

# **INDUSTRIAL WASTEWATER CLEANUP**

**Recent Developments**

**Albert Yehaskel**

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# FOREWORD

The detailed, descriptive information in this book is based on U.S. patents, issued since January 1977, that deal with recent developments in industrial wastewater cleanup.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. patent literature in this field. By indicating all the information that is significant, and eliminating legal jargon and juristic phraseology, this book presents an advanced, technically oriented review of recent developments in industrial wastewater cleanup.

The U.S. patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial, timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure." These patents include practically all of those issued on the subject in the United States during the period under review; there has been no bias in the selection of patents for inclusion.

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially useful information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development. The information contained in this book will allow you to establish a sound background before launching into research in this field.

Advanced composition and production methods developed by Noyes Data were employed to bring this durably bound book to you in a minimum of time. Special techniques are used to close the gap between "manuscript" and "completed book." Industrial technology is progressing so rapidly that time-honored, conventional typesetting, binding and shipping methods are no longer suitable. We have bypassed the delays in the conventional book publishing cycle and provide the user with an effective and convenient means of reviewing up-to-date information in depth.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor and patent number help in providing easy access to the information contained in this book.

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# INTRODUCTION

In the next few years, water will certainly be regarded with increasingly greater respect. The Environmental Protection Agency and the Federal Water Pollution Control Act will both have a tremendous impact in all industries that pour forth polluted or untreated water to our waterways and streams.

By 1984, the Environmental Protection Agency's best-available-technology standards are slated to go into effect. Until then, many industries have already begun and many more will begin the massive task of implementing today's technologies in the design of treatment plants. In some cases, the treatment plants more than meet the EPA's stringent rulings.

For example, some pharmaceutical manufacturing plants have already implemented facilities for purifying effluents and recycling the water for continuous use. This process alone has saved them a huge water bill and in a few years the savings will pay for the facilities. Furthermore, the paper industry has spent over \$3 billion to add end-of-pipe effluent treatment systems and other pollution control equipment to its pulp and paper mills.

Many towns and boroughs throughout the country are reporting water contamination in their wells due to underground leaching. These municipalities are now employing or intend to construct water treatment facilities to take care of this problem. Purification by filtration, activated carbon and other advanced techniques will be the most widely used techniques for treating raw water.

There is very little doubt that many of the ills caused by water pollution will have to be treated with new technology and more stringent laws.

This book gives the reader an in-depth look at over 275 methods, processes, new apparatuses and applications as exemplified by the patent literature of the last two years. Many of these methods and procedures have achieved wide industrial application in the abatement of water pollution.

# SOLID-LIQUID SEPARATION PROCESSES

## FLOCCULATION AND COAGULATION

### Ultrasonic Wave Treatment

A. Porath-Furedi; U.S. Patent 4,055,491; October 25, 1977 describes an apparatus and method for using ultrasonic waves for removing microscopic particles from a liquid medium, such as algae from a solar or refuse pond, or blood cells from blood. The apparatus includes an ultrasonic generator propagating ultrasonic waves of over one megacycle per second through the liquid medium to cause the flocculation of the microscopic particles at spaced points.

In two cases, the ultrasonic waves are propagated in the horizontal direction through the liquid medium, and baffle plates are disposed below the level of propagation of the ultrasonic waves. The baffles are oriented to provide a high resistance to the horizontal propagation of the ultrasonic waves and a low resistance to the vertical settling of the flocculated particles.

