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# Alternative Flotation Techniques for Wastewater Treatment: Focus on Electroflotation

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During the last decades (dissolved-air) flotation has found several applications in water and wastewater treatment. Flocculation is generally required in advance for a satisfactory separation and a membrane process is often applied downstream. Examples from the literature given in the present review include heavy metals, textile dyes, food, paper industry, oily effluents, laundry wastewaters, sludge etc. and are accompanied by typical laboratory results. Among the used techniques, the process known as electroflotation (or electrolytic flotation), which often incorporates electrocoagulation, was particularly focused in this paper due to certain advantages it offers; this process is certainly suitable for small-scale applications.

**Keywords** effluents; electrocoagulation; electrodes; electroflotation; industrial liquid wastes

## INTRODUCTION

Although the froth flotation process was developed at the turn of the previous century, it is still the best available technology in mineral processing. As high-grade ore deposits are depleted, low grade, fine grained, and complex ores have to be mined and processed. Beneficiation of these ores requires, of course, fine grinding for liberation of valuable minerals. Flotation techniques which produce small bubbles could enhance the separation of the minerals. It has been shown that the bubble size plays an important role in the flotation recovery of fine particles (1). Fine particles float better with small bubbles. As the bubble size decreases the probability of particle-bubble collision (and hence flotation separation) increases. Electroflotation or (perhaps, better) electrolytic flotation is an unconventional separation process owing its name to the bubbles generation method it uses, i.e., electrolysis of the aqueous medium (Scheme 1). Two electrochemical factors of practical importance in flotation of minerals are the pulp potential and galvanic interactions and may be this was the reason

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electroflotation was tried to pyrite. This technique was compared with the other better established (2).

According to the specific technique used for the generation of the necessary, for flotation, bubbles; for flotation two broad categories exist:

- dispersed-air flotation (or froth flotation, for minerals), and
- dissolved-air flotation, being applied to water.

Electroflotation (denoted hereafter as EF) is usually included in the first category. Generally, flotation requires smaller tanks and produces better treated water quality, compared to sedimentation.

The term micro-flotation was used by another scientist for a similar technique to intensify separation of a previously flocculated emulsion (3). The water phase with residues of oil flocs was passed into a flow-type electrolyzer with insoluble electrodes, where it was saturated with microbubbles of electrolysis gases. The chemical reactions taking place at the anode are given as follows.

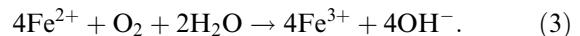
For an iron anode, for example:



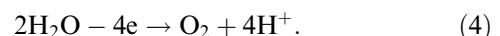
at alkaline conditions:



while at acidic conditions:



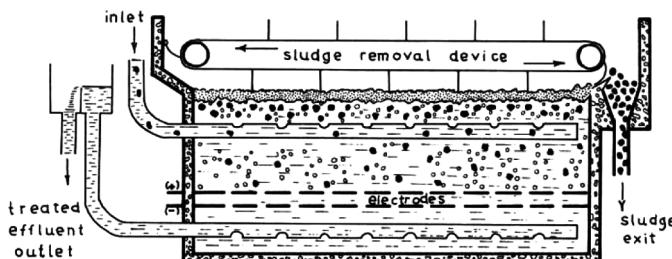
In addition, there is the oxygen evolution reaction:



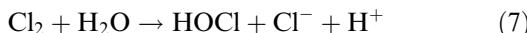
The reaction at the cathode is:



When there are chlorine ions (i.e., seawater), there are more reactions taking place:



SCH. 1. Schematic representation of an electroflotation unit.



When an effluent is brought between two electrodes, of which one is the positive anode and the other is the negative cathode, and electricity is supplied to the electrodes, an electric field is built up between them through the use of the suspension conductivity. Even without any other addition of chemical reagents, a preliminary coagulation occurs within the particulate matter of the effluent, which results in the grouping of the negative and positive particles together.

Furthermore, with the decomposition of water into its constituents, free atomic oxygen is evolved in the diffusion layer of the anode. It is carried by convection into the waste water and immediately combines with the present organic and inorganic constituents, resulting in its oxidation. In a similar manner, there is also a transformation brought about by the electrically excited hydrogen, resulting in reduction of the contained constituents, as suggested in other review papers (4). The principle of electrolyzing sea water, i.e., using sea water in order to influence the conductivity of the dispersion during electrolytic flotation, is quite interesting. During electrolysis, alkalinity is created at the cathode (i.e., if separated electrodes were used), and phosphorus can be precipitated together with flocculent magnesium hydroxide. It is noted that phosphate supply is a limiting factor in algae growth.

It is true that the technique of electroflotation largely originated in the ex-USSR; as it was seen in a series of papers (that were later translated), with the application for instance of the clarification of grape liquor, and the treatment of sewage waters and effluents from the electrochemical treatment of metals (5). Various designs of the flotation cell were then proposed including the idea of consumable anodes. The operation of other electrochemical processes accompanying EF and taking place simultaneously with the main process, namely electrodialysis,

electrophoresis, electrocoagulation etc. was presented by Romanov during a summer school (6).

Work followed in various countries and specific patents appeared at the patent in Reference (7). EF was effectively used to separate chromate oxyanions, a toxic water pollutant (8), also, the removal of metal ions from dilute aqueous solutions or effluents, such as in the examination of a multi-component system consisting from ferrocyanides, oxy-quinolates and hydroxides of metals by Nebera and co-workers (9). It is known today that electroflotation has certain advantages when it is compared with other flotation techniques (10). Photographs of the EF constructed cells were later presented (11).

The electrode system and mainly a dimensionally stable oxygen evolution anode is the most important part and thus, considered as the heart of an EF unit (12). A compact electroflotation device, followed by a sand filter, was used to remove Ni, Zn, Pb, Cu/CN in polluted groundwater obtained from directly under a contaminated site (13).

