State-of-the-Art Electroflocculation

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The electroflocculation principle has been known since the beginning of the century, but until recently it has not been used in industrial applications. The 'Purifier' described in the paper is an electroflocculation unit which can separate oil, organic substances and heavy metals from water. It is most competitive with concentrations of less than 5000 parts per million oil or organic substances in water. The paper describes the major working principles of the 'Purifier'.

Oil-polluted water and water polluted with other organic substances is a problem in many different industries. Demands from the authorities and general public for a cleaner environment will increase, and the authorities might reduce the legal effluent concentrations to 20 mg of organic substances per litre of effluent. When the effluent is characterised as hazardous waste, it is illegal to drain it into the sewer. It might only consist of 0.5% oil, while the rest is pure water. These huge volumes of low-concentration oily waste are expensive to treat. If the oil could be separated from the water it would be much less costly to treat the oily waste, because of the lower volume. The oily sludge can probably be incinerated, and the water reused in the industrial process with a reduction in the cost of new process water.

The electroflocculation unit is capable of separating many kinds of organic substances and heavy metals in addition to oil. The degree of separation is in most cases above 99%, and the power consumption is about 1 kWh/m^3 of wastewater. Current units can treat about 1 m^3/h of wastewater in a continuous process. The best results are when the wastewater contains 5000 ppm organic substances or less.

History

Electrolytic processes to separate oil in wastewater were described in the patent literature as early as 1903. The process was used to treat condensed water from steam engines, before it entered the steam boiler as feedwater. The unit used iron sheets as the anode material; the iron was oxidised during the process, and had to be replaced after a while. The electrolysis cell operated with a potential of 150 V and with a fairly high current.[1]

This process was further developed by Weintraub, Gealer Golovoy and Dzieciuch into a continuous process to clean oily wastewater from metal-cutting, forming, rolling and finishing operations. An electrolytic cell which can treat 3.8 l/min of wastewater was designed and patented in 1980. The wastewater which was fed into the unit contained from 300 to 7000 mg oil/litre of water. The processed water contained less than 50 mg/l for 90% of the time, and less than 25 mg/l for 83% of the time. The unit can be improved to reach an effluent oil concentration of 10 mg/l. The power consumption was calculated to be 1.6 kWh/m^3.[1]

One of the first experiments with electroflotation was in 1911, treating domestic sewage in the United States. This method has not become generally used because the electrodes tended to scum after a while and, because of this, the efficiency decreased with time.[2]

Flotation processes are used extensively in the mining industry. In 1904, it was proposed for the first time to use electrolysis to make gas bubbles to 'float' minerals. The process was used in some mines in Broken Hill, Australia. However, the operation was not successful, because the power consumption was too high and because the technology was not well enough developed.[3]

In 1946, Rivkin et al.[3] obtained a patent for a method for electroflotation of ore. They designed several laboratory-scale electroflotation cells, which gave an improved flotation rate compared to other flotation techniques. This method is not reported to have been taken into commercial use by the industry.[3] Other experiments with electrolytic cells have been reported, but it appears that electroflotation of minerals is still at the laboratory/experimental stage. This is because only a limited amount of research has been done on the mechanisms and the

consumption of 0.48 kWh/m^3 of water, but they used a residence time of 10 – 20 min.[4]

Electroflotation

In flotation processes, air or gas is bubbled through a liquid containing particles which float or are emulsified in the water. The process consists of four basic steps: (1) gas bubble generation, (2) contact between gas bubble and oil drop, (3) gas bubble adsorption on the surface of the particle, and (4) the gas bubbles and oil drops rising to the surface.[5] At the surface a layer of foam will be created. This foam consists of gas bubbles and the flotated particles, and can be removed by skimming. The rate of flotation depends on several parameters, such as the surface tension between the water, particles and gas bubbles; the gas bubble diameter; the size of the particles; the water's residence time in the electrolytic cell and the flotation tank; the particle and gas bubble zeta potentials; and the temperature, pH and particle size distribution.