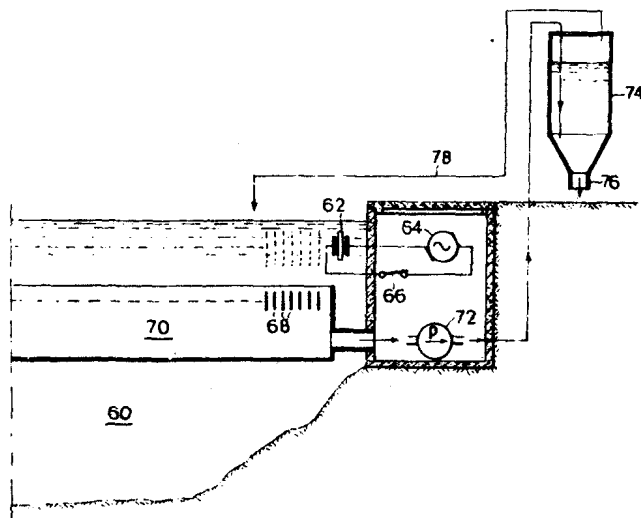
The ultrasonic generator is periodically energized to flocculate the particles, and then deenergized to permit the settling of the flocculated particles through the baffle plates from where they are removed. The following represents one of many useful applications of this process.

Figure 1.1 illustrates the process utilized in a system for removing algae growing in a pond. This application is particularly of potential commercial importance because of recent work directed towards the utilization of solar energy for growing algae, particularly *Dunaleilla*, in solar ponds for producing fuel, and for growing other algae in other ponds for producing food protein.

Another possible application is in the reclamation of water and/or protein from refuse where, according to one system, algae is grown in a sludge pond and must be separated in order to reclaim the water and/or protein. The pond illustrated in Figure 1.1 is generally designated 60 and may be a natural pond, or an artificially created one, filled with water exposed to solar radiations. Where the

algae is to be grown and harvested for fuel or protein production, the pond would be a solar pond filled with salt water. Where water (or protein) is to be reclaimed, it would be a sewage pond. It has been found that the growth of algae can be promoted in the pond usually at a level slightly below the upper surface of the pond. The ultrasonic wave generator 62 would be immersed in the pond at the level of growth of the algae to propagate ultrasonic waves in the horizontal direction. The generator is driven by an oscillator 64 and its energization and deenergization are controlled by a switch 66.

**Figure 1.1: Application of Ultrasonic Wave Treatment in Removing Algae**



Source: U.S. Patent 4,055,491

Below the level of propagation of the ultrasonic waves are the baffle plates 68 having a high resistance to the horizontal propagation of the ultrasonic waves, and a lower resistance to the vertical settling of the flocculated algae particles. The latter settle in a chamber 70 below the baffle plates 68, and are pumped via pump 72 to a settling tank 74.

The flocculated particles settle at the bottom of the tank and are removed via the lower outlet 76. The water at the top of the tank is removed via a conduit 78 and may be reintroduced back into the pond 60. The algae in the above application have a diameter of 5 to 9 microns; the frequency of the ultrasonic generator 62 is therefore preferably about 2.8 megacycles per second.

### Magnetic Floccs

J.A. Neal; U.S. Patent 4,089,779; May 16, 1978; assigned to Georgia-Pacific Corporation describes a process for the clarification of an aqueous liquid by imparting magnetic characteristics to flocculated particles by addition of a ferromagnetic organic composition to the liquid to associate the ferromagnetic

composition with the flocculated particles. This process is achieved by adding to an aqueous liquid flocculated with a metal hydroxide, a water-soluble ferromagnetic lignosulfonate, ferromagnetic sulfonated tannin, or a ferromagnetic sulfonated phenol condensed with an aldehyde. The ferromagnetic composition is added in conjunction with an insoluble metal hydroxide flocculating agent or compound added for the formation of the insoluble metal hydroxide to flocculate the finely divided particles in the liquid.

The ferromagnetic organic composition becomes associated or combined with the floc or flocculated particles to impart magnetic characteristics to the particles. The flocculated contaminants may then be removed from the liquid by using a magnetic filter or by settling in the presence of a magnetic field which will considerably increase the rate of settlement. The ferromagnetic organic compositions may be prepared by dissolving an iron compound and a lignosulfonate, sulfonated tannin or sulfonated phenol-aldehyde in water, adding 1 equivalent of alkali per equivalent of iron, and reacting the mixture in a manner to permit the formation of magnetite or other magnetic oxides of iron.