If one has a search Wikipedia on the internet, one can find the term "water war" classified as a colloquial term often used to describe an armed conflict motivated around the use or possession of water resources within a state's boundary or between two or more states. Apart from water scarcity, creating also desertification, there is a lot of water that needs to be treated, for example in China, where between 200–300 million people throughout the country-side do not have access to a safe source of water (14). People in developing countries get their water often from rivers or wells with elevated concentrations of heavy metals, such as arsenic, as in Bangladesh. Maybe the aforementioned justify this manuscript effort. Further, a new interest in the technique has recently been shown in the literature.

## RECENT WORK

Perhaps, a common application of flotation is to oil effluents, due obviously to density reasons and here we are talking about a large quantity of effluents. Many techniques are available including a variety of filters, chemical dosing, and reverse osmosis, gravity separation, ultrafiltration, microfiltration, biological process, flotation, membrane bioreactor, carbon adsorption, chemical coagulation, electrocoagulation, electroflotation, etc., for the separation of oil–water emulsions. The advantages and disadvantages of these processes were summarized (15) and the latter method was tested in a batch cell with a set of perforated aluminium electrodes.

Similar electrodes were used elsewhere (16). Wastewater from dyeing and finishing processes in the textile manufacturing industry constitutes a substantial source of pollution, which exhibits intense color, high chemical oxygen demand, fluctuating pH, and suspended particles. Indeed, the textile industry utilizes about 10,000 pigments or dyes,

but most of them are substances toxic to human and aquatic life; it was reported that up to 15% of the dyes used are released into wastewaters.

As fats and proteins are partially hydrophobic they can be easily separated by flotation rather than sedimentation, so EF was tried with satisfactory results. The existing technologies for tannery effluents were said to be inadequate to separate low-density colloidal size suspended solids (17).

The production of clarified and stable apple juice is a subject of interest for the beverages industries. The clarification step which remained long discontinued implied the addition of a large quantity of pectolytic enzyme and of clarifying agents to the freshly pressed juice, to induce the precipitation of proteins and other suspended matter; fining treatments were followed by a separation step usually consisting of decantation and classical filtration on filter-press, or flotation by dispersed gas. The development of membrane separation processes (to replace the traditional approach) has enabled the automation of the whole production and in a considerably shorter time (18). The use of gelatin in combination with EF was found to aid the clarification process.

The coagulation-electroflotation process was used to treat paper industry effluents which contain an important rate of suspended solids (19). The methodology of experimental research with an orthogonal central composite design was adopted; the regression equations obtained was optimized to find the best conditions of treatment in batch mode. Tests of treatment in continuous mode were then carried out successfully by determining the optimal residence time of the effluents to be treated. Based on hydrodynamics and purification efficacy in static membrane flotation experiments, the integrated flotation unit combining co-current membrane flotation and countercurrent electroflotation treatment was designed.

The most widely used methods, such as traditional coagulation, flotation, adsorption, and chemical oxidation or a combination of these were said to be insufficient for laundry wastewater treatment (20). Because of the large variability of the amount and composition of laundry wastewater (in Taiwan), developing a new treatment method was necessary. The experimental results showed that the removal efficiency was better, reaching to about 62% when applying ultrasound to the electrocoagulation cell. The performance of the monopolar connection of electrodes was better than that of the bipolar connection in that work.

The aim of another paper was to develop an electroflotation/electrocoagulation cell to study the combined process and the influence of some relevant parameters, such as collector concentration, tension, and current density variation, on the removal of zinc from synthetic solutions (21). The removal of heavy metals from dilute aqueous solutions is often not acceptable using classical

methods, which do not achieve levels in accordance with environmental quality standards.

Use of effective technologies for the treatment of wastewaters containing heavy metals will allow creating water recycling systems for the industrial facilities. That will help to save wastewater discharge fees and freshwater supply payments (22). That article presented a study of wastewater treatment efficacy with flotation and membrane filtration for copper cations removal. Since ceramic membranes were used as air diffusers, this method of flotation treatment was called membrane flotation; the reverse osmosis and nanofiltration techniques were studied too.

A Ti/Pt-IrO<sub>2</sub> electrode, as anode, was tested for anaerobic digestion effluents (23). The anaerobic digested effluents typically contain high amounts of ammonia, phosphate, total suspended solids, and persistent organic substrate; they have been used as fertilizers for recycling nutrients in agricultural fields, but their excessive application is the probable cause of nitrogen pollution in farming areas.

Leachate has a complex structure and high pollutant load, and its treatment is quite hard to supply the discharge standards. Therefore, many pretreatment and combined treatment methods have been proven to treat leachate (24). In this paper, treatment of leachate by electrocoagulation was investigated in a batch process. Moreover, process economy is as important as removal efficiencies during the process evaluation task; various direct and indirect cost items including electrical, sacrificial electrodes, labor, sludge handling, maintenance, and depreciation costs have been considered in the calculation of the total cost (25).

A 20 L external-loop airlift reactor was used as an electrochemical cell in order to carry out water depollution using batch electrocoagulation without mechanical agitation, pumping requirements, or air injection (26). Mixing and complete flotation of the pollutants were achieved using only the overall liquid recirculation induced by H<sub>2</sub> micro-bubbles generated by water electrolysis. A red dye from the Moroccan textile industry was used in a case study to validate this innovative application of these reactors.

The combined electrocoagulation and electroflotation process was shown to remove fluoride from drinking water effectively; the energy consumption was also discussed (27). Long-term consumption of water containing excessive amounts of fluoride has detrimental effects on the human body. Adsorption is effective in defluoridation, but its operation was argued to be complex. The membrane processes also are known to be effective means for defluoridation; nevertheless, a common problem is their poor selectivity. They are suitable for treatment of brackish water containing high content of fluoride, which needs both defluoridation and desalination simultaneously.