There are many different flotation methods. The conventional process is to use a compressor to blow air through nozzles in the bottom of the flotation tank. The problem is the distribution of the air bubbles, and to make small enough bubbles. Small gas bubbles are more efficient than larger gas bubbles, since they have a larger surface area per unit volume of gas. Smaller gas bubbles also have the advantage that they have lower buoyancy, and so will have a longer residence time in the electrolyte. This increases the possibility for collisions between bubbles and oil particles.

Another method is dissolved-air flotation, which gives a better bubble distribution in the water. The disadvantages is that it is not a continuous process, and it is difficult to control the bubble flux. During the process air is injected into the water under pressure; when the pressure is released, the water is supersaturated with air, which is released as air bubbles.[6] This is the same process that happens when a bottle of carbonated water or beer is opened.

A method which follows the same principle, but which uses a very low pressure, is vacuum flotation. The water is saturated with air at atmospheric pressure, and when a vacuum is applied, air bubbles will be released.[6] This process has the same advantages and disadvantages as dissolved-air flotation.

Electroflotation is a continuous method. The bubbles are generated by electrolysis of water; the water flows between two electrodes, and is reduced to hydrogen at the cathode and oxidised to oxygen at the anode. One advantage is that the gas bubbles generated are essentially at the same, very small size. However, the power consumption can be high if the process is not well designed and optimised. Another advantage is that it is easy to adjust the gas bubble flux, by varying the current across the electrodes. The distribution of the gas bubbles is also good, because the bubbles are produced over the whole area of the electrode.
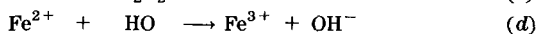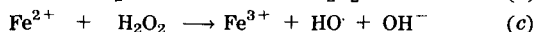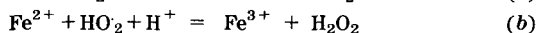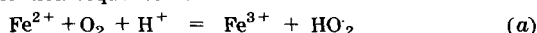
Electroprecipitation

Tennant Company

Electroprecipitation is a flocculation process where the flocculating agent is ions of metal which are precipitated from the anode. The metal ions will settle in the electrolyte, but on the way down they collide with particles in the electrolyte, and adsorb onto the surface of these particles. The best anode material is iron or aluminium, because they give trivalent ions; most other cheap and easy accessible metals give bivalent ions. Trivalent ions have a

breakdown of emulsions is brought about with the assistance of hydroxyl radicals which are generated during ferrous-ion oxidation. The reaction sequence is:

$$Fe^{2+} + O_2 + H^+ = Fe^{3+} + HO_2 \qquad (a)$$
$$Fe^{2+} + HO_2 + H^+ = Fe^{3+} + H_2O_2 \qquad (b)$$
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^{\cdot} + OH^- \qquad (c)$$
$$Fe^{2+} + HO \longrightarrow Fe^{3+} + OH^- \qquad (d)$$

The ferrous ion/hydrogen peroxide solution taking part in reactions (c) and (d) is recognised as Fenton's reagent, and is a powerful oxidising system. The emulsion is destabilised by both oxidative destruction of the chemical emulsifier and by neutralisation of the emulsion/droplet charge.[1]

No mechanism has been suggested with aluminium as the anode. Aluminium ions are very unstable, and it is suggested that aluminium ions react with hydroxyl ions and make a network as soon as they are released from the anode. The network of aluminium hydroxide will adsorb onto colloidal particles. Colloidal particles are defined as particles which in the dispersed state have an extension in at least one dimension of between 1 nm and 1 μm. The upper limit is not distinct, since particles which are larger than 1 μm are also treated as colloidal particles if they have properties like colloidal particles.[7]

