of Cu(II) from aqueous solution in a loop flotation column which had a vertical draft tube and a specially designed porous gas sparger to produce microbubbles. Suitable operating conditions were determined by studying the effects of gas velocity, pH, surfactant addition rate and the concentration of Fe\textsuperscript{3+} on the removal efficiency. The loop flotation column was observed to possess higher final removal efficiency as well as reduction rate of Cu(II) than conventional bubble flotation column and could be widely used in wastewater treatment. Wang et al.\textsuperscript{104} performed experiments on flotation of Cu(II) by CGAs made from SDBS to explore a new method for separating heavy metal ions from dilute solution. The results showed that the flotation efficiency between pH of 5 and 6 had an optimum value to CGAs flow rate and amount. At pH above 7, the flotation efficiency could be as high as 99% at the optimum condition. In CGAs based flotation, introduction of flocculating agent to the system was not needed.
4.3.4 Separation of fine particles of CuO from silica

Waters et al.\textsuperscript{105} carried out laboratory scale flotation experiments by CGAs generated using the anionic surfactant SDS to separate CuO from SiO\(_2\) by flotation and compared the results with conventional batch flotation using air bubbles where the interaction between the surfactant-adsorbed particles and bubbles was hydrophobic in nature. The attraction between the anionic CGAs and the CuO particles was initially due to electrostatic interactions. CGAs were produced as a very dense froth which allowed the drainage of unattached particles, mostly silica, either non-selectively entrained or released by bursting bubbles into the pulp resulting in higher concentration grade of CuO but ultimately leading to poor overall recovery. Initially, the CGAs showed high selectivity but with the progress of time, froth depth decreased due to the stability of the aphrons, allowing the drainage of unattached CuO particles from the froth into the pulp. Consequently, the deeper froth for the CGA system, resulted in a higher concentrate grade but a lower recovery. Flotation using CGAs initially resulted in a higher concentrate grade of 62\% and the recovery was just 25.2\% much lower than the performance of the conventional flotation. However, a two stage flotation was designed so that the froth from CGAs did not overflow the column, resulted in the recovery of CuO concentration grade of 81.8\% and a recovery of 76.5\%, while the conventional batch flotation yielded a concentrate grade of 59.1\% CuO at a recovery of 58.3\%.

4.3.5 Froth flotation of minerals by nanobubbles

Earlier research results indicated that significant recovery improvements of coal and phosphate particles could be achieved using cavitation generated nanobubbles.\textsuperscript{92, 106} The nanobubbles attached themselves with the coal and phosphate particles. In the process, the surface hydrophobicity increased, elevating the probabilities of particle-bubble collision and attachment and also reducing the probability of detachment.

Nanobubbles, when used to float phosphate fertilizer, almost doubled the flotation rate constant and thus greatly increased throughput. The flotation rate constants for 0.85–1.18, 0.60–0.85 and 0.425–
0.60 mm size range particles were 0.62 min\(^{-1}\), 0.83 min\(^{-1}\) and 0.97 min\(^{-1}\), respectively when no nanobubbles were present. The flotation rate constants of phosphate particles in these three size fractions increased to 1.3 min\(^{-1}\), 1.7 min\(^{-1}\) and 2.0 min\(^{-1}\), respectively in the presence of nanobubbles. Nanobubbles increased the Acid Insoluble (A.I.) rejection. The A.I. rejections of +0.425–1.18, +0.60–0.85, and +0.425–0.60 mm phosphate particle size fractions in the presence of nanobubbles were higher than in the absence of nanobubbles. The laboratory-scale flotation column test results indicated that for a given A.I. rejection, depending on the characteristic of phosphate samples, the nanobubble increased \(\text{P}_2\text{O}_5\) recovery by up to 10%-30%. The recovery rate of hard-to-float particles was more improved than that of easy-to-float particles. This reduced the collector dosage by a third or half of the original. The coarse phosphate flotation rate constant almost doubled and the flotation selectivity index increased up to 25% by the nanobubbles.\(^9\)\(^2\)