The conventional technology for treating wastewater from industrial Cu production, which consists of lime

neutralization/FeCl<sub>3</sub> coagulation and flocculation, does not satisfy the requirements for direct wastewater discharge. The residual selenium concentration, the large sludge quantities generated as well as the expense of reagents were just some of the shortcomings of this technology. To combat these problems, a new hybrid process combining electrocoagulation and microfiltration was drawn up and verified in experiments (28).

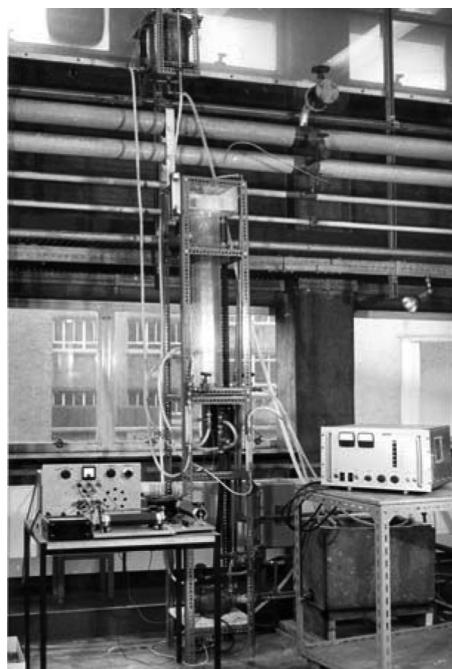
The two main bubble generation techniques were examined and compared in a review (29). Dissolved-air flotation, which is the established technique in water treatment, is quite different as shown from the dispersed-air flotation one; the bubbles size produced during EF was also commented upon. Muller (30) stated that for the 21st century electroflotation would be among the key electrochemically based technologies.

### TYPICAL RESULTS

The flotation cell used in the bulk of this reported work consisted of a vertical Perspex tube (150 mm diameter and 1 m effective height). Sample points were fitted at intervals up the column and various electrode configurations could be mounted on its flanged base. The electrodes used for batch operation of the column comprised two horizontal, circular stainless steel discs equal to the column diameter. The lower electrode, the cathode, was made of sheet steel and the anode, mounted above and parallel to it, was perforated to allow the upward passage of gas bubbles from the cathode (10).

The rig (see also Scheme 2) could be simply modified for continuous operation by the provision of an external pumped circuit feeding the test effluent to a point near the electrodes, designed in such a way to minimise entry turbulence in the cell. A constant head tank was added in the arrangement for the introduction of the feed. An overflow weir at the top of the column collected the thickened solids and the treated liquid effluent could be withdrawn continuously from a point just below the weir. A minimum suspended solids removal of 90% was obtained, with a flow rate of 5 cm<sup>3</sup> s<sup>-1</sup>. Modifications/alterations of the above arrangement will be briefly described in the following.

The experimental programme, carried out (during the seventies) in the then Chemical Engineering Department of the University of Newcastle upon Tyne, U.K., investigated some of the key parameters of electroflotation. The choice of electrolyte to render the solution conducting was made by considering the results obtained from runs carried out with an initial paint concentration of 1,000 mg L<sup>-1</sup> at a current density of 100 A m<sup>-2</sup>. As a result, 0.1% sodium chloride was added to the paint effluent used in subsequent work, which proceeded to investigate the effect of current density and initial paint concentration on the flotation performance. Samples were withdrawn as a function of time throughout the runs and



SCH. 2. Photograph of the EF laboratory rig (at Merz court); at the right, in front of the feed tank is the transformer/rectifier used with the bipolar electrodes.

at the end of each experiment the paint had separated at the top of the column into a well-defined layer. This floated layer was very stable and showed no tendency to remix with the clear solution below when the current was switched off. The thickness of the layer (between 25–50 mm) depended upon the current density employed, the greater thickness corresponding to higher current densities at the electrodes.

Analysis using a Unicam spectrophotometer with a 10 mm glass cell and a wavelength of 430 μm was found to be convenient and reproducible; the small samples necessary could be withdrawn from the column with the minimum of disturbance.

Another laboratory-prepared sample, which was an emulsified oil-water dispersion, has been tested. A machine cooling oil (Revol oil) was used. The oil contained an emulsifier, and when it was diluted in water, it gave a very stable white emulsion. In this way, the effectiveness of the electrolytic flotation as a liquid/liquid separation method, and mainly its applicability on emulsions was examined. In this case, much lower initial concentrations were suitable (on the order of 100 mg L<sup>-1</sup>) for satisfactory flotation removal. The chemical analysis was by the spectrophotometer at 225 mμ wavelength (and silica cells) for the chromophoric groups of the hydrocarbons.

Batch flotation tests were used to obtain data to evaluate a continuous flow electroflotation unit, to foresee the way it should work and predict the expected result. The

basic information desired from the batch tests included answers to questions including the following (10a):

1. Will the material being considered float?
2. How rapidly will it float?
3. What kind of electrodes does it need?
4. What degree of effluent clarification can be expected?
5. What will be the rate of flotation?
6. How do changes in current density and feed concentration influence these answers?

The answers to these questions are important when one is considering the design of a flotation equipment for a particular application. Attention should be paid on the possible sensitivity of the process with respect to each application.

Before a viable electroflotation process could be developed it is necessary to find electrode materials of adequate mechanical and electrical properties with an extended lifetime. The basic requirement for the electrodes is to evolve very fine bubbles by electrolysis of the influent fluid. To accomplish this in practice a number of criteria must be satisfied:

1. no electrode corrosion,
2. avoidance of scaling,
3. capability of operating perhaps at high current densities, and
4. should not produce objectionable gaseous products.