The network of aluminium ions is built up from a chain with three hydroxyl ions per aluminium ion. The chains can be several hundred ångstrøms long, but only a few particle diameters thick. The chains are created by a condensation polymer reaction mechanism. The process depends on pH and temperature to create the correct crystals. At 25°C the pH in the water must be between 4 and 10, and at 100°C between 3 and 7, in order to create large crystals. Outside these pH ranges the aluminium ions will react to make less complex compounds with hydrogen and oxygen.[8]

Electroflocculation

Electroflocculation is a combination of the processes of electroflotation and electroprecipitation. Our electroflocculation unit consists of an electrolytic cell with an aluminium anode and a stainless-steel cathode. The anode must be more easily oxidisable than the cathode to give the correct effect. Balmer and Foulds[9] tried many different electrode materials, such as iron, steel, copper, brass, zinc, alloys of aluminium, bronze and phosphor bronze. All of these materials produced enough flocs, and gave a high degree of separation. They concluded that the cheapest and most easily accessible electrode materials should be used.

An electrolytic cell can be designed in many different ways.[10] Here we will discuss a specific unit, which has been designed and patented by Jan Sundell; this unit is called the 'Purifier'. The distance between the electrodes is 3 mm; this distance is an important design variable when it comes to optimising the operating costs of the unit. The operating costs are dependent on the power consumption, which can be expressed as

$$P = U \times I \qquad (1)$$

where P is the power consumption (W), U is the voltage (V) and I is the current (A). Using Ohm's Law ($U = R \times I$, where R is the resistance in ohms), it is also possible to rewrite Eqn. 1 as

$$P = R \times I^2 \qquad (2)$$
$$P = \frac{U^2}{R} \qquad (3)$$

The relationship between current and power consumption is shown in Eqn. 2, and a change in current will change the power consumption in the second power. The amount of gas which evolves at the electrodes is dependent on the current flowing across the electrodes.

To reduce the power consumption without changing the current and the degree of separation, one can reduce the resistance in the electrolyte. Reducing the distance between the electrodes or increasing the conductivity of the electrolyte will reduce the power consumption without changing the degree of separation, because the current is not changed. Ohm's Law states that the power consumption will decrease as the distance between the electrodes

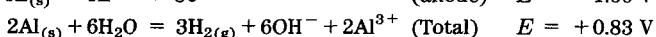distance between the electrodes gives a low power consumption.[9]

In some types of wastewater the conductivity is too low, and it is necessary to add some salts to increase the number of dissolved ions in the electrolyte. The simplest method is to add table salt (NaCl), but it has also been reported that 0.01N CaCl$_2$ has been used to increase the conductivity of the electrolyte.[1]

There is an optimum arrangement with a certain power consumption and a certain degree of separation. When the current in the electrolytic cell is increased, the gas bubble flux increases; this increases the separation effect. However, when the concentration of gas bubbles is increased, the possibility that two gas bubbles collide also increases. This reduces the separation effect since larger gas bubbles are less effective than smaller gas bubbles, because they have a smaller surface area/volume ratio. In addition, gas bubbles have a lower conductivity than the electrolyte; this increases the power consumption.

When the gas bubble concentration increases, the result is that the degree of separation increases as the current increases up to a certain level. The concentration of the gas bubbles gives a large contribution to the electrolyte resistance, and eventually too many of the gas bubbles will coalesce. The degree of separation will then slowly decrease as the current across the electrodes increases.[11] At a certain point, increasing the power consumption will no longer affect the degree of separation.

The electrode reactions

The anode and cathode reactions are as follows:

$2H_2O + 2e^- = H_{2(g)} + 2OH^-$	(cathode)	$E = -0.83$ V
$2H_2O = O_{2(g)} + 4H^+ + 4e^-$	(anode)	$E = +0.40$ V
$Al_{(s)} = Al^{3+} + 3e^-$	(anode)	$E = -1.66$ V
$2Al_{(s)} + 6H_2O = 3H_{2(g)} + 6OH^- + 2Al^{3+}$	(Total)	$E = +0.83$ V

Hydrogen gas will evolve on the cathode, and oxygen gas will evolve on the anode; oxygen gas will only evolve at high current densities. It is an advantage that hydroxyl ions are developed at the cathode, because they maintain the pH in the electrolyte. To create the correct aluminium complexes, the pH must be close to 7.