4.4 CGAs as carrier

The ability of microbubble suspensions to deliver oxygen, microorganisms and micronutrients to a target site can be harnessed for successfully enhancing the aerobic biodegradation of the pollutants inside the matrix. Unlike the normal bubble, microbubbles shrink when their size is below a critical value. The internal pressure of the microbubble increases as the bubble size decreases according to the Young–Laplace equation (Equation 5):

\[
\Delta P = \frac{2\gamma}{r}
\]

where \(P\) is the pressure difference, \(\gamma\) is the surface tension, and \(r\) is the radius of the bubble. As described by Henry’s law, the entrapped gases tend to diffuse from a high-pressure area inside the bubble to a comparatively low-pressure environment of the surrounding aqueous solution and gradually diffuse into it. With decreasing bubble size, buoyancy also decreases resulting in a slow upward flotation having a longer retention time in aqueous solutions.\(^10\)\(^7\) Therefore, supplying oxygen through microbubbles enables a high level of oxygen transfer and is applicable to oxygen consuming
processes such as aquaculture, hydroponic cultivation, aerobic fermentation and aerobic treatment of sewage.56-108-109

4.4.1 Carrier of microorganism, nutrient and oxygen

Aerobic biodegradation of organic compounds can be aided by delivering oxygen by microbubble suspension in the subsurface. Several researchers used microbubbles to successfully enhance the aerobic biodegradation of phenol, p-xylene and pentachlorophenol and also to transport microorganisms in a soil column.110-113 Jackson et al.110 reported that the total number of bacteria in the effluent was at least 2 or 3 times greater in magnitude after the passage of the CGA suspension than that obtained by passage of either surfactant or water as the eluting agent, respectively. Save and Pangarkar114 utilized CGAs for harvesting of microorganisms such as Saccharomyces cerevisiae and studied the effect of various operating parameters, viz. pH, biomass loading, dispersed and continuous phase velocity, surfactant type and concentration.

CGAs were found to be highly effective in floating and separating microorganisms.115 On introduction of CGAs in a microorganism infested effluent, microorganism-bubble complexes were formed by adsorption mechanism and subsequently floating on the surface. A statistical analysis was done in the form of two-way cross-classification of parameters to assess the impacts of sparging rate of the CGAs and operating height on the concentration of yeast cells in a flotation column. Hashim et al.45 deduced that the adsorption of yeast on the aphrons followed the Langmuir model under certain experimental conditions. However, the mechanism of bubble attachment and detachment changed from a monolayer to a multilayer one with changes in the pH and feed concentration.

Kommalapati and Roy116 studied the bioenhancement of soil microorganisms by utilizing natural surfactant solutions obtained from fruit pericarps of Sapindus mukorossi under anaerobic conditions to solubilize hydrophobic organic compounds from soil. Natural surfactant of concentrations 0.1, 1 and 2% along with two different nutrient media such as basal salt media (BSM) and heterotrophic media were used in the experimental studies. Natural surfactant solution was found to serve as both carbon
and energy source for anaerobic microorganisms and was observed to be biodegradable to a considerable extent. The microbial growth increased significantly with increasing surfactant concentration from 0.1 to 2% by weight, probably due to higher availability of nutrient in more concentrated solution.

Rothmel et al.\textsuperscript{117} reported a high rate of degradation of trichloroethylene (TCE) in a sand column due to the enhanced transport of the inoculum and supply of oxygen by the microbubble suspension of anionic surfactant Steol CS-330. Mobilization was 75\% when the foam was injected followed by artificial groundwater and then by foam again. When the TCE-degrading bacterial strain ENV 435 was simultaneously added with the second pulse of foam, 95–99\% degradation of the residual TCE was observed.