The iron compound is dissolved in the water in an amount at least twice the stoichiometric amount of iron, expressed as ferric iron, necessary for reaction with the sulfonate groups of the lignosulfonate, sulfonated tannin, or the sulfonated phenol condensation product. Usually a change in the oxidation state of the iron may be required in the presence of the alkali to obtain the iron in both the ferric and ferrous states in the desired proportions, i.e., approximately those present in magnetite. The following example illustrates the process.

*Example:* An aqueous solution of ferric sulfate and a ferromagnetic lignosulfonate was prepared. The ferric sulfate was added in an amount such that the solution contained 200 ppm of iron. The ferromagnetic lignosulfonate was added in an amount such that the iron content of the lignosulfonate was 11.5 ppm or about 5.7% of the iron content of the ferric sulfate. The pH of the solution of the ferric sulfate containing the ferromagnetic lignosulfonate was raised to pH 8 by addition of sodium hydroxide precipitating the ferric iron as ferric hydroxide.

The sample was placed in a container about 1.25 cm deep which was on top of a permanent ceramic magnet. The magnets produced a magnetic field of about 400 gauss at the surface. The ferric hydroxide precipitate containing the magnetic lignosulfonate settled at a rate of 1.5 cm/min. The same precipitate in absence of the magnetic field settled at a rate of about 0.6 cm/min.

The ferromagnetic lignosulfonate contained 24% iron and exhibited a magnetic attractive force of about 1.25 g/g which was about 48% of the magnetic attractive force obtained with magnetite measured in a magnetic field of about 240 oersteds. The ferromagnetic lignosulfonate was prepared by adding ferrous sulfate to a lignosulfonate solution and adding about 1 equivalent of sodium hydroxide for an equivalent of the iron while the mixture was reacted at 95°C with agitation under atmospheric conditions to oxidize a portion of ferrous iron to ferric iron. After the reaction was completed, additional ferrous sulfate was added followed by sodium hydroxide and heating continued.

### Flocculation by Electrolytic Treatment

*L.P. Casanovas and J.L.J. Vellas; U.S. Patent 4,038,163; July 26, 1977; assigned to Societe d'Etudes et de Diffusion de Procedes et Brevets SA, Switzerland describe a process for purifying an aqueous liquid containing impurities. This method uses a vat provided with metallic electrodes and connected to a circulating pump and to a filter containing at least one filtering layer of low granulometry built up from accumulation of flocculates.*

The process for the electrolytic treatment of aqueous liquids is characterized in that a scattered emission of metallic ions is produced in the aqueous liquid from metallic electrodes submitted to the action of an electric current, the quantity of which, when applied to the electrodes, determines the quantity of ions sent out. Some of the metallic ions sent out are combined with hydroxyl ions which are in the liquid, thus creating colloidal particles having a high absorbing power and causing a fine flocculation.

The fine flocculate is continuously retained during formation in the form of a porous filtering mass of fine flocculate. This is traversed by the liquid still comprising metallic ions. The quantity of metallic ions which is electrically produced is selected to allow penetration of metallic ions through the porous mass in the treated liquid. The treated liquid comprises some free metallic ions raising the resulting electrical potential of the treated liquid in comparison with the potential of the liquid before the metallic ions emission.

According to another important characteristic of this process, the porous mass of flocculate is constituted by impregnating with the nascent flocculate a filtering mass with low granulometry, the flocculate being retained in the filtering mass until it shows a loss of pressure substantially quadruple to the loss of pressure noticed during the beginning of treatment. The filtering mass impregnated with the flocculate forms a self-regulating buffer of the quantity of free metal ions not having caused a flocculation and which are drawn away from the porous mass of flocculate to maintain a high electrical potential of the treated liquid.

### Electrolysis with Aluminum Anode

*A process described by P.A. Valanti; U.S. Patent 4,048,031; September 13, 1977; relates to a method and a device for purifying emulsions and contaminated water with the acid of electrolysis. An arrangement is provided for moving at least one aluminum anode with respect to a cathode, to maintain a fixed determined distance between the anode and cathode.*

An emulsion or contaminated water to be treated is run in the region between the electrodes, and means are provided for preferably running the emulsion or water along the aluminum anode before it reaches the space between the electrodes. The flock is then removed from the resultant flocculated liquid.