Typical batch results are shown in Fig. 1, where three different current densities were examined. Flotation retention time was found to decrease by increasing current density or decreasing the initial paint concentration. It is worth noting here that the higher current densities, although they lead to higher achievable removal rates, simultaneously introduce increased operating costs, so it becomes a matter of best optimization.

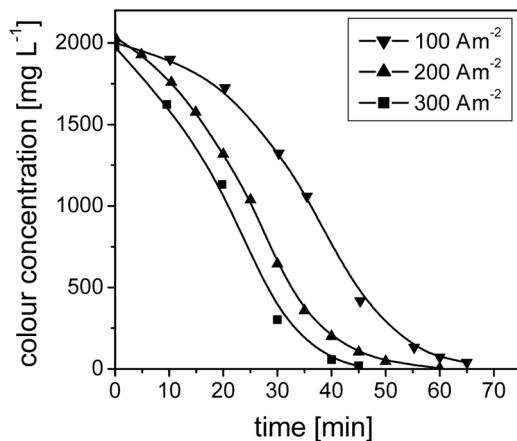


FIG. 1. The effect of current density in EF of a paint emulsion solution.

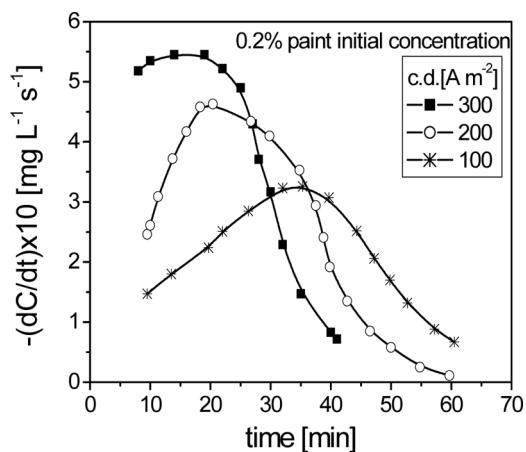


FIG. 2. Variation of flotation rate during a batchwise run.

The families of curves obtained when plotting the flotation rate exhibited an increasing rate of solids removal until about 80% has been removed when the rate falls (Fig. 2); the higher the current density, the greater was the rate of removal. It was observed that the flotation rate reached a maximum, which increased with higher feed concentrations (10b). A constant maximum rate of solids removal was reached at any given current density.

The effect of the initial pH value on electrolytic flotation is quite critical, as in any other flotation technique. The final (treated) paint concentrations of the effluent and the relative retention times have been found to depend strongly on the pH, correlating well with the corresponding values (10a). In this system, flotation removal rates were very high within a narrow pH range and very low outside it. For instance, it was high in a too alkaline solution, with the addition of KOH electrolyte (Fig. 3); in the latter figure, other results were plotted for comparison.

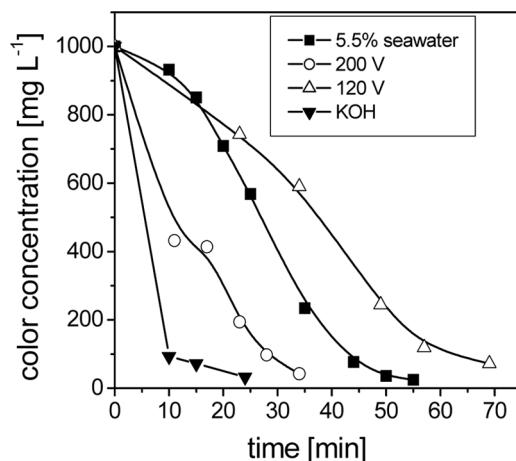


FIG. 3. The addition of electrolytes or the use of bipolar electrodes, at different electrical potential difference.

Increasing the conductivity of the effluent by salt addition decreased the necessary voltage (hence, the power input). Thus power savings, due to increased conductivity, could easily cover the purchasing price of sodium chloride for the 0.1% addition (4a). When increasing the conductivity, attention should be paid to anode corrosion, mainly by the chloride ion.

The running cost of EF is largely a function of the conductivity of the effluent. Of course, there is the possibility of using sea water in combination with the effluent for water or wastewater treatment plants that are located near the coast. The data, for example, from experiments with 0.1% NaCl gave a voltage of around 22 V for an interelectrode gap of 2.54 cm; for a gap of 0.32 cm, a voltage of only 2.8 V was found to be sufficient. The use of a supporting electrolyte is often seen in the literature, too (31). For example, the application of sodium sulphate in this case.

A bipolar arrangement is characterized by the fact that only the terminal electrodes are connected to the source of electric current, while the rest of the electrodes conduct each other through the solution conductivity (10a); some experimental results with this set (at two different voltages) were also presented in Fig. 3. Increasing the power input, the retention time was decreased. It can be seen, however, that the voltage was rather high, although the design could be improved from the initial quite random one, by determining the optimum plate thickness and their spacing.

The two electrodes of the horizontal set, usually applied in EF, could also be separated by a cation exchange membrane, as only one of the previously mentioned gases is usually necessary (10a). In the lower part/separated electrode an electrolyte was circulated to remove the created gas and in the meantime increase the conductivity. The same idea was applied for mineral processing (32); a modified Hallimond tube was used as the bench EF cell.

It was noticed that only one gas (hydrogen) activated the process, when the emulsified oil/water emulsion was studied, while the other acted as a depressor or merely contributed in the transfer of the coagulated matter to the flotation cell surface (Fig. 4). In the meantime, when the separation between the gases was applied, an electricity savings was noticed at laboratory scale. These advances could be achieved on an industrial scale by changing the surface area of the working electrodes, i.e., using electrodes having the shapes of a plate and a rod.

