

## Review of Recent Patents on Coagulation / Flocculation (C/F) Process: Methods and Applications with Emphasis on Phosphates Removal

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**Abstract:** The present review describes the most recent patents and outlines the progress made over the last decade in the field of wastewater treatment focusing on the application of Coagulation/Flocculation (C/F) process, which is mainly used as primary treatment for the effective removal of colloidal particles and organic matter. Various materials/chemical reagents have been developed in recent years as coagulation/flocculation agents. Among them are inorganic-based coagulants, organic-based flocculants, as well as hybrid materials, or tannin-based polymeric coagulants. Furthermore, a recent patent application for treating wastewater is using nanoparticles of clay as anionic coagulant agent. In many sensitive catchment areas, the effective removal of phosphorus is also required. Several alternative processes, methods and treatment systems have been provided in recent patents for lowering the concentration of phosphorus in wastewaters, noting that the conventional use of alum or ferric chloride for phosphorus removal is rather problematic due to acidity of coagulants, being added to the wastewater. A coagulation-sedimentation apparatus is specifically designed to treat water at higher rates and a more recent patent discloses a system for continuous optimization of the relevant wastewater treatment.

**Keywords:** Al-based coagulants, coagulation, Fe-based coagulants, flocculation, phosphates removal, tannin-based polymeric coagulants, wastewater treatment.

### 1. INTRODUCTION

Extensive research activity has been directed on the wastewater treatment field over the past few years, including the publication of several related patents focusing on the application of Coagulation/Flocculation (C/F) process.

C/F process is considered as a typical physico-chemical treatment for contaminated waters, or industrial wastewaters. This technology is mainly used as primary treatment for the effective removal of particulate and/or organic matter. Knowing their specific differences can lead to a better understanding of clarification and dewatering operations of the wastewater treatment [1].

*Coagulation* is the destabilization of colloids (0.01-1.0 $\mu$ m) by neutralizing the electrical forces that keep them apart. *Flocculation* is the action usually of (organic) polymers, (otherwise named as polyelectrolytes) to form bridges between the flocs and bind the particles into larger agglomerates, or clumps. Once the suspended colloidal particles are flocculated into larger particles, they can be easily removed from the solution by sedimentation, provided that a sufficient density difference exists between the suspended matter and the liquid [2, 3].

In many sensitive catchment areas, supplementary phosphorus removal is also required (as tertiary wastewater treatment process) and this is performed by the addition of appropriate chemical reagents. The benefits of sequential chemical addition for coagulation operations have been shown on several occasions. A common case is phosphorus precipitation [2]. Many countries set 1mg/L and 2mg/L as the limit for total phosphorus concentrations in discharges of wastewater treatment plants. One of the reasons for this low limit is that P concentrations below 0.5mg/L have been shown to be the limiting value for algal growth [4], i.e. at P concentrations below 0.5mg/L algal growth in a natural, freshwater environment is essentially inhibited or blocked.

### 2. PATENTED COAGULATION/FLOCCULATION (C/F) PROCESS FOR WASTEWATER TREATMENT

In a patent appeared on July 1985, Larry [5] indicated a process for treating wastewater containing an undesirable level of organic matter, wherein the coagulated solids are flocculated by treatment with a non-polymeric, cationic flocculating agent, comprising a salt of a fatty acid (aminoalkyl alkanolamide), followed by treatment with an anionic polymeric flocculating agent, while the use of the cationic agent alone is ineffective in providing acceptable flocculation, and an anionic flocculating agent must also be added to fully flocculate the precipitated, coagulated solids. The cationic flocculating agent is used in the process in an effective amount which ranges from about 50 to 800mg/L. Commer-

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cially available anionic polymers include Hydrad 771 supplied by Calgon Co. and Herculoc 1031 supplied by Hercules, Inc. The anionic polymer is added in amounts up to about 100 mg/L, preferably from 10 to 60 mg/L. Furthermore, the invention relates to a process for treating wastewater, obtained in connection with polymerization processes and chemical compounding, with an organic non-polymeric cationic flocculating agent.

Large amounts of wastewater are generated in connection with the running of chemical plants where for example, chemical compounding and latex polymerization processes, are carried out on a daily basis. Such wastewater is loaded with suspended and dissolved organic materials including mixed polymer latex wastes and also including various ionic and non-ionic organic surfactants at solids concentrations typically ranging from 0.05 up to 5 (% weight). Based on ecological considerations, disposal of such untreated wastewater by downstream dumping, or draining in leach fields, is undesirable and often restricted or prohibited by statute.

It is well known that treatment of turbid waters and relevant wastewaters as aforementioned, involves the application of precipitation and coagulation with subsequent flocculation, whereby the ultra-fine particles and particles in colloidal form are coalesced into various dimensioned flocks, which are thereafter can be separated by flotation, precipitation or sedimentation. A variety of processes are known for the primary treatment of such wastewaters. A representative process comprises the precipitation, coagulation and flocculation of the solids therein by chemical means and thereafter, by subjecting the wastewater to a subsequent separation step of dissolved air flotation, so as to float the sludge formed of the coagulated particles up to the surface.