Choi et al.\textsuperscript{118} experimented with CGA suspension generated from sodium dodecyl sulfate (SDS), dodecylethylidimethylammonium bromide (DEDAB), saponin and a protein hydrolysate, collagen as oxygen carrier for aerobic biodegradation of contaminants in soil. It was observed that the microbubble suspensions were separated into a liquid and gas phase directly after injection, the liquid phase moving faster than the gas phase. A plug-flow pattern was noticed in the flow of the gas front. The experimental results from both homogeneous and heterogeneous cells confirmed that the microbubble flow could overcome the heterogeneity in porous media although the flow in the low-permeability zone was accompanied by a large pressure drop. Again, Choi et al.\textsuperscript{119} performed an experiment on phenanthrene biodegradation in a sand column with a saponin-based microbubble suspension prepared from \textit{Quillaja} bark containing \textit{Burkholderia cepacia} RPH1, a phenanthrene-degrading bacterium. On introducing three pore volumes of the microbubble suspension containing \textit{B. cepacia} RPH1 into the sand column contaminated with phenanthrene concentration of 100 mg Kg\textsuperscript{-1}, the oxygen content declined to 5\% from an initial value of 20\% within 5 days. Correspondingly, 34.4\% of initial phenanthrene was removed in 8 days. Based on the stoichiometric calculation of oxygen consumed, assuming complete mineralization, 15\% of the initial amount was completely biodegraded in the column and the rest underwent incomplete biodegradation. On repeated
introduction of microbubbles, it was observed that 75.4% of phenanthrene was recovered. The total recovery of bacterial cells in the effluents was greater, around 42% in the case of the microbubble suspension compared to surfactant solution, which was only 8%, indicating higher efficiency of the microbubble suspension in transporting *B. cepacia* RPH1 through the porous medium. Other researchers observed that in a gas-liquid system, microorganisms tend to attach to the gas–liquid interface. Park et al. carried out an identical study on phenanthrene biodegradation by *B. cepacia* RPH1 using saponin-based microbubble suspension prepared from *Quillaja* bark and obtained similar results. The gas saturation increased in the column after passing the first PV of the microbubble suspension. At the bottom of the column, the gas saturation was 0.84 while at the middle and top, it was 0.28 and 0.09, respectively. The decrease of phenanthrene mainly occurred at the lower part of the column where the supply of oxygen by the microbubble was concentrated. Bacterial cells were found to be distributed almost uniformly throughout the column. The biodegradation efficiency could be enhanced by applying more pore volume of microbubble suspension.

### 4.4.2 Mass Transfer by CGAs

Wagner and Pöpel investigated the influence of different types and concentrations of surfactants (anionic and nonionic) on oxygen transfer rate. Oxygen transfer rates of fine bubble aeration systems for wastewater treatment frequently gets reduced down to 40% to 70% compared to clean water conditions due to presence of surfactants in wastewater, resulting in uneconomic performance. The oxygen transfer rate was measured by aeration coefficient or gas–liquid volume mass transfer coefficient ($k_{l,a}$). The nonionic surfactants reduced the oxygen transfer more strongly than anionic surfactants at the same surface tension. The influence of surfactant on $k_{l,a}$ was proposed to be the result of two conflicting effects, viz. the increase of the surfactant concentration promoting the formation of microbubbles thus generating a large surface area, which greatly favours the gas–liquid mass transfer. The arrangement of surfactant molecules on the gas–liquid interface might hold back the oxygen transport through the interface and reduces $k_{l}$ to a different extent depending on their
The conflicting factors shaped the final effect of CGAs dispersions on the mass transfer coefficient $k_{L,a}$ and it was determined by their relative magnitudes.\cite{123}

Dai et al.\cite{124} studied CGAs produced from four surfactants, viz. SDS, HTAC, NP-10 and MAPK for enhancing gas–liquid mass transfer of oxygen by CGAs dispersion and concluded that it is indeed a complicated phenomenon depending on stirring velocity, type and concentration of surfactants and temperature. With the increase in surfactant concentration, the $k_{L,a}$ of oxygen increased for SDS, decreased for MAPK, increased for HTAC up to 0.363 gm L$^{-1}$ and then decreased while NP-10 had little effect on $k_{L,a}$. In the case of SDS dispersion, the mass transfer was found to reach a maximum value at a stirring velocity of 8000 rpm and increased with temperature up to 308 K. Higher temperatures increased $k_{L,a}$ due to the acceleration of molecular diffusion but the influence was weakened above 308 K because of reduction in O$_2$ solubility. For SDS, the effect of enlarging surface area predominated over the increase of interface resistance resulting from the arrangement of surfactant molecules on the interface. SDS concentration of 2.75 gm L$^{-1}$ was found to enhance $k_{L,a}$ by a factor of 3 compared to surfactant-free systems.

Gong et al.\cite{125} numerically analyzed the effect of the bubble-induced liquid flow on mass transfer in microbubble plumes using a two-way coupling Eulerian–Lagrangian approach to simulate oxygen bubble plumes with initial bubble diameters from 100 μm to 1 mm and a maximum local void fraction of less than 2% in compact rectangular tanks. The bubble-induced liquid flow was found to be suppressed when bubbles are injected uniformly. So, the uniform injection of microbubbles provided much better mass transfer efficiency than concentrated injection.