In general, the electric field gradient between the electrodes aids in the flocculation of suspended solids. Furthermore, when an electric current is applied to a dispersion, the oxidation-reduction potential changes depending on the type of electrode treatment. Also, nascent hydrogen and oxygen are highly active and as they attack the solid surfaces, a change in the flotation characteristics of these can be realized. Any one or more of these effects could be operated during EF. These have been described by the general term

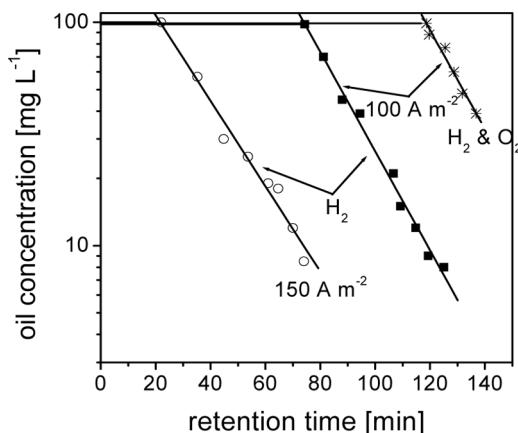


FIG. 4. Separating the electrodes, with a membrane (at different current density): testing with an oil-water emulsion.

electrochemical effect of the process, which is not found in other flotation techniques (33ii). Nevertheless, there should exist a certain differentiation between the previously mentioned electrochemical effects and the application of gas bubbles as the transport medium in the flotation process. The use of flotation cells with consumable anodes is also of interest, since their slow dissolution provides a continuing injection of metal hydrolyzable cations into the system [usually Fe(III) or Al(III)], which then subsequently aids flocculation. More or less, the two processes of electrocoagulation and electroflotation are taking place simultaneously.

The effective EF results obtained have been attributed, among others, to the generation of uniform and tiny bubbles. It is known that the separation efficiency of a flotation process depends strongly on the size of the bubbles. This is because smaller bubbles provide larger surface area for particle attachment. A new method was developed to measure the bubble size distribution, in dissolved-air and induced air flotation, based on the bubbles' capture (without movement) combining microscopy with digital image processing procedures (34). The influence of increasing the saturator pressure (in dissolved-air flotation) on mean bubble size has been a subject of argument in the literature.

Average sizes of as small as 5  $\mu\text{m}$  and as large as 200  $\mu\text{m}$  were reported in different papers dealing with electroflotation (35a). Surprisingly in our case, the bubble size decreased with increased current densities, and at the same time the number of bubbles increased; a direct measurement method was used here. EF bubbles (both hydrogen and oxygen) had a mean diameter of around 50  $\mu\text{m}$ . The data obtained were plotted on normal probability paper, in good agreement with the Gaussian distribution (33i).

## DISCUSSION – PROCESS DEVELOPMENT

The knowledge of the rate at which suspended matter will be separated and floated in a flotation unit is very

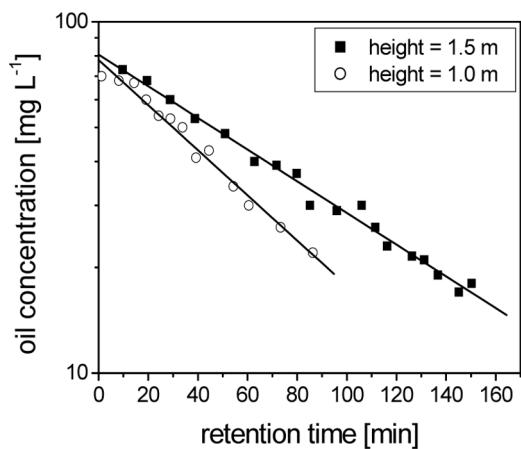


FIG. 5. Batch experiments at a different tank height but also in a pilot plant.

important. Also, an operator should be able to identify the main variables that control this removal rate (4a). The understanding of the process can lead to a substantial improvement in the EF design. A macroscopic approach was followed in the kinetics study. This usually consists of the analysis of suspended matter concentrations as a function of time. It is pointed out, as shown, that the conditions governing the entire period of the batch process were not constant. Figures presenting results of the kinetics study are usually given in a semilogarithmic plot (as Figs. 4 and 5).

It was observed that for most of the experimental time, except perhaps the initial period, the first-order equation, as known from chemical reaction kinetics, could satisfactorily describe the process,

$$\ln(C/C_0) = -k t, \quad (9)$$

where  $k$  denotes the flotation rate coefficient,  $C$  is the concentration at time  $t = t$ , and  $C_0$  at time  $t = 0$ .

Flotation kinetics were previously discussed (36). In batch tests the ratio  $dC/dt$  is a measure of the flotation rate and will be equal to the rate of clarification (in effluent treatment) if the amount of removed constituents (suspended solids or oil) that returns to the solution from the floated layer is negligible. In mineral processing attention was, however paid to the fact that flotation is applied mostly as a selective separation process and that only certain mineral particles (either useful or gangue) have to be transferred towards the slurry surface.

If the same equation is applied to continuous flow experiments, where at the steady state  $dC/dt = 0$ , the aforementioned equation, as it stands and is used in the figures, breaks down. Batchwise tests can be used to gain preliminary information on the flotation characteristics of a system, while continuous flow experiments may give the

final design data. For instance, studying the performance of (dissolved-air) flotation thickeners for waste activated sludge, the negative effects which occurred at laboratory-scale were not found in full-scale experiments which resulted in bubble sizes of 45–60  $\mu\text{m}$  (37).