There are many mechanisms which are at work in the electrolytic cell. These include an electrophoresis mechanism, which makes the negatively charged oil particles attracted to the anode. This results in a faster flocculation than would be the case with conventional flocculation or flotation methods.[9]

Gas bubble formation

The gas bubbles which are created by electrolysis have an important function in the separation process. Reay and Ratcliff found that the rate of flotation of polystyrene particles is dependent on the gas bubble- and particle diameter.[12] The rate of flotation at a constant gas rate varies as $d_{particle}^2$ and d_{bubble}^{-3}. This means that the rate of flotation is at its highest when the particles are as large as possible and when the gas bubbles are as small as possible. Collins and Jameson found that the rate of flotation of polystyrene latex particles with a diameter of $4-20$ μm varied as $d_{particle}^{1.5}$.[12] They also found that the exponent showed little dependence on the charge on the particle, but that the actual rate of flotation was strongly influenced by the particle charge, which was varied in the $30-60$ mV range.

There is a specific ratio between the sizes of the particles and the bubbles where there is a higher probability of direct collisions between gas bubbles and particles.[13] A direct collision makes the gas bubble adsorb onto the particle, and many direct collisions during a short time give a high rate of flotation.

If a collision between a particle and a gas bubble is to be successful, the energy barrier represented by the water film between the actual particle and the actual gas bubble must be overcome. The collision velocity and the particle mass determine the energy which is available during the collision; larger particles hit the gas bubbles with a greater force than smaller gas bubbles. The relative velocities of a particle and a gas bubble increase with the difference in their dimensions. If the gas bubble hits a relatively small particle, the force from the collision will make the particle rebound from the gas bubble. The highest probability for a successful collision is when the gas bubble collides perpendicular

efficiency for bubbles less than 100 μm in diameter can be described by

$$E_c = \left(\frac{d_{particle}}{d_{bubble}}\right)^N \qquad (4)$$

where $N = 1.90$ when $\rho_{particle}/\rho_{fluid} = 1.0$, and $N = 2.05$ when $\rho_{particle}/\rho_{fluid} = 2.5$. This assumes that the stream around the sphere follows Stokes' Law for a flow around a rigid sphere; that electrical interactions between bubbles and particles do not have any effect on the particle trajectory or on E_c, and that bubble motions are not affected by the presence of the particles.[12]

The size of the gas bubbles

The following conditions affect the gas bubble departure diameter:[14]

☐ Gas bubble contact angle.
☐ Cathode surface morphology.
☐ Current density.
☐ Polarisation potential.
☐ Gas bubble charge.

Parameters which are fixed or which are impractical to adjust in order to obtain fine-sized gas bubbles are pH, temperature, reagent concentration and the electrode material.

Khosla et al.[14] and Glembotskiy et al.[15] have reported that the gas bubble size decreases with increasing current density. Glembotskiy et al.[15] have also found that the hydrogen gas bubble size increases with increasing temperature, and that the smallest gas bubbles were formed at pH 7. Khosla et al.[14] have also successfully used pulsed electrolysis to generate very small gas bubbles; with a pulse cycle time varied in the range of 30 ms and the current density varied from 2 to 0.5 A/m^2, they observed an increasing number of small gas bubbles ($< 10-15$ μm). Others[11,12] have reported gas bubble diameters of 20 μm during electroflotation with a constant current density.

Gas bubble formation on the cathode

There are three basic steps in the development of gas bubbles: nucleation, growth and detachment. Nucleation occur in energy-favourable places like pits and scratches. These places have a higher voltage than the rest of the cathode surface (see Reference 16, p. 305). Khosla et al.[14] reported that with pulsed electrolysis the energy-favourable places are less important as nucleation sites, and that nucleation is more uniform over the cathode surface.