4.5 A soil flushing system design

Surfactant foam technology achieved better mobility control in porous media and improved the removal efficiencies of several remediation processes. It removed hydrophobic organic compounds\cite{67,113,126} and heavy metals\cite{127} from contaminated soils. In situ foam flushing has also been proved to be an efficient process for NAPL contaminated soil remediation.\cite{128} Wang and Mulligan\cite{127} came up with a
conceptual design of a surfactant foam flushing installation as illustrated in Figure 5. Surfactant foam can be flushed through the contaminated zone where it washes and sweeps the soil, in the process extracting contaminants and bringing them to the surface for further treatment. The sweep efficiency of surfactant foam in a porous medium can be determined by the value of capillary number ($C_a$), a dimensionless number defined as the ratio of viscous forces to capillary forces. According to Wang and Mulligan\textsuperscript{129}, depending on the Darcy velocity ($u$), fluid viscosity ($\mu$) and interfacial tension ($\sigma$), the capillary number is commonly formulated as in Equation 6:

$$C_a = \frac{\mu}{\sigma}$$

\textit{Figure 5: A scheme of soil flushing system by microbubbles, adopted from Wang and Mulligan}\textsuperscript{129}

\textit{Table 2: Performance of CGAs for pollutant removal (see at the end)}
5. CONCLUSION

CGAs constitute a unique system of highly stable spherical microbubbles having few colloidal properties. Their characteristic properties such as extremely high interfacial area, thick multilayer surfactant shell, hydrophobic inner shell, charged outer surface, lack of profuse capillary drainage, low buoyancy, ability to flow through pipes and its behavior as shear thinning fluid under different flow rate and surfactant concentrations favor the utilization of CGAs in several separation processes.

The properties of microbubbles get affected by the generation technique employed thus leading to application in different fields having different requirements such as size, monodispersity, surface properties and stability. Besides sophisticated methods such as pressurizing dissolution methods, multiphase flowing methods, the usage of fine nozzles, orifices and pores, the simple and inexpensive classical method by high speed stirrer and homogenizer can be used for normal separation processes.

Over the years, CGAs had been used principally for five objectives such as (i) pollutant removal from soil, (ii) pollutant separation from fluid phase, (iii) particle separation by flotation column, (iv) carrier of gas, nutrients and microorganisms and (v) for protein separation. In this review, the last field of application has been left out since only contaminant treatment was the context of this review paper.

The mechanism involved in all of these processes can be summarized as: (i) phase separation between gaseous and liquid phase of CGAs and induction of contaminant in one of the phases (ii) displacement, solubilization, dispersion, channeling and electric repulsion at the surface of soil particles (iii) higher interfacial area of CGA suspension leading to closer contact between remediation fluid and contaminant (iv) mechanism of oil-drop emulsification and imbibition into the foam lamellae structure (v) bubble entrained floc flotation, and (vi) ionic interactions.

Three types of surfactants are mostly used for preparing CGAs, viz. anionic, cationic and neutral, depending on the contaminant to be removed, if the ionic interaction plays a role in the removal mechanism. Cationic pollutants such as heavy metals can be easily removed by the anionic surfactants.
while anionic species such as polystyrene and some dyes are effectively arrested by cationic surfactants. However, if the treated matrix contained strong cationic and anionic species, then non-ionic surfactants were found to be most effective in removing pollutants without getting trapped in the matrix. Some natural surfactants have been also tested by researchers, such as soapnut extracts and *Quillaja* bark extracts. Using CGA suspension is advantageous due to the fact that this material harnesses all the functionalities of surfactant washing with additional inclusion of gaseous phase to ensure better removal and also creating air ventilation in the confined contaminated matrix. Also, using non-toxic organic and natural surfactants for CGAs preparation ensures eco-friendliness of the process. Generally, soil washing is not considered as an environment friendly option but CGAs address this problem effectively. By transporting air, nutrients and microorganisms to contaminated soil matrix, it opens up a completely new avenue for biological treatment of soil and aquifers. Another advantage is that considerably less amount of surfactant chemical is required to attain the same result with CGAs as compared to conventional surfactant solution.

While using CGAs for wastewater treatment and particle flotation is much explored and comparatively easy, quite a few challenges are to be overcome regarding its application in soil and aquifer remediation. There may be channeling of the flow of CGAs in some types of soils leaving some inaccessible area of the soil untreated. Also, it may be difficult to apply in deeper portions of soil, especially if the soil has low porosity. Again, it has never been applied in the field in large scale.