### Calcium Chloride

*A process described by R.V. Sebelik and W. Schaefer; U.S. Patent 4,108,768; August 22, 1978; assigned to Winchester Chemical Co., involves removing oils and greases (hexane solubles) and metal ions from laundry waste waters. It has*

been found that when an industrial waste water containing hexane soluble impurities, for example, a laundry waste water, is adjusted in pH to a value of at least 11.6 and calcium chloride is added to that waste water in an amount of at least 1,700 ppm, based on the total weight of laundry waste water, a substantial portion of the hexane solubles will attach to or be incorporated in a metal hydroxide floc.

The calcium hydroxide floc is coagulated or agglomerated by the addition of any well-known metal hydroxide coagulants, such as a high molecular weight polyacrylamide, and the coagulated floc or floc clumps are removed by floc flotation and skimming. The calcium chloride will react at this very high pH to effectively flocculate a substantial portion of the oils and greases (hexane solubles) in addition to a substantial portion of the contaminating metal ions in the laundry waste water. Calcium chloride has been the only chemical found to be effective at this very high pH level of at least 11.6 and it is necessary that the laundry waste water be adjusted in pH to at least 11.6 for the calcium chloride to become effective in clarifying the laundry waste water.

### Manganese and Iron Removal

*R.R. Davis, A.M. Langberg and A.P. Debus; U.S. Patent 4,028,241; June 7, 1977; assigned to Hungerford & Terry, Inc. describe a system for recovering treated water used to backwash and rinse filters used to remove manganese and iron impurities from water. The process provides a recovery basin into which water used to backwash and rinse a manganese oxide filter is deposited. A coagulating agent such as a polyelectrolyte is added to the backwash and rinse water. The coagulating agent and water is agitated in the recovery basin, and then the precipitates or other impurities removed from the filter are allowed to settle to the bottom of the recovery basin.*

The treated water from which the impurities have settled is then returned to the filter inlet and passed through the filter in normal filtering operation so that the water used to backwash and rinse the filter exits from the filtering system as pure treated water. Settling is preferred to other methods for separating the removed precipitates from the backwash and rinse water.

A polyelectrolyte is used because the time required for the precipitates removed from the filter to settle from the backwash and rinse water would be on the order of hours, days or weeks, while on the other hand, with the polyelectrolyte, settling requires less than 1 to 2 hours.

### Polyquaternary Compounds

*A process described by M.T. Dajani; U.S. Patent Reissue 29,241; May 31, 1977; assigned to Nalco Chemical Company relates to the clarification of water which contains suspended solids and which has at least 0.1 ppm of chlorine dissolved therein. This comprises the addition of a poly quaternary compound to the water, coagulating the suspended solids. The range of addition is between 0.5 to 5 ppm of these compounds.*

These compounds are polymers which contain a plurality of basic nitrogen sites in the form of quaternary groups. They may be prepared by polymerizing a quaternary ammonium monomer, such as, dimethyl diallyl ammonium chloride, or by alkylation of already formed polyamine compounds. Examples of typical

polyamines which may be converted to polyquaternary compounds are: polyethyleneimine, polyethyleneamine, condensation polymers of ammonia or alkylene polyamines and polyhalides such as ethylene dichloride, etc. One requirement is that the polyquaternary compound be water-soluble at the dosage level which is employed in the process. Usually this only requires solubility in the order of about 10 ppm. The following examples illustrate the process.

*Example 1:* A number of polyquaternary compounds were tested on a turbid water which contained approximately 150 ppm of suspended solids and 6 ppm residual chlorine. These polyquaternary compounds were evaluated under a standard testing procedure where 1.5 ppm of the quaternary compound was added to the turbid water, mixed for 5 minutes at 200 rpm, mixed for 10 minutes at 50 rpm and then allowed to settle for 15 minutes.

After the settling period, a 200 ml aliquot of the water was siphoned and its turbidity measured using a standardized Hellige Turbidimeter. The results of these tests are shown in the table below. In each case, the ability of the quaternary compound to clarify the standard water was dramatically shown when contrasted with its parent polyamine.