Growth is driven by expansion caused by a high internal pressure and transport of dissolved gas through the gas/liquid interface because of supersaturation of gas in the electrolyte.[14] Another mechanism which make gas bubbles grow is coalescence. This occurs when two gas bubbles touch, and coalesce into a single gas bubble. Sides (Reference 16, p. 309) described a mechanism called radial specific coalescence, and observed that smaller gas bubbles moved radially towards a larger gas bubble and coalesced.

Another mechanism which make two gas bubbles coalesce is

when one gas bubble rolls across the cathode surface, and coalesces with every gas bubble which comes into its path. This gas bubble will often grow larger than necessary before it detaches. Sides (Ref. 16, p. 312) reported that when the electrode was tilted a few degrees from the horizontal, the bubbles coalesced and made a large front of gas bubbles, which 'scavenged' other bubbles in its path. This is unfavourable for the rate of flotation, because gas bubbles with smaller diameters are more effective than gas bubbles with larger diameters.

The third step is detachment. Its occurence is dependent on the bubble contact angle and the size of the gas bubble. Pulsating electrolysis gives the gas bubbles a shock, which makes the gas bubbles detach earlier than they would without the pulses. A surface-active substance in the electrolyte will reduce the surface tension between the electrolyte, the surface of the cathode and the gas bubbles, and make the gas bubbles detach sooner. Venczel (Ref. 16, p. 316) added gelatine, glycerine and beta-naphthochinolin to the electrolyte; in most cases the bubble diameter decreased. The reason suggested is that the surface-active substance results in increased wettability of the electrode.

The 'Purifier' reported here has been tested with soap in the electrolyte. This test gave a higher degree of separation with oil-in-water emulsions. The disadvantage is that a surface-active substance works as an emulsifier and stabilises the oil emulsion, but it is probably possible to find surface-active substances which increase the wettability of the cathode without working as an emulsifier for pollutants in the water.

The 'Purifier', an electroflocculation unit designed by Jan Sundell

Before the wastewater enters the electrolytic cell, it is coarsely filtered in a hydrocyclone. This removes the larger particles, and improves the total degree of separation. It was mentioned earlier that there is a problem with the anode, which will tend to scum.[2] This problem is solved in the Purifier. Jan Sundell has designed and patented a system which keeps the anode clean all of the time, and makes the anode wear evenly.

In the electrolytic cell aluminium ions precipitate from the anode and flocculate the unwanted particles like oil, most kinds of organic compounds and heavy metals. At the same time the hydrogen gas bubbles which form at the cathode cause the flocculated particles to float. The residence time of the wastewater in the electrolytic cell is less than 1 s, but this depends on the flow velocity of the water. The water flows into a sedimentation tank, where the residence time is short, but depends on the temperature, the concentration of impurities etc.

This process forms both a sediment and a layer floating on the surface, which are removed at regular intervals. The sediment is drained regularly, and the surface layer is skimmed off. The sludge is dewatered in a filter, and the removed water is recycled into the electrolytic cell. The sedimentation tank is tapped for clean water at regular intervals.

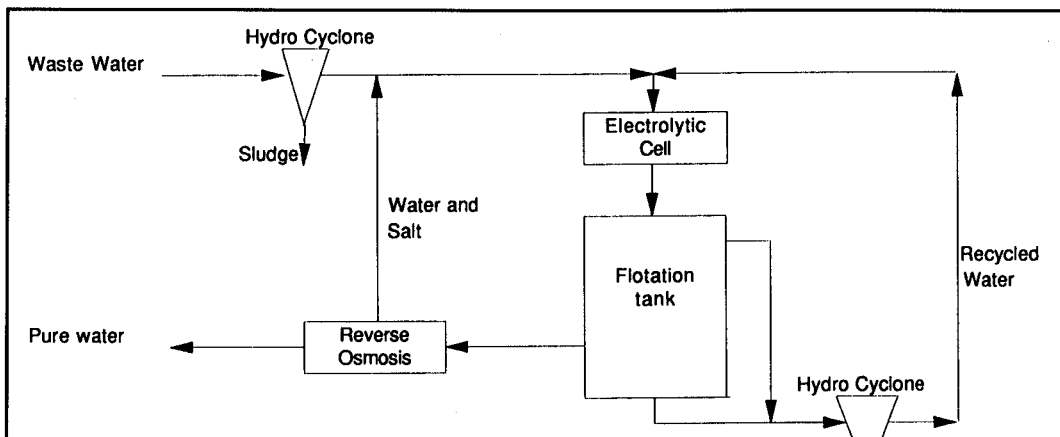If the wastewater conductivity is too low, it is necessary to add