Extensive research should be undertaken to apply this promising technology for soil and groundwater treatment, keeping in mind the extremely complex texture and chemistry of the soil environment. Also, heavy metal removal by CGAs are to be explored both in soil and liquid matrix since mostly treatment of organic and oily contaminants have been mostly explored for the past two decades.
ACKNOWLEDGEMENTS

We fully acknowledge our gratitude towards University of Malaya, Kuala Lumpur, Malaysia for the financial assistance and to Ms Papia Roy for her compilation work on CGA at an earlier date.

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2 List of Figures:

3 Figure 1: Schematic diagram of structure of CGAs according to Sebba

4 Figure 2: Photomicrographs of the microbubble dispersion at different times. Photo A represents $T = 0$ s; B represents $T = 360$ s; C represents $T = 1080$ s; and D represents $T = 1620$ s.\(^{20}\)

6 Figure 3: Schematic of three successive steps of in froth floatation: bubble-particle collision, attachment and detachment, adopted from Fan et al.\(^{92}\)

8 Figure 4: Effect of nanobubble on coarse particle froth flotation, adopted from Fan et al.\(^{92}\)

9 Figure 5: A scheme of soil flushing system by microbubbles adopted from Wang and Mulligan.\(^{129}\)

10 List of Tables:

11 Table 1: Methods of CGAs and microbubble generation

12 Table 2: Performance of CGAs for pollutant removal
Table 1: Methods of CGAs and microbubble generation

<table>
<thead>
<tr>
<th>Method</th>
<th>Instruments used</th>
<th>Principle</th>
<th>Diameter of Microbubble</th>
<th>Gas hold-up</th>
<th>Production efficiency (in different units)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Classical Method</td>
<td>High speed stirrer in a baffled beaker</td>
<td>Above 4000rpm, the waves beat up against the baffles and are forced to re-enter the liquid carrying a thin film of gas. Such a thin film is unstable and breaks into minute gas aphrons encapsulated by a soapy shell.</td>
<td>&gt;25µm</td>
<td>&gt;60% of gas in solution</td>
<td>1 KWh for 10,000L CGAs</td>
<td>130</td>
</tr>
<tr>
<td>2 Sonication</td>
<td>Sonicator</td>
<td>Sonicator is operated with 0.5 inch ultrasound probe at a power level of 300 W for 3 minutes. High frequency sound waves produce CGAs in a surfactant solution.</td>
<td>26 µm for 1% L-150A (38% sucrose laurate ester, 10% ethanol, 52% water) 46 µm for 1% SDS</td>
<td>40% for 1% L-150A 42% for 1% SDS</td>
<td>2.5×10⁷ ml⁻¹ for 1% L-150A 8.3×10⁷ ml⁻¹ for 1% SDS</td>
<td>59</td>
</tr>
<tr>
<td>3 Homogenization</td>
<td>Homogenizer</td>
<td>At &gt; 4000 rpm speed, high speed rotor automatically draws solution axially into dispersion head and then forces it radially through the slots in rotor-stator arrangement. The turbulence forms CGAs.</td>
<td>68 µm 1% L-150A solution (38% sucrose laurate ester, 10% ethanol, 52% water) 72 µm for 1% SDS</td>
<td>15% for 1% L-150A 11% for 1% SDS</td>
<td>6.25×10⁷ ml⁻¹ for 1% L-150A 4.36×10⁷ ml⁻¹ for 1% SDS</td>
<td>59</td>
</tr>
<tr>
<td>4 Dispersed Air Flotation</td>
<td>Bubble Diffuser</td>
<td>Compressed air is forced through small pores of four sintered-glass disks to produce the micro bubbles.</td>
<td>75 µm - 655 µm</td>
<td></td>
<td></td>
<td>131</td>
</tr>
<tr>
<td>5 Electroflotation</td>
<td>Conventional electrode system containing a cathode and an anode.</td>
<td>Very small bubbles of hydrogen and oxygen were formed at the cathode and anode respectively, and their bubbles float in water.</td>
<td>22 - 50 µm</td>
<td></td>
<td>0.034 m² min⁻¹ W⁻¹</td>
<td>132-133</td>
</tr>
<tr>
<td>6 Dissolved Air Flotation (DAF)</td>
<td>Liquid pressure pump, air compressor &amp; injector, a central air dissolving tube &amp; pressurized water release unit.</td>
<td>Air is pressurized into solution at approximately 483 kPa (70 psi). The aerated solution is then released through needle valves to atmospheric pressure, forming bubbles that rise to the surface of the liquid.</td>
<td>33 to 143 µm, with a mean of 60 µm</td>
<td></td>
<td>0.054 m² min⁻¹ W⁻¹</td>
<td>133-135</td>
</tr>
<tr>
<td>7 Electrostatic Spraying of Air</td>
<td>Air pump, Capillary tip</td>
<td>Gas flows through a charged capillary acting as electrode for the application of a high-voltage-induced electric field which breaks up 10 to 180 pm with average size of 30 pm.</td>
<td></td>
<td></td>
<td>0.022 m² min⁻¹ W⁻¹</td>
<td>133-136-138</td>
</tr>
</tbody>
</table>
the gas bubbles flowing into solution