The sludge is separated from the liquid by mechanical means and is thereafter properly buried, or disposed, whereas the treated wastewater can be alternatively disposed of by spray irrigation in slow rate land treatment of leach fields. Commonly, the flocculated sludge can be separated from the wastewater by the application of known settling procedures. It is noticed that many wastewater treatment processes utilize polymeric flocculants, comprising of cationic, anionic or non-ionic polymers, which are often added during the primary treatment of wastewater to further aid in the flocculation of solids by lowering the charge of contaminant particles, as well as by causing interparticle bridging, thereby increasing the size of particle aggregates. Typically, a cationic polymer is added to a wastewater in concentrations from about 50 to 800mg/L, followed by the addition of an anionic polymer from about 10 to 100mg/L [5].

The patent of Hideo *et al.* [6] in 1988, discloses a method of producing coagulated colloidal particles with close-packed structure which comprises the following steps:

- 1). Adding a coagulant to aqueous colloidal particles at a temperature lower than the softening temperature of colloidal particles and under such conditions that the coagulant will be present in discrete units in the dispersion, before it will be brought into solution by diffusion;

- 2). Allowing the molecules of coagulant to gradually diffuse from the coagulant units into the surrounding dispersion, thereby coagulating the colloidal particles on the surface of each coagulant unit, causing the coagulated particles to grow from inside to outside of each unit, and producing coagulated particles of desired size with regularly packed structure;
- 3). Separating the coagulated particles thus formed from the dispersion; and
- 4). Drying, or heating in an aqueous phase, the coagulated particles separated above at a temperature lower, than the softening point of these colloidal particles.

A specific objective of this invention has to provide a method of producing high-purity polymer particles containing less amounts of water-soluble and oil-soluble impurities (e.g. inorganic salts, organic additives or residual monomers). A further objective was to provide a method of producing polymer particles, which can be rapidly dissolved or dispersed in water, or in an organic solvent to form a clear solution, or a homogeneous dispersion of fine particles.

Another object of this invention was to provide a method of producing polymer particles, which undergo little change in state, have high bulk density and form no fine powder and hence, which are easy to handle and transport and are free from blocking and creating troubles during storage. Also another objective has to provide a method of producing polymer particles with give homogeneous moldings and which can be directly subject to injection-molded, i.e. without prior pelletization. The method of this invention is basically different from the conventional coagulation processes, although there seems to be no substantial difference in actual operation. The fundamental difference is that the coagulated particles in the conventional processes are aggregates in which primary latex-like particles are randomly packed.

Conventional processes may be roughly classified into three types, each of which is described below with emphasis placed on actual operations.

- 1). The first method is to simply mix a latex-like particle and a coagulant together.

Since the rate of coagulation is very high, the following steps take place successively:

- a). Formation of coagulum the moment that the coagulant comes into contact with the latex;
- b). Fragmentation of this coagulum by external force (for example by stirring); and
- c). Mixing of the coagulant molecules released by fragmentation with the latex, ultimately resulting in bulk coagulation of the whole latex system. The coagulated particles can thus be obtained as a nearly homogenous slurry.
- d). The random coagulum obtained by this method contains enough water, is thixotropic in nature, and do not behave as a liquid, even at a concentration as

low as 20%. Therefore, it requires dilution with water before coagulation.

- 2) The second method is to add a latex-like particle to an aqueous coagulant solution in the form of discrete droplets, or in the form of a continuous flow (linear or zonal) e.g. through a nozzle.

This method is intended to produce coagulated particles just in the shape of the discrete droplets, or to break down the linear or zonal coagulum formed in the latex into particles.

Thus, the particles obtained by the aforementioned methods (1) and (2) give an amorphous powder of a broad particle size distribution.

- 3) The third method is to spray the latex into a coagulator condition.
  - a). High-purity particles with water- and oil-soluble impurities (e.g. inorganic salts, residual monomers and organic solvents) will be readily removed.
  - b). Easy dispersion and solution in solvents.
  - c). Excellent properties and characteristics of particles [6].

Another relevant patent involved with methods for treating wastewater was held by Wood and Vasconcellos and published in 1995 [7]. This invention relates to treatment of oily wastewater by utilizing water soluble block co-polymers, containing water soluble and water insoluble monomers. These polymers provide effective flocculation, specifically for induced-air flotation and dissolved-air flotation processes.

Water soluble block co-polymers, containing water soluble and water insoluble monomers, proved useful as flocculants for oily wastewater treatment. There is an increasing usage of water soluble polymers and co-polymers in wastewater treatment industries. These compounds have shown desirable use for the purpose of flocculating contaminants from different contaminated waters.