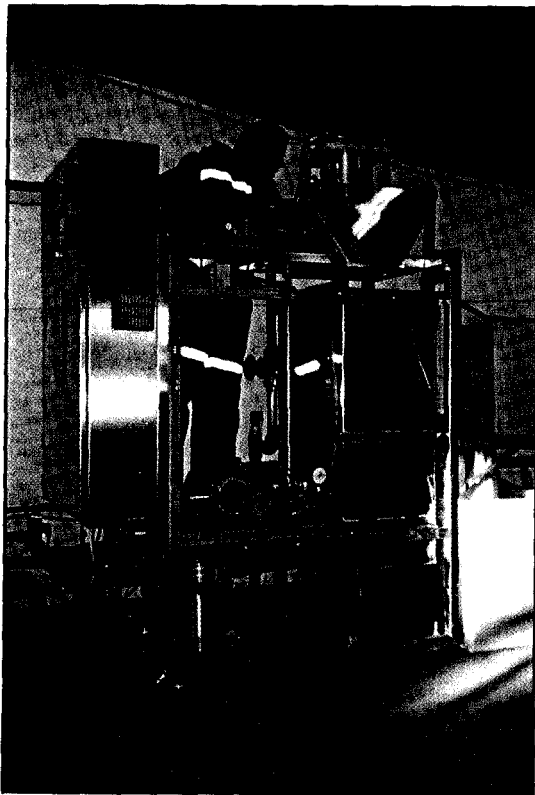**Figure 1. Flowsheet for the Purifier.**

Figure 2. The Purifier unit, including electrolytic cell, sedimentation tank and process control system.

sodium chloride to increase the conductivity. If the recipient cannot accept salt water, it will be necessary to remove the salt. This is done with the use of a reverse osmosis unit. The unit produces two streams, one with pure water and the other with a mixture of salt and water. The latter stream is recycled back to the electrolytic cell for reuse of the salt.

The Purifier has achieved prominent results with the separation of different kinds of pollution from water. Especially good results have been achieved in the separation of oily emulsions, and it has also achieved a high degree of separation with several kinds of organic substances and heavy metals. Table 1 gives values which were achieved during testing of the Purifier (the analysis was performed by the KM Laboratory in Karlstad).

The US company Environomics has also developed a process which uses the electroflocculation principle, which has achieved good results for separation of polyaromatic hydrocarbons (PAHs), oil, organic compounds and heavy metals from wastewater.

References

1 Weintraub, M.H., Gealer, R.L., Golovoy, A. and Dzieciuch, M.A.: 'Development of electrolytic treatment of oily waste water', *Environmental Progress*, February 1983, **2**(1), p. 32.

2 Fukui, Y. and Yuu, S.: 'Collection of submicron particles in electro-flotation', *Chem. Eng. Sci.*, 1980, **35**, pp. 1097–1105.

3 Mallikarjuan, R. and Venkatachalam, S.: 'Elektroflotation — A review'. International Symposium on Electrochemistry in Mineral & Metal Processing (165th meeting of the Electrochemical Society), Cincinnati, Ohio, USA, May 1984, pp. 233–256.