Another observation is that a deviation was apparent at the start of batch EF experiments, where a retardation appeared. Nevertheless, this fact was expected to be overcome during continuous flow. This period, which was explained as the time needed for destabilization of the treated dispersion, was affected by the current density and the added chemical or other flocculent concentrations. As it was shown rather clearly, the application of a common cationic polyelectrolyte reduced the necessary retention time, producing also cleaner effluent; these experiments took place at a larger scale (4a). The scale-up was on the order 1:21.8, where the relative calculations were based on the different tank surfaces; a horizontal set of electrodes was used with platinum expanded mesh as anode and stainless steel 304 sheet as cathode. In the larger scale the same kinetic pattern was followed, although with increased retention times.

The principles of scale-up in chemical technology are generally rather well established. This knowledge would not only benefit operation and prediction, but also electroflotation plant design, placing it on a more concrete basis, and thus reducing the excessive reliance on costly trial-and-error development of new and improved units. Experiments also were carried out at varying tank depth (height). In Fig. 5 some of the results for oil/water emulsion treatment are presented, using EF.

The flotation rate was calculated from the respective chemical kinetics equation as a function of retention time, enabling the flotation rate to be presented in figures or used in calculations. A constant maximum rate of solid removal was reached at any given current density (10b). There was, however, a limited concentration of the dispersion system to be treated in the flotation cell, above which the unit was not actually in operation, i.e., the generated bubbles were only helping to mix the liquid.

An investigation of hydrodynamics was also undertaken, as the efficiency is expected to be a function of the residence time distribution (35b). The stimulus-response technique was used in this experimentation. The tracer input signal was an electrolyte and had the form of a step function. Assuming that the flow regime was composed of various flow types, a theoretical multiparameter model, known from Levenspiel (and Chemical Reaction Engineering), was applied, and the experimental data of EF were fitted accordingly; the age distribution function,  $I$ , was used as given by:

$$I = \frac{Q_1}{Q} \exp \left\{ -\frac{Q_1}{Q} \frac{V}{V_B} \left( \theta - \frac{V_p}{V} \frac{Q}{Q_1} \right) \right\} \quad (10)$$

where  $Q_1$  is the flowrate of the dispersion (effluent) passing through the tank,  $Q$  is the total volumetric flowrate of the feed,  $V$  is the total volume of the flotation cell,  $V_B$  is the backmix flow volume,  $V_p$  is the plug flow volume, and  $\theta$  is the dimensionless time, i.e., the time divided by the mean residence time ( $T = V / Q$ ) of the effluent in the vessel; the above equation can then be rearranged.

A flotation unit is fundamentally a form of reaction vessel, with a separation occurring instead of a chemical reaction. Consequently, a detailed knowledge of the flow characteristics involved in a particular tank may be expected to comprise an important feature of its design. The advantages of different operation modes in continuous flow have also been discussed; it was found that the plug flow region was about the same for both operation modes, countercurrent and co-current, in relation to the bubbles rise. It was arranged by varying the inlet port of the feed near the top of the tank or at the bottom near the electrodes, respectively. As might be expected, differences were noticed in the mixed flow and dead-water regions, while no bypass was found. In the countercurrent flow, there was more backmix flow (~87.7%), while in the co-current operation, a stagnant region appeared (~6.7%) (4a).

A simple equation was subsequently used to describe the process in continuous operation, based also on the assumption of a first-order kinetics equation. Under steady-state conditions, a mass balance was computed around the EF vessel:

$$r = Q_{in}C_i - Q_{out}C = k_i/CV \quad (11)$$

where  $r$  is the overall flotation rate,  $Q$  is the volumetric flowrate,  $C_i$  and  $C$  are the inlet and exit concentrations, respectively, and  $k_i$  is the flotation rate constant; the latter is really a complex function of various parameters, e.g., the particle and bubble size, the particle characteristics, the concentration of collector, if applied, etc. This equation, which was suitably rearranged, gave promising results in comparison with the experimental data (35b).

The inherent assumption in the mass balance equation was that the concentration was independent of the distance, a principle that holds for a perfectly mixed vessel. A regression analysis of these equations for the two different dispersion applications gave significant results. Therefore, within the range investigated, these assumptions were quite well justified. The significance of this work is that the effluent concentration from the electroflotation unit could be foreseen with reasonable approximation as a function of the feed concentration entering the unit, if the other operating parameters (i.e., flow rate, current density) are kept stable. Finally, if the outlet concentration is expressed or known (for instance, the limit imposed by the Water Control Authorities), it is then possible for the optimum flow rate to be predicted by calculation.

The same analysis was applied to the results on thickening of activated sludge by Yongacoglou (in her 1974 report), with certain necessary assumptions (see Fig. 6). The nearest current density was taken from the corresponding batch tests for the calculation of  $k_i$ . Another assumption referred to the mean holding time, calculated as the ratio of sludge height over the overflow rate, and also, as before, the gas flow rate used for flotation (which is surely much smaller than the effluent throughput) will carry the particulate matter over the weir and no liquid will be lost. Although there were some apparent discrepancies in the relation, the positive conclusion was that always the calculated exit concentrations were greater than the respective experimental ones. Therefore, the applied model represented a simple and reasonable tool in electroflotation treatment.

An economic comparison was given (in the form of a table) with the relative costs of EF vs. dispersed-air flotation for the same laboratory application (4a). A comparison of running expenses between flotation systems by Gardner (38) showed that electroflotation requires significantly less power on units of  $5\text{ m}^2$  area or less, i.e., units able to accept flows in the range up to  $13.9\text{ m}^3\text{ s}^{-1}$ . The advantage decreases with an increase in the size of the cell.

Elsewhere (39), in another comparison, EF clearly showed advantages over either dissolved-air flotation, settling or (the so-called) impeller flotation. Observations as far as the surface load of flotation cells is concerned were reported for the separation of activated sludge during continuous flow experiments (40). Comparing them with the dissolved-air flotation results, it was clear that the laboratory scale electroflotation procedure was very satisfactory, offering a growing field of applications. Furthermore, a re-evaluation between the efficiency and the relevant cost was proposed.