The efficacies of the polymers or co-polymers used will vary depending upon the type of monomers selected to form the polymer or co-polymer, the molecular weight of synthesized molecule and in the case of a co-polymer, the placement of selected monomers on the backbone of co-polymer; the latter characteristic is the specific focus of this invention.

Co-polymers may be synthesized without attention to the distribution of two base monomers along its backbone resulting in a random distribution of these monomers. Synthesis may be controlled however, to form a copolymer having long sequences of monomers, e.g. A and B, as follows:



This formation results in compounds referred to as block co-polymers, which exhibit unique properties and as a result are more desirable than random co-polymers, or a blend of the two homopolymers synthesized from the respective mono-

mers. The industrial importance of block co-polymers has increased markedly in recent years for these reasons [7].

Very recently, Coste, Bucaille and Logette, issued an interesting patent [8], disclosing a method for treating water charged with colloidal impurities, either dissolved or suspended, in a treatment plant, wherein said method comprises: the step of contacting said water, in an advanced oxidation area, with hydrogen peroxide in the presence of at least one transition-metal salt; a flocculation step that comprises contacting said water, in a flocculation area, with at least one flocculation additive and with at least one ballast comprising at least one non-soluble granular material denser than water and used as a biomass carrier; the step of feeding the water and floc mixture thus obtained into a settling area; the step of separating the treated water at the upper portion of said settling area from a mixture of sludge and ballast resulting from the settling of said flocs; the step of extracting the sludge and ballast mixture at the lower portion of said settling area; and the step of recycling at least a portion of the sludge into said advanced oxidation area.

In 2013, a relative patent entitled "Method for Treating Water by Ballasted Flocculation Implementing a Natural Flocculent" [9], that has been published by Leveeq and Sauvignat, discloses also a method for treating water by ballasted flocculation comprising a step for injecting into said water at least a flocculent, a step for injecting into said water at least one particulate material that is denser than water, and a step for retrieving treated water, characterized in that said ballasted flocculation and is performed under agitating at a mean speed gradient between 100 and 1400s<sup>-1</sup> and in that said flocculent consisted of at least one natural carbohydrate polymer having an anionic charge density between -900 and -4000mueq/g.

### 3. PREPARATION OF SEVERAL APPLIED COAGULANT AGENTS

#### 3.1. Hybrid Materials Used in C/F Process

The introduction of common inorganic coagulants, such as aluminum or iron-based substances, plays a major role in neutralizing the surface charge of suspended particles or colloidal systems and facilitates the particle aggregation and subsequent gravity settling [10]. The flocculation process involves the addition of appropriate floc-forming chemical reagent, performed usually after coagulation, to agglomerate the non-settable or slow-settling colloidal solids and it plays a major role in the fate and transport of contaminants in aquatic environments by bridging the aggregated flocs to form larger agglomerates, usually in the presence of technical or natural polymeric materials [11, 12].

Various materials have been developed in recent years for coagulation and/or flocculation purposes. Among them is the use of inorganic-based coagulants, of organic-based flocculants, as well as hybrid materials [13, 14]. Hybrid materials used in coagulation/flocculation of wastewaters are materials obtained from the addition of effective components into the original material to enhance the aggregating power.

**Table 1. Classification of Hybrid Materials Used in C/F Process [15].**

Hybrid Materials	Description
Inorganic-inorganic hybrid	Inorganic Polymeric Coagulants (IPCs), referred as pre-hydrolyzed coagulants, such as polyaluminum chloride (PAC), polyferric chloride (PFC) and polyferric sulfate (PFS), which are prepared by partial neutralization of inorganic salts, e.g. $AlCl_3$ , $FeCl_3$ and $Fe_2(SO_4)_3$ , and by controlling the basicity
Inorganic-organic hybrid	Organic Polymeric Flocculants such as polyacrylamide (PAM) and poly-dimethyl-diallyl-ammonium chloride (PDMDAAC), which are introduced in inorganic coagulants and IPCs
Inorganic-natural polymer hybrid	Chitosan (amino-polysaccharide produced by deacetylation of chitin)-based hybrid materials have received diverse modifications, where several inorganic additives have been introduced to enhance the performance during coagulation/flocculation of wastewater
Inorganic-bio-polymer hybrid	Consisting of bio-polymer (MBFGA1 and Puffulan) and inorganic substance (PAC), where the biopolymer is associated with inorganic coagulant to form new hybrid materials
Organic-organic hybrid	It consists of two different organic groups. Specific terms, such as copolymer, grafted-polymer and chemically-modified polymer are used to represent the organic-organic hybrid, and used to address this group of materials
Organic-natural polymer hybrid	These organic-natural polymers can be synthesized by grafting certain proportion of organic group into the main chain of natural polymer, e.g. SAG-g-PAM hybrid

The hybrid materials, which are used for coagulation and/or flocculation purposes, can be classified into the following groups, using combinations among each other: inorganic, organic, natural polymer and bio-polymer, as shown in Table 1 [15].