4 Kaliniichuk, E.M., Vasilenko, I.I., Shchepanyuk, V.Yu., Sukhoverkhova, N.A. and Makarov, I.A.: 'Treating refinery waste waters to remove emulsified oils by electrocoagulation and electroflotation', *Int. Chem. Eng.*, July 1976, **16**(3), p. 434.

5 Hosny, A.Y.: 'Electroflotation technique for removing petroleum oil waste', *Bull. Electrochem.*, January 1991, **7**, p. 38.

6 Chambers, D.B. and Cottrell, W.R.T.: 'Flotation: two fresh ways to treat effluents', *Chem. Eng.*, August 1976, **83**, p. 95.

7 Mørk, P.C.: 'Overflate og kolloidkjemi, 3rd edition' (Institutt for Industriell Kjemi, Norges Tekniske Høgskole, Norway, 1991.

8 Diggle, J.W. and Vijh, A.K.: 'Oxides and oxide films', *in:* Alwitt, R.S.: 'The aluminium-water system, vol. 4' (Marcel Dekker, New York, 1976), Chap. 3, pp. 169–254.

9 Balmer, L.M. and Foulds, A.W.: 'Electroflocculation/electroflotation for the removal of oil from oil-in-water emulsions', *Filtration & Separation*, November/December 1986, **23**(6), p. 366.

10 Hogan, P. and Kuhn, A.T.: 'Die Electroflotation bei der Abwasserbehandlung', *Oberflache-Surface*, 1977, **18**(10), p. 255.

11 Hosny, A.Y.: 'Separation of oil from oil/water emulsions using an electroflotation cell with insoluble electrodes', *Filtration & Separation*, September/October 1992, **29**(5), pp. 419–423.

12 Collins, G.L. and Jameson, G.J.: 'Experiments on the flotation of fine particles — The influence of particle size and charge', *Chem. Eng. Sci.*, 1976, **31**, pp. 985–991; Reay, D. and Ratcliff, G.A.: *Canadian J. Chem. Eng.*, 1975, **53**, p. 481.

13 Klassen, V.I. and Mokrousov, V.A.: 'An introduction to the theory of flotation' (Butterworths, London, 1963).

14 Khosla, N.K., Venkatachalam, S. and Somasundaran, P.: 'Pulsed electrogeneration of bubbles for electroflotation', *J. Applied Electrochem.*, 1991, **21**, p. 986.

15 Glembotskiy, V.A., Mamakov, A.A. and Sorokina, V.N.: 'The size of gas bubbles formed under electroflotation conditions', *Electrochemistry in industrial processing and biology*, **661.931**, p. 66 (Scientific Information Consultants, London).

Table 1. Results from test runs with the Purifier.

	Before the Purifier, mg/l	After the Purifier, mg/l	Degree of separation	Example
1. Oil in water	350	0.3	99.9%	Car wash unit
2. Aliphats in cooling water	260	2.4	99.1%	Ship
Aromats in cooling water	62	0.6	99.0%	
3. Lead, Pb^{2+}	5.3	< 0.05	> 99%	Printing office
Copper, Cu^{2+}	110	1.2	98.9%	
Zinc, Zn^{2+}	160	0.22	99.9%	

Table 2. Results from Environomics Inc (1993).

Wastewater from laundry	Before separation, mg/l	After separation, mg/l	Degree of separation	Type of compounds
	3.4	0.079	97.7%	Polyaromatic
Naphtalene	5.7	0.240	95.8%	hydrocarbons
2-bis ethylhexylphtalate	3.4	< 0.33	> 91%	(PAHs)
Pyrene	3.4	< 0.33	> 91%	
Fluoranthene	3.4	< 0.33	> 91%	
Chrysene				
Total oil and grease	5500	40	99.3%	Oil fractions
Oil and grease	4000	10	98.8%	
Phenol	3.4	0.052	98.5%	Organic
TSS	3500	22	99.4%	compounds
Ethylbenzene	21	< 0.007	> 99.97%	
Toluene	23	0.014	99.94%	
Xylene	168	0.051	99.97%	