**Table 1: Effect of Chlorine on the Activity of Polyamines and Their Methyl Chloride Quaternary Equivalents**

Clarification Agent	Residual Turbidity, (ppm SiO <sub>2</sub> )
(1) Ammonia-ethylene dichloride condensation polymer	50.0
(2) Methyl chloride quaternary of (1)	4.2
(3) Polyethyleneimine	56
(4) Methyl chloride quaternary of (3)	3.5
(5) Condensation polymer of tetraethylene pentaamine and epichlorohydrin	62
(6) Methyl chloride quaternary of (5)	4.7

*Example 2:* A synthetic turbid water was prepared by suspending 200 ppm kaolin clay in deionized water. To this water, 1 ppm of residual chlorine was added. Experiments were then run to determine the amount of clarification agent necessary to achieve a specified residual turbidity. Specifically, a polyamine prepared by a condensation polymerization of ammonia and ethylene dichloride was added at dosage levels necessary to achieve a residual turbidity of 50 ppm, 30 ppm, 10 ppm and 5 ppm.

At the same time, similar tests were run using a quaternary derived from the above described polyamine alkylated with methyl chloride. The results of these tests are shown in the table below. Substantially smaller amounts of the quaternary compound were necessary to achieve equivalent results.

**Table 2: Dosage Requirements to Achieve Varying Residual Turbidity**

Clarification Agent	Dosage, ppm			
	50	30	10	5
Polyamine	4.2	4.5	5.6	—
Polyquaternary	0.8	1.0	1.5	1.7



A number of other polyquaternaries were prepared and evaluated in similar manners. For example, N-butyl chloride, alkyl chloride and benzyl chloride alkylation products of several polyamines were prepared. Evaluation of these materials showed results similar to that shown in the above examples.

### Inorganic Flocculating Composition

A process described by L. Casale; U.S. Patent 4,035,259; July 12, 1977; assigned to Caffaro, SpA, Societa per l'Industria Chimica ed Elettrochimica, Italy relates to an inorganic flocculating composition consisting of water-soluble salts of Al, Fe, Mg and Ca, obtained by attacking clays containing the above chemical elements, the attack being carried out with an acid capable of forming water-soluble salts of the chemical elements. This process is carried out in the following stages:

slurrying the raw clay so as to obtain a semifluid slurry having a percentage contents of solids between 33 and 55% on a weight basis, the clay particles having a size of not more than 1 mm in diameter;

treating the stirred slurry or suspension with an acid which is capable of forming with Al, Fe, Mg and Ca, water-soluble salts with an increase of the temperature up to approximately 90°C;

completing the acid attack on the clay by a heat treatment of the mixture, preferably in an autoclave at a temperature of about 150°C and a pressure of about 4 atm; and

a gradual cooling of the mixture and filtration, with separation of a solid residue and liquid phase, the latter constituting the flocculation composition.

Field tests as conducted with the compositions according to this process, more particularly those obtained by attacking a clay with sulfuric acid, have shown the property of such compositions of destroying the stability of colloidal slurries, thus permitting the coagulation of the particles in suspension and the subsequent flocculation. More specifically, such a composition is characterized by: a high coagulating and clarifying power; colorless residual sludges; turbidity less than 1 JU in the treatment of superficial waters; a wide range of the working pH; and compatibility, in the case of treatment of superficial waters, with oxidizing preliminary treatments, more particularly chlorination. The following example illustrates the process.

*Example:* A bentonite clay is used, which has the following average contents of its principal components.

	Percent
SiO <sub>2</sub>	59-60
Al <sub>2</sub> O <sub>3</sub>	18-19
Fe <sub>2</sub> O <sub>3</sub>	3-4
CaO	2-3
MgO	4-5

The raw clay, which has the form of clods of various size, is slurried in a wet mill, by metering the quantity of water which is necessary to obtain a semifluid slurry in which the percentage of dry matter can vary from 33 to 35%, with a