The coagulation process presents usually high removal efficiency of different pollution control parameters, mainly of chemical oxygen demand (COD) and suspended solids (SS). The process is based on the use of  $Al(III)$  or  $Fe(III)$  salts alone, or in combination with calcium salts and the use of polymers as flocculants [16-18]. Alternative aluminum-based coagulants, such as polyaluminum chloride [18], polyaluminum silica chloride and polyaluminum ferric chloride [19, 20], and polymer addition [21] were studied to improve coagulation efficiency [22].

The preparation, characterization and application of such composite coagulants are under intensive investigation during the last decade. The basis for their production is commonly a known and widely used pre-polymerized inorganic coagulant, i.e. in the case of aluminum, the polyaluminum chloride (PACl). The generally applied concept is the introduction of various additives in the structure of a pre-polymerized coagulant, in order to produce a homogenous, stable in time product with higher Molecular Weight (MW) and improved coagulation-flocculation performance, than the initial reagent (i.e. PACl). The challenge to confront is the desirable combination of higher efficiency and cost-effectiveness, which are the basic prerequisites for the development of new products. Various additives are being examined, which can be classified into two main categories: inorganic and organic. In the case of inorganic additives, silica in the form of polysilicates is usually applied, whereas as organic additives, several polymers can be used, e.g. anionic, non-ionic or cationic polyelectrolytes. It is expected that the addition of negatively charged polysilicates, or of anionic

polyelectrolytes will reduce at a certain extent the charge neutralization ability of the composite coagulants, e.g. when compared to PACl, a reduction which will be compensated by the enhancement of the respective aggregation abilities, thus implying improved flocculation properties. The same behavior is expected in the case of non-ionic polyelectrolytes (PE) addition. In the case of cationic polyelectrolytes, both the charge neutralization and the flocculation abilities are expected to increase in the composite coagulants [23, 24]. It should be mentioned that the tendency in the coagulation field nowadays is the production of modified composite coagulants, by the introduction of several additives to produce the so called pre-polymerized coagulants, in order to improve their efficiency and to make them equal, or even more efficient, than the commonly applied organic polymers [19, 20, 25-36].

#### Composite Coagulants Developed

Extensive studies on polysilicate coagulant combined with ferric salt and aluminum salt have been conducted by several researchers all over the world [20-27]. Zouboulis and Tzoupanos [29, 31], systematically examined several silica-based polyaluminum chloride derivatives, leading to the development of the most effective polyaluminum silicate chloride (PASiC) and Zouboulis and Moussas [28] examined several silica-based polyferric sulphate derivatives, such as polyferric silicate sulphate (PFSiS).

Today, there is a prompt need for the development of new PAC-based coagulants such as poly-aluminum-ferric-silicate-chloride (made of aluminum, ferric and silicate) to improve the coagulation performance. The ferric salts can generate thicker and heavier flocs than aluminum salts, but their strong tendency to hydrolysis and polymerization may result in flocs instability and corrosion problems. Nevertheless, the combination of aluminum and ferric salts [37] may

improve the hydrolysis process, the stability of hydrolyzed ferric salts, and the formation of larger flocs. Recently, several investigators [35-42] have studied the simultaneous addition of Al (III), Fe (III) and polysilicic acid solution (pSi), so that the polymerization of pSi and the hydroxylation of metal ions would be synchronized and the coagulation efficiency of poly-aluminum-ferric-silicate-chloride is mainly affected by the Al/Fe/Si ratio and the respective preparation techniques.

### 3.2. Patented Preparation of Coagulants/Flocculants Reagents

There are several patents dealing with the preparation of such materials that are used for C/F purposes. In 1999 Dulko issued a patent [43], and continued in 2000 [43] with an additional one, that describes a process for the production of polyaluminum chlorides and polyaluminum chlorosulfates, useful as coagulants in water treatment. Compared with other inorganic purification agents, these compounds generally work more efficiently, produce less by-product sludge, work better in cold water, settle faster and change (reduce) the pH of water to a lesser extent. The compounds are also used in the production of paper, foods and pharmaceuticals.

Those inventions are directed to a process, which avoids many of the problems, associated with the previously aforementioned methods. It can be used to produce compounds with basicities greater than 70%, using as starting material, basic aluminum chlorides and basic aluminum chlorosulfates of low basicity (25% or less). The produced polyaluminum chlorides and polyaluminum chlorosulfates remain fluid, i.e. they do not coalesce into a gel, and the formation of calcium sulfate precipitates can be avoided. Further on, they can be produced without the addition of heat, thus avoiding the formation of undesirable by-products. As a result, the process is particularly well-suited to large-scale industrial applications. In addition, this process permits the formation of products with unique properties that are also part of the invention. Polyaluminum chlorosulfates can be produced, which have greater than 75.3% basicity and preparations of greater than 70% basicity can be produced, without substantial amounts of calcium carbonate. In addition, concentrated preparations of high basicity polyaluminum chlorides and polyaluminum chlorosulfates can be obtained which contain  $Al_{13}$ , i.e. the form of aluminum generally believed to be the most efficient for removing impurities from water.