<table>
<thead>
<tr>
<th></th>
<th>Method</th>
<th>Description</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Gas Sparger System</td>
<td>Air or process gas is combined with water in a common manifold, and the mixture is injected at high pressure through a series of small orifices of 25-50 μm range.</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Microbubble generator for bioreactor systems</td>
<td>Liquid effluent and oxygen or another gas are admitted through the chamber under pressure and then passed into a venturi chamber to further reduce the size of bubbles</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Rotational Porous Plate Micro-air-bubble generator apparatus.</td>
<td>Compressed air is ejected into water through small holes on the porous plate which is rotated to tear the bubbles in suitable sizes which were transported to the mixing box with turbulent flow thus dissolving the bubbles as they moved downwards.</td>
<td>10 to 20 μm, 1.3 × 10^7 and 6.6 × 10^2 number mm⁻³</td>
</tr>
<tr>
<td>11</td>
<td>Spherical Microbubble Generator with flowing water tube</td>
<td>Pressurized water is introduced into a spherical pipe in a way that outlet velocity becomes higher than the inlet velocity, lowering the pressure at inlet, thus sucking in air into water stream through a number of small holes drilled on the pipe wall. The air sucked is broken into a great number of microbubbles.</td>
<td>120 μm mean diameter, It can operate at low energy of 40 Watts</td>
</tr>
<tr>
<td>12</td>
<td>SPG membrane generator from Shirasu-porous-glass (SPG) membranes</td>
<td>Air is pressed through SPG membranes of 43–85 nm pore diameters at a transmembrane pressure ratio of 1.0–2.0 while 0.05–0.5 wt.% SDS solution was flowed along the inner surface of the membrane.</td>
<td>360–720 nm</td>
</tr>
<tr>
<td>13</td>
<td>Lotus Ceramics Generator</td>
<td>Microbubbles were generated by introducing N₂ gas through the ceramic tube by immersing it into water at a minimum pressure of 20 kPa.</td>
<td>70 to 105 μm at flow rates of 0.15–0.25 L min⁻¹ in the thin sample and 0.3–0.7 L min⁻¹ in the thick sample</td>
</tr>
</tbody>
</table>

http://onlinelibrary.wiley.com/doi/10.1002/jctb.3691/abstract;jsessionid=280188B3A0B1EFACF575151D84E8B24A.f04t04
Table 2: Performance of CGAs for pollutant removal