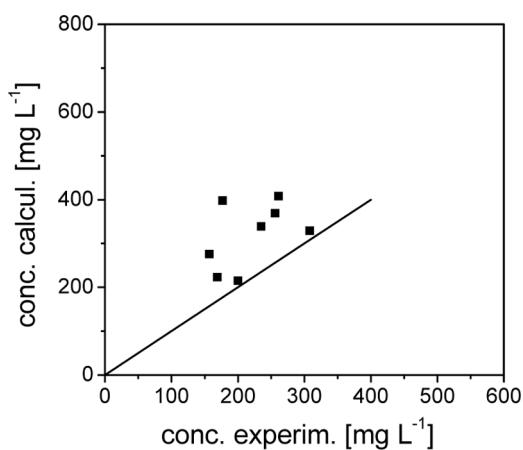


FIG. 6. The mass balance model for EF continuous flow of sludge thickening: experimental vs. calculated effluent concentrations (Yongacoglou's results).

In conclusion electroflotation offers certain advantages over other flotation techniques of bubble generation (dispersed-air or dissolved-air). Among others, the following points are perhaps the most important.

1. The electrode grids can be arranged to provide good coverage of the whole surface area of the flotation tank, avoiding any bypass.
2. The electric field gradient between electrodes aids flocculation and flotation, even without the presence of any surfactant.
3. Gas production (evolution), flotation time, and the other operating conditions can be checked quickly and are relatively easily controlled.
4. The equipment is reliable and safe in operation.
5. Ionic strength of the effluent solution (slurry) to be treated is not a crucial parameter, as in the other flotation techniques.
6. By-product recovery is a potentially profitable aspect of electroflotation treatment, so proteins, fats, oil, organics, but also toxic or valuable metals could be recovered from waste streams, especially when no other chemical reagents (like surfactants) are added to help the pollutant separation.

A new interest on the technique has been recently shown in the literature, with preliminary work presented in some of them. Perhaps with the progress in electrochemistry in the last few decades, including suitable electrode materials and hence possibly in designing a more suitable EF cell, the process and the aforementioned results can be looked at again from a new and better position.

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## REFERENCES

1. Kydros, K.A.; Gallios, G.P.; Matis, K.A. (1994) Electrolytic flotation of pyrite. *J. Chem. Tech. Biotechnol.*, 59: 223–232.
2. Matis, K.A.; Gallios, G.P.; Kydros, K.A. (1993) Separation of fines by flotation techniques. *Sep. Tech.*, 3: 76–90.
3. Rulyov, N.N. (1999) Hydrodynamic destruction of waste emulsions in the process of their separation through ultra-flocculation and micro-flotation. *Coll. Surf. A*, 151: 11–15.
4. (a) Matis, K.A.; Zouboulis, A.I. (1995) Electrolytic Flotation: An Unconventional Technique. In: *Flotation Science and Engineering*, Matis, K.A., ed., Dekker: New York, 385–413; (b) Matis, K.A.; Gallios, G.P. (1986) Dissolved-air and Electrolytic Flotation. In: *Mineral Processing at a Crossroads*, Wills, B.A.; Barley, R.W., eds.; Martinus Nijhoff: Dordrecht, 37–70.
5. Kharlan, N.G.; Mamakov, A.A.; Yagubets, A.N.; Karyakin, V.V. (1969) Electroflotation purification of the working liquid during electrochemical treatment of metals. *Elektronnaya Obrabotka Materialov*, 5 (29): 47–51; Mamakov, A.A. (1968) Electroflotation clarification of grape liquor (survey). *ibid.*, 3 (21): 78–86; Matov, B.M. (1966) Consumable-anode electroflotation cell. *ibid.*, 4: 94–96 (Translated as *Applied Electrical Phenomena*).
6. Romanov, A.M. (1998) Electroflotation in Waste Water Treatment: Results and Perspectives. In: *Mineral Processing and the Environment*, Gallios, G.P.; Matis, K.A., eds.; Kluwer: Dordrecht, 335–360.
7. Raworth, Moss & Cook, Improvements in Processes for the Flotation Separation of a Liquid from a Solid or an Immiscible Liquid in Suspension. U.K. Patent 1,194,850, appl. 14 June 1967.
8. Zouboulis, A.I.; Matis, K.A. (1989) Electrolytic flotation of chromium from dilute solutions. *Envir. Tech. Let.*, 10: 601–612.
9. Nebera, V.P.; Zelentsov, V.I.; Kiselev, V.A. (1980) Electroflotation of ions from Multicomponent Systems. In: *Fine Particles Processing*, Somasundaran, P., ed.; SME-AIME: New York, 886–894.
10. (a) Matis, K.A. (1980) Treatment of industrial liquid wastes by electroflotation. *Wat. Pollut. Control*, 79: 136–142; (b) Backhurst, J.R.; Matis, K.A. (1981) Electrolytic flotation in effluent treatment. *J. Chem. Tech. Biotechnol.*, 31: 431–434.
11. Matis, K.A. (1992) Electrolytic Flotation. In: *Innovations in Flotation Technology*, Mavros, P.; Matis, K.A., eds.; Kluwer: Dordrecht, 301–304.
12. Chen, G. (2004) Electrochemical technologies in wastewater treatment. *Sep. Purif. Tech.*, 38: 11–41.
13. Poon, C.P.C. (1997) Electroflotation for groundwater decontamination. *J. Hazardous Mater.*, 55: 159–170.
14. Anon. (2009) Cash flows from China's water. *Chem. Eng. News*, 87 (19): 18–21.
15. Bande, R.M.; Prasad, B.; Mishra, I.M.; Wasewar, K.L. (2008) Oil field effluent water treatment for safe disposal by electroflotation. *Chem. Eng. J.*, 137: 503–509.
16. Belkacem, M.; Khodir, M.; Abdelkrim, S. (2008) Treatment characteristics of textile wastewater and removal of heavy metals using the electroflotation technique. *Desalination*, 228: 245–254.
17. Murugananthan, M.; Raju, G.B.; Prabhakar, S. (2004) Separation of pollutants from tannery effluents by electro flotation. *Sep. Purif. Tech.*, 40: 69–75.
18. Araya-Farias, M.; Mondor, M.; Lamarche, F.; Tajchakavit, S.; Makhlof, J. (2008) Clarification of apple juice by electroflotation. *Innovative Food Sci. Emerging Tech.*, 9: 320–327.
19. Ben Mansour, L.; Ksentini, I.; Elleuch, B. (2007) Treatment of wastewaters of paper industry by coagulation-electroflotation. *Desalination*, 208: 34–41.
20. Wang, C.-T.; Chou, W.-L.; Kuo, Y.-M. (2009) Removal of COD from laundry wastewater by electrocoagulation/electroflotation. *J. Hazardous Mater.*, 164: 81–86.
21. Casqueira, R.G.; Torem, M.L.; Kohler, H.M. (2006) The removal of zinc from liquid streams by electroflotation. *Miner. Proces.*, 19: 1388–1392.
22. Sudilovskiy, P.S.; Kagramanov, G.G.; Kolesnikov, V.A. (2008) Use of RO and NF for treatment of copper containing wastewaters in combination with flotation. *Desalination*, 221: 192–201.
23. Lei, X.; Maekawa, T. (2007) Electrochemical treatment of anaerobic digestion effluent using a Ti/Pt-IrO<sub>2</sub> electrode. *Bioresource Tech.*, 98: 3521–3525.
24. Ilhan, F.; Kurt, U.; Apaydin, O.; Gonullu, M.T. (2008) Treatment of leachate by electrocoagulation using aluminum and iron electrodes. *J. Hazardous Mater.*, 154: 381–389.
25. Kobya, M.; Bayramoglu, M.; Eyyaz, M. (2007) Techno-economical evaluation of electrocoagulation for the textile wastewater using different electrode connections. *J. Hazardous Mater.*, 148: 311–318.
26. Essadki, A.H.; Bennajah, M.; Gourich, B.; Vial, Ch.; Azzi, M.; Delmas, H. (2008) Electrocoagulation/electroflotation in an external-loop airlift reactor-Application to the decolorization of textile dye wastewater: A case study. *Chem. Eng. Proces.*, 47: 1211–1223.