#### Polyaluminum Chlorides

Poyaluminum chlorides are products of aluminum chloride hydroxide,  $AlCl(OH)_2$ ,  $AlCl_2(OH)$ , and  $Al_2Cl(OH)_3$ . A representative formula is:  $Al_2Cl_{(6-n)}(OH)_n$ , where  $n = 2.7$  to 5 for products formed via the process described in the following. It is thought that when these products are diluted, polymeric species, such as  $Al_{13}O_4(OH)_{28}(H_2O)_{12}$  are formed.

#### Poyaluminum Chlorosulfates

These compounds can be best described by the formula:  $Al_2(OH)Cl_{(6-n-2k)}(SO_4)_k$ , wherein  $n = 2.7$  to 5 and  $k$  is greater

than 0 and less than 4.3. The main difference between basic aluminum chlorosulfates and polyaluminum chlorosulfates is the amount of hydroxyl substitution; where  $n$  is less than or equal to 1.5 for the former and between 2.7 and 5 for the latter. The polymeric species formed upon dilution may be expressed as  $Al_{13}O_4(OH)_{28}(H_2O)_{12}$ .

#### Basic Aluminum Chlorides

These are compounds having the general formula  $Al_2(OH)_nCl_{(6-n)}$ , where  $n$  is greater than zero and less than, or equal to 1.5. It is believed that solutions of these compounds contain  $Al(H_2O)_6$ ,  $Al_2(OH)_2(H_2O)_8$ , and  $Al(OH)(H_2O)_5$ .

#### Basic Aluminum Chlorosulfates

These are compounds of the general formula  $Al_2(OH)Cl_{(6-n-2k)}(SO_4)_k$ , wherein  $n$  is greater than zero and less than or equal to 1.5, and wherein  $k$  is greater than zero, but less than 0.5. It is believed that solutions of these compounds contain all of the compounds present in basic aluminum chloride, as well as:  $Al(H_2O)_6$  and  $Al_2(OH)_2(H_2O)_8$  [43-47].

Another recent patent application was published in 2008 by Kojima *et al.* [44]. In a wastewater treatment process according to this invention, at least one of a coagulation-sedimentation treatments and a pressure flotation treatment are conducted, by using a polysilicato-iron coagulant [44].

Earlier in 1995 Clarke and Newton issued an interesting patent [40], disclosing a process for the production of flocculant agent from acidic aqueous liquor, containing dissolved salts of aluminum and/or iron such as a waste liquor from the acid activation of a montmorillonite clay mineral, by contacting this liquor with a basic material, such as magnesite, capable of reacting with the dissolved salts to precipitate aluminum and/or iron values, and separating the precipitate in the form of a cake, or slurry from the remaining liquor, then treating the cake or slurry with HCl to redissolve aluminum and/or iron values, preferably introducing into the digestion liquor metallic aluminum and/or iron (the case where the solution contains ferrous iron is preferable) and contacting the solution with an oxidizing agent to convert iron (II) to the ferric form (III), and finally separating suspended solid matter from the resulting solution. The flocculant product, which may comprise a solution of basic poly- (aluminum and/or iron) halide, gives a sufficiently low residual aluminum concentration, when used to treat water. A novel magnesium-containing poly- (aluminum/iron) halide product is also provided. This invention relates to flocculant agents, as well as to a process for manufacturing them from waste acidic liquors and to a process for the treatment of water, aqueous effluents, such as sewage effluents, or other aqueous liquids by using the prepared flocculants [45].

Nanotechnology is an extremely broad technology area, including and co-ordinating many separate disciplines, with the potential for application in a broad range of environmental products, in addition to applications being appointed in the biomedical, electronics, sensors and other industries.

Nanoscale research is important in many environmental areas, including molecular studies of mineral surfaces, the transportation of ultrafine colloidal particles and aerosols. By using nanoscale research, it is expected that specific benefits will be gained, including better understanding of molecular processes in the environment, development of manufacturing processes that reduce pollution, creation of new water purification techniques, improved processes for the composition of artificial photosynthetic processes for clean energy, development of environmental biotechnology, and better understanding of the role of surface microbiota in regulating chemical exchanges between mineral surfaces and water or air.