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Pollutant and Concentration</th>
<th>Soil flushing agent</th>
<th>Flushing condition</th>
<th>Percentage removal of pollutants at different flow modes</th>
<th>Mechanism of pollutant removal &amp; influencing factor</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil (bulk density=1.5g m cc$^{-1}$ porosity = 0.4)</td>
<td>Oily waste</td>
<td>CGA suspension (8mM SDS)</td>
<td>flushing solution pumped into column in a upflow, downflow and horizontal flow modes at a rate of 2.6 mL min$^{-1}$ at 50 psi pressure</td>
<td>56 47 49</td>
<td>A</td>
<td>9</td>
</tr>
<tr>
<td>Soil (bulk density=1.5g m cc$^{-1}$ porosity = 0.45)</td>
<td>Automatic Transmission Fluid (ATF)</td>
<td>CGA suspension (8mM SDS)</td>
<td>flushing solution pumped into column in a upflow and downflow modes at a rate of 2.6 mL min$^{-1}$</td>
<td>41 50 -</td>
<td>E, B, F, G, H</td>
<td>61</td>
</tr>
<tr>
<td>Sandy soil (river bank soil washed with water &amp; nitric acid)</td>
<td>Diesel Oil</td>
<td>CGA suspension</td>
<td>Flushing media were introduced at the top of the column in downflow mode</td>
<td>- 96 -</td>
<td>I</td>
<td>63</td>
</tr>
<tr>
<td>Soil (bulk density=1.46 gm cc$^{-1}$ porosity = 0.42)</td>
<td>Naphthalene</td>
<td>Solution of 0.15, 20, 50 mM Tergitol</td>
<td>flushing solution pumped into column in a downflow mode at a rate of 2.6 mL min$^{-1}$</td>
<td>- 3, 30, 66</td>
<td>B</td>
<td>47</td>
</tr>
<tr>
<td>Soil (bulk density=1.6g)</td>
<td>HCB 70-80 mg Kg$^{-1}$</td>
<td>Water Flood</td>
<td>12 pore volumes (120 ml each) flushing media were pumped from the top of the column</td>
<td>- 0.02 -</td>
<td>D</td>
<td>66</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Soil (bulk density=1.6g m cc(^{-1}), HCB 2 mg Kg(^{-1}), porosity = 0.4)</th>
<th>Water Flood</th>
<th>12 pore volumes (120 ml each) flushing media were pumped from the top of the column at downflow mode at a Rate of 2.5 ml min(^{-1})</th>
<th>-</th>
<th>0.02</th>
<th>-</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soapnut solution 0.5%</td>
<td>-</td>
<td>3.16</td>
<td>-</td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soapnut solution 1%</td>
<td>-</td>
<td>13.84</td>
<td>-</td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CGA suspension of 0.5% Soapnut solution</td>
<td>-</td>
<td>7.55</td>
<td>-</td>
<td>B, (-)G, (-)Q</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CGA suspension of 1% Soapnut solution</td>
<td>-</td>
<td>15.1</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil (bulk density=1.6g m cc(^{-1}), HCB 90-110 mg Kg(^{-1}), porosity = 0.4)</td>
<td>Water Flood</td>
<td>12 pore volumes (120 ml each) flushing media were pumped from the top of the column at downflow mode at a Rate of 2.5 ml min(^{-1})</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
<td>D</td>
</tr>
<tr>
<td>Soapnut solution 0.5%</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soapnut solution 1%</td>
<td>-</td>
<td>2.26</td>
<td>-</td>
<td>C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CGA suspension of 0.5% Soapnut solution</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>B, (-)G, (-)Q</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CGA suspension of 1% Soapnut solution</td>
<td>-</td>
<td>1.7</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass bead column N-pentadecane</td>
<td>Solution of Triton SP-190 (400 ppm)</td>
<td></td>
<td>-</td>
<td>19</td>
<td>-</td>
<td>C, J</td>
</tr>
<tr>
<td>Foam of Triton SP-190 (400ppm) Gas:liquid=5:1</td>
<td></td>
<td></td>
<td>-</td>
<td>36</td>
<td>-</td>
<td>J, K</td>
</tr>
<tr>
<td>Foam of Triton SP-190 (400ppm) Gas:liquid=10:1</td>
<td>9 pore volumes of surfactant solution</td>
<td>-</td>
<td>74</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution of Triton SP-190 (1000 ppm)</td>
<td>introduced from the top of the column and allowed to flow through the glass beads at a desired volumetric flow rate</td>
<td>-</td>
<td>35</td>
<td>-</td>
<td>C, J</td>
<td></td>
</tr>
<tr>
<td>Foam of Triton SP-190 (1000ppm) Gas:liquid=5:1</td>
<td></td>
<td></td>
<td>44</td>
<td>-</td>
<td>J, K</td>
<td></td>
</tr>
<tr>
<td>Foam of Triton SP-190 (1000ppm) Gas:liquid=10:1</td>
<td></td>
<td></td>
<td>85</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution of Triton SP-190 (2000 ppm)</td>
<td></td>
<td></td>
<td>38</td>
<td>-</td>
<td>C, J</td>
<td></td>
</tr>
<tr>
<td>Gas:liquid=10:1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pumice stone 750 mg Kg(^{-1})</td>
<td>Water Flood</td>
<td>Continuous operation conducted at up-flow mode with surfactant solutions and CGAs at flow rate of 11</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(-)Q</td>
</tr>
<tr>
<td>3% BioNonex solution</td>
<td>47</td>
<td>-</td>
<td>-</td>
<td>B, C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7% BioNonex solution</td>
<td>68</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3% BioNonex CGAs</td>
<td>55</td>
<td>-</td>
<td>-</td>
<td>B, C, D, M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wastewater Slurry</td>
<td>CGAs</td>
<td>FL</td>
<td>pH</td>
<td>Ionic Strength</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>------</td>
<td>----</td>
<td>----</td>
<td>---------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>Fine cellulose fibres</td>
<td>CGAs of SDS solution (1 gm m^-3)</td>
<td>In a flotation column, slurry and CGAs passed in counter-current direction</td>
<td>70</td>
<td>-</td>
<td>-</td>
<td>L, M, R</td>
</tr>
<tr>
<td>Polystyrene wastewater</td>
<td>CGAs of SDBS solution</td>
<td></td>
<td>98</td>
<td>-</td>
<td>-</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>CGAs of HTAB solution</td>
<td></td>
<td>95</td>
<td>-</td>
<td>-</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>CGAs of Tween-20 solution</td>
<td></td>
<td>35</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Magnesium hydroxide wastewater</td>
<td>CGAs of SDS solution</td>
<td></td>
<td>55</td>
<td>-</td>
<td>-</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>CGAs of HTAB solution</td>
<td></td>
<td>53</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CGAs of Tween-20 solution</td>
<td></td>
<td>50</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2-Octanol Methyl orange</td>
<td>CGAs of HTAB</td>
<td>CGAs or air sparged from bottom</td>
<td>95 in 6-7 mins</td>
<td>-</td>
<td>-</td>
<td>M, N</td>
</tr>
<tr>
<td></td>
<td>Air spurring</td>
<td>&lt;95 in 20 mins</td>
<td>-</td>
<td>-</td>
<td>(-)N, (-)M</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>CGAs of surfactant having same charge as dye</td>
<td>CGAs introduced at bottom of flotation column</td>
<td>40</td>
<td>-</td>
<td>-</td>
<td>L</td>
</tr>
<tr>
<td>Methylene blue &amp; Methyl orange</td>
<td>CGAs of surfactant having opposite charge as dye</td>
<td></td>
<td>95</td>
<td>-</td>
<td>-</td>
<td>N</td>
</tr>
<tr>
<td>Sweet whey</td>
<td>Lactoferrin and lactoperoxidase</td>
<td>CGAs of AOT</td>
<td>10–30 mL CGAs mixed with 1–10 mL whey, and the mixture was allowed to separate into two phases at pH = 4 and ionic strength = 0.1 mol L^-1</td>
<td>90% total recovery, 25 times higher in CGAs phase than in liquid phase</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>Trichloroethylene</td>
<td>Microbubble of Steol CS-330</td>
<td>Injection of foam followed by artificial groundwater (AGW) and then by foam again through 8 inch column</td>
<td>75% degradation of contaminants</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>foam/AGW/foam + bacterial strain ENV 435</td>
<td>95–99% degradation of contaminants</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>Sand (porosity = 0.35)</td>
<td>Phenanthrene</td>
<td>Microbubble prepared from saponin mixture extracted from <em>Quillaja</em> bark</td>
<td>microbubble suspension injected from bottom at 10 mL min⁻¹</td>
<td>75.4%</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