27. Zuo, Q.; Chen, X.; Li, W.; Chen, G. (2008) Combined electrocoagulation and electroflotation for the removal of fluoride from drinking water. *J. Hazardous Mater.*, 159: 452–457.

28. Mavrov, V.; Stamenov, S.; Todorova, E.; Chmiel, H.; Erwe, T. (2006) New hybrid electrocoagulation membrane process for removing selenium from industrial wastewater. *Desalination*, 201: 290–296.

29. Matis, K.A.; Lazaridis, N.K. (2002) Flotation techniques in water technology for metals recovery: Dispersed-air vs. dissolved-air flotation. *J. Min. Metall. A*, 38: 1–27.

30. Muller, K. (1992) Electroflotation from the Double Layer to Trouble Waters. In: *Electrochemistry in Transition*, Conway, B.E.; Murphy, O.J.; Srinivasan, S., eds.; Plenum: New York, 21–37.

31. Khelifa, A.; Moulay, S.; Naceur, A.W. (2005) Treatment of metal finishing effluents by the electroflotation technique. *Desalination*, 181: 27–33.

32. Ketkar, D.R.; Mallikarjunan, R.; Venkatachalam, S. (1991) Electroflotation of quartz fines. *Int. J. Miner. Proces.*, 31: 127–138.

33. Matis, K.A. (1980) (i) Bubble measurements in electrolytic flotation (Short paper). *Chim. Chron. (New Ser.)*, 9 (1): 71–76; (ii) Matis, K.A. (1980) Electrolytic flotation in industrial effluent treatment. *ibid.*, 11 (2): 159–171.

34. Rodrigues, R.T.; Rubio, J. (2003) New basis for measuring the size distribution of bubbles. *Miner. Eng.*, 16: 757–765.

35. (a) Matis, K.A.; Backhurst, J.R. (1984) Laboratory Studies of Electrolytic Flotation as a Separation Method. In: *Solid-Liquid Separation*, Gregory, J., ed.; Ellis Horwood: London, 29–40; (b) Matis, K.A.; Mavros, P. (1991) Foam / froth flotation: Part II. Removal of particulate matter. *Sep. Purif. Methods*, 20: 163–198.

36. Ek, C. (1992) Flotation kinetics. In: *Innovations in Flotation Technology*, Mavros, P.; Matis, K.A., eds.; Kluwer: Dordrecht, 183–209.

37. de Ruk, S.E.; van der Graaf, J.H.J.M.; den Blanken, J.G. (1994) Bubble size in flotation thickening. *Wat. Res.*, 28: 465–473.

38. IChemE (1975) *The Application of Chemical Engineering to the Treatment of Sewage and Industrial Liquid Effluents. Symp. Ser. 41*, Univ.; York.

39. Il'in, V.I.; Sedashova, O.N. (1999) An electroflotation method and plant for removing oil products from effluents. *Chem. Petrol. Eng.*, 35 (7–8): 480–481.

40. Mayer, J.; Zhang, L.; Hahn, H.H. (1990) Liquid-solid Separation by Electro-flotation: An Attractive Alternative to Dissolved-air Flotation. In: *Chemical Water and Wastewater Treatment*, Hahn, H.H.; Klute, R., eds.; Springer-Verlag: Berlin, 151–159.