The integration of nanotechnology into a biological treatment plant may allow both nanoparticle adsorption and enhanced microbial degradation to take place on the nanoparticle surface and enable the recycling of the nanoparticles. In the wastewater treatment industry, important benefits of the use of nanotechnology concepts may include the movement of the boundary between the efficacy of physical (primary and of biological (secondary) treatment. For example, it may be possible to develop nanotechnological advances that remove contaminants by charge, complexation or adsorption, that conventional polymer chemistry cannot remove and that currently require the design, capital expenditure and installation of a secondary biological treatment plant.

This is the subject of the patent application published in 2008 by Mitchell and Engstrom [46], which relates to a process for treating wastewater, by using clay nanoparticles. The nanoparticulate clay (bentonite or hectorite) comprises also an anionic coagulant. This patent provides for a blend of nanoparticles that operate via a different mechanism, than current industrial techniques and therefore, allow for the elimination or the reduction in size of secondary biological treatment.

This invention combines the processes of coagulation and adsorption to accomplish the removal of cationic, anionic and nonionic contaminants. By using natural products, such as clay, the present invention is also applicable for use in the food industry application. The combination of anionic nanoparticle coagulant clay and contaminant bridges between the clays creates the opportunity for synergies with conventional coagulants. In particular, blends or mixtures of the anionic nanoparticle coagulant clay and conventional coagulants can be exploited to remove a broader array of contaminants, than is possible when using either coagulant individually. These synergies will create a layered adsorption onto the cationic nanoparticles of anionic contaminants. This invention also includes processes for recovering spent coagulants and recycling them. The recovery process may be accomplished through any of a number of known techniques, including desorption [43].

Delamination of the bentonite particles is essential in the present invention in order for the cationic contaminants to be adsorbed and bridge gaps between the clay particles. There is additional potential for the use of polymeric nanoparticles

and polymeric nanospheres (1-50nm) that can be designed with various surface chemistries and then blended to provide a wide range of coagulant surface chemistries for contaminant removal. Alternatively, nanocapsules having specific chemistries can be made that can be used to remove specific contaminants. By using coagulant nanotechnology of the present invention, the scope and performance of physical primary treatment is greatly enhanced and the need for secondary biological treatment may be greatly reduced or eliminated. This is particularly true for certain technologies, e.g. protein recovery in kill facilities, metal recovery in plating wastes. Synergies between conventional coagulants and the nanocoagulants of the present invention provide significant opportunities for the removal of a broad spectrum of contaminants, because the chemistries have a different operating mechanism [43].

Finally, tannin-based environmentally friendly polymeric coagulants are disclosed in a patent appeared on June 2008, by Shyadligeri and Madhavan [40]; these are co-polymers of naturally occurring tannins, dialdehyde and diamines. In a preferred embodiment, the dialdehyde is glyoxal and the diamine is dimethylamino propylamine. The present invention relates to a process for clarifying wastewater, and in particular the oily waste water from the production of pharmaceuticals, food and beverages. The tannin component can be obtained from various wood and vegetation materials found throughout the world. Tannins are a large group of water-soluble complex organic compounds. Almost every tree or shrub that grows contains some tannins in the leaves, twigs, barks, wood or fruit.

The resulting polymeric coagulants are able to be used for clarification of various wastewater streams, for instance they can be used to treat wastewater in the food and beverage industries, oil refineries and steel industry. Actual dosage ranges for these reagents are mainly depended upon the characteristics of the wastewater to be treated. These compounds can be also used in conjunction with additional flocculants to improve the overall treatment efficiency of wastewater [48].

## 4. PHOSPHORUS REMOVAL FROM WASTEWATER

### 4.1. Sources of Phosphorus in Wastewater

Domestic and industrial wastewater can be relatively rich in phosphorous, nitrogen, and carbonaceous contaminants that are essential nutrients for the growth of organisms. Phosphorus bans or limitations in synthetic detergents or changes in detergent formulas by the manufacturers have served to reduce the levels of phosphorous in domestic wastewater. However, several industrial and food process waste streams are inherently high in phosphorous content, e.g. those produced from a potato processing facility. The discharge of a phosphorous-rich wastewater into a receiving stream may stimulate accelerated algal growth, which can result in oxygen depletion and stream eutrophication.

Phosphorus in the wastewater comes from toilet wastes as well as bath, laundry, and kitchen wastewater. Toilet

**Table 2. Domestic Wastewater Phosphorus Contribution by Different Sources in a Household [49].**

Source of Phosphorus	Contribution, Grams Per Person Per Day	Contribution, Percentage of Total
Garbage disposal (kitchen)	0.1	4%
Toilet	1.6	59%
Bath, sinks, and appliances	1.0	37%
Total phosphorus	2.7	

wastes contribute 30%-70% of P in the form of nucleic acids and adenosine tri-phosphate excreted in feces. Detergents (laundry) and dish soaps (kitchen and sinks) used in the household contribute another 30%-70% of P Household products (e.g. soaps, cleaners, and personal care products) and found that P was detectable in 97% of 156 products and that much of this P can make its way into household wastewater. The U.S. EPA (2002) estimates that each person in the United States contributes 2.7grams of total P to wastewater each day Table 2. Of this total P, toilet wastewater contributes the highest amount (59%), followed by baths, sinks, and appliances (37%), and garbage disposals (4%) [49].