A - Phase separation between liquid and gas phase  
B - Increased contaminant solubility and mobilization by micellar solubilisation  
C - Increased contaminant solubility and mobilization by reduced interfacial tension between contaminant and solution  
D - Displacement of contaminant by solvent media/CGA due to density difference  
E - Water solubilisation  
F - Dispersion (surfactant molecules adsorb on the surface of emulsion by creating a dispersion of droplets, which reduces interfacial tension and retards particle flocculation during mixing)  
G - Channelized flow of CGAs through matrix  
H - Electric repulsion at the surface of soil particles  
I - Higher interfacial area leading to closer contact between remediation fluid and contaminant favouring mobilization of the contaminant and its removal  
J - Surfactant-enhanced emulsification of contaminant  
K - Imbibition of contaminant into the foam lamellae structure  
L - Bubble entrained floc floatation depending on concentration of surfactant & particle size  
M - Finer bubble size  
N - Ionic charge (cationic/anionic) of CGA facilitating attachment of bubbles with the contaminant molecules  
O - Enhanced transportation of the microbial inoculum and supply of oxygen by the microbubble suspension  
P - CGAs acting as ion exchangers  
Q - Pore clogging and lower hydraulic conductivity  
R - Difference of Electrokinetic Potential between contaminant particle and CGA/colloidal system  
(-) - negative effect / less effect / opposite dimension