#### 4.2. Phosphorus Removal from Wastewater

Phosphorous is most efficiently removed from wastewater, when it is in the form of orthophosphates, as many orthophosphate salts are not soluble in water. Although organic phosphonates and polymeric phosphates forms can be readily converted into orthophosphates, by treating them with strong, hot oxidizing acid conditions, this is not practical on large scale wastewater treatment plants. Fortunately, microbiological processes can perform the conversion of organic or polymeric phosphates forms to orthophosphates.

Phosphorus does not exist in elemental form in the natural environment because elemental P is extremely reactive and readily combines with oxygen (O) to form phosphate ( $\text{PO}_4^{3-}$ ). In wastewater, P exists as one of several possible phosphate compounds including orthophosphate, polyphosphates, and organic phosphate [50]. Phosphorus forms in septic tank effluent are broadly divided into the following two categories:

1). **Inorganic Phosphate** is contributed by detergents and household cleaning products such as soaps. These are present as the following:

- **Orthophosphate** is also referred to as "available or reactive P" and may be present in several dissolved forms. These include  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ .
- **Polyphosphate** is orthophosphate molecules linked together in "chains" and is derived from detergents and other cleaners; they are also known as condensed phosphates. These include pyrophosphate ( $\text{P}_2\text{O}_7^{4-}$ ) and triphosphate ( $\text{P}_3\text{O}_{10}^{5-}$ ). Polyphosphates

in water are unstable and eventually convert to orthophosphate.

2). **Organic Phosphate** is contributed by human excreta (feces) and food residues. Organic phosphates are present in sugars, phospholipids, and nucleotides.

Gold and Sims (2001) [51] reported that 85% of the P in septic tank effluent (i.e. wastewater that has passed through the septic tank but has not entered the drain field) is in the form of orthophosphate. The remaining 15% exists in organic or inorganic forms in suspended solids. Most of the inorganic P in septic tanks originates from detergents and soaps. In addition, a small amount of inorganic P is released when organic material is decomposed by microbes.

Traditional methods to remove solids, such as settling, filtration and centrifuging, will remove the majority of all insoluble phosphorous species with the solid fraction as shown in Fig (1). However, the removal of remaining soluble phosphorous species can be performed, by using the following methods: removal by phosphate-accumulating microorganisms, precipitation by a metal ion and precipitation as struvite.

Soluble phosphorous can be removed by aerobic or facultative microorganisms that can incorporate the phosphorus into their cell mass. Once incorporated within the biomass, the phosphorous can be removed from the system as waste activated sludge [52].

Most often, phosphorous is removed from wastewaters by chemical precipitation, using salts of multivalent metal ions, commonly calcium, aluminum or iron. Calcium is conventionally applied in the form of lime (as calcium hydroxide), aluminum in the form of alum (aluminum sulphate), and iron in the form of ferric chloride. In addition to using a source of multivalent metal ions, polymers are also sometimes added to aid in the formation of appropriate flocs size. The precipitation/flocculation process is generally followed by the removal of the precipitated/flocculated phosphorous, using mechanical means, such as by sedimentation or filtration. More recently, polymeric aluminum products such as PASS (polyaluminum silicate-sulphate), PASiC (aluminum-silicate polymer composite), and PAC (hydroxylated poly-aluminum chloride) have also been patented (PASS), or tested (PASIc and PAC) in full-scale applications (PASS) and in laboratory experiments (PASIc and PAC). The PASS

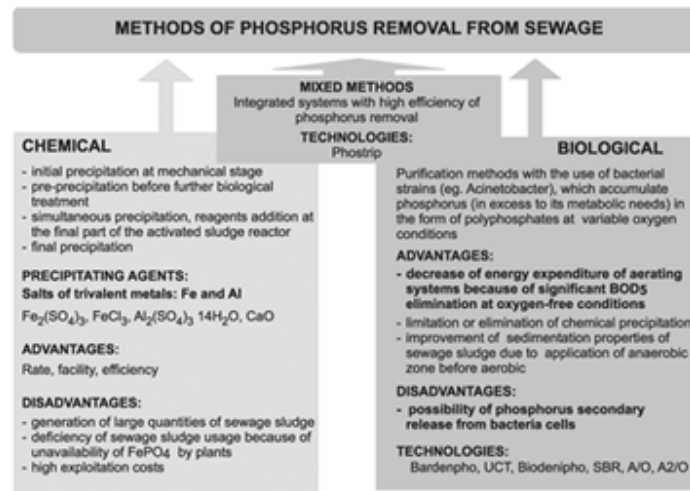


Fig. (1). Methods of Phosphorus removal from wastewaters [47].

formula as an example is defined in US5149400 (1992) by Haase *et al.* [53] as:



Where

- A is 1.0
- B ranges from 0.75 to 2.0
- C ranges from 0.3 to 1.12
- D ranges from 0.005 to 0.1
- X is greater than 2.0, but less than or equal to 4.0, such as  $3-B+2C+2D(X-2)$  and
- E is larger than 4, when the product is in aqueous form.

The use of these coagulants/flocculants is generally followed by the removal of resulting precipitate, e.g. by sedimentation or filtration.

Several patents have been issued, which are directed to the removal of phosphorus from wastewater. The most relevant patents are considered to be the following:

US4981675 (1991) by Handy Chemicals Inc. [53], which described water treatment methods using a polymeric basic aluminum silicate sulfate. The respective treatment conditions were:

- 1). 8-9°C at a pH of 6.65 to 6.93 and a concentration of 3-8mg/L  $Al_2O_3$
- 2). 25°C and at a pH of 7.14-7.38 at a concentration of 3-8mg/L  $Al_2O_3$

and US6165369 (2000) by General Chemical Corporation [54], which presents a water treatment method that includes the use of polyaluminum silicate sulfate in conjunction with finely-divided, acid-insoluble solid particles.

According to commonly applied procedures, a flocculent agent can be added to the wastewater, while it is in the biological reactor. In certain cases the addition of flocculent occurs, when the wastewater has been partially, but not fully treated in a biological reactor, e.g. as the third stage of a four-stage Rotating Biological Contactor (RBC). Because the biological reactions using aerobic bacteria must be carried-out at a pH level around 6.8 or higher, the coagulant/flocculent agent according to this procedure is introduced into wastewater, which has been properly adjusted by using another chemical, in order to have a pH of around 6.8 to 7.6.

Thus, in the existing systems a portion of the phosphorus present in wastewater is expected to be used for microbial metabolism and another portion of it precipitates-out and forms flocs in the biological reactor. This precipitate in some systems is removed from the last stage of biological reactor and returned to the primary settling tank where it is allowed to accumulate. This is done in order to minimize the amount of precipitate that is fed to the next stage of wastewater treatment process [55].

Relevant processes, methods and systems are provided in recent patents appeared on May 2007 [55], and on July 2009 [55] by Bolduc for lowering the concentration of phosphorus in wastewater. The process includes the addition of a suitable amount of an aluminum-based coagulant/flocculent to the



wastewater, for example an aluminum-silicate coagulant/flocculent product, while maintaining the pH of the wastewater at between 4.5 and 6.7. This step provides an eventual effluent stream of precipitated aluminum-based, phosphorus-containing flocs dispersed in the wastewater. The next step involves the physical removal, e.g. by filtration, the precipitated aluminum-based, phosphorus-containing flocs, which is dispersed in the wastewater. These steps are able to provide a wastewater effluent containing less than about 0.03mg of total phosphorus/L of wastewater [55].

Another recent patent regarding the reduction of phosphorous-containing compounds, is that by Kelley and Handley published in 2011 [52, 56]. Methods and compositions utilizing aluminum, magnesium, and calcium-based additives for the treatment and neutralization of wastewaters are described for removing several contaminants, including phosphorous-containing compounds, total suspended solids (TSS), biological oxygen demand (BOD), fats, oils, and greases (FOG), and total Kjeldahl nitrogen (TKN). Methods and compositions to control pH, sulfur and sodium loads present in wastewaters and precipitated solids are also described.

Aluminum hydroxyphosphate is formed from the alum treatment of orthophosphate-containing wastewater. Alum (aluminum sulfate) reacts with water and orthophosphate to form the insoluble aluminum hydroxyphosphate. The pH for successful phosphate removal by alum treatment lies in a very narrow range (around 6) and two molecules of alum are required for every one of phosphate removed. At pH below 5 or above 7, the removal of phosphate is either incomplete, or a fine solid is forming, which has poor settling efficiency.

Iron, in the form of ferrous or ferric salts, has been used to precipitate the orthophosphates as the insoluble iron hydroxyphosphate. Soluble iron ions combine with alkalinity and phosphate to form the insoluble ferric hydroxyphosphate and the floc ferric hydroxide, which helps to increase the rate of settling. The ideal wastewater pH for this to occur is around 6. Most of sludge from this removal is moved into an anaerobic digester. A common iron salt for this purpose is ferric chloride.

In principle, release of phosphorus (and other compounds) can be done in two ways: using acid or base. The positive feature of using acids is high recovery grade. From the other hand, a lot of other metals including heavy metals are also released causing separation problems and increasing complexity of process technology. Leaching with base has up to 50% lower recovery efficiency however metal leaching is also reduced. Another point that should be taken into account while using base leaching is that calcium presented in sludge will more likely bind phosphorus into calcium phosphate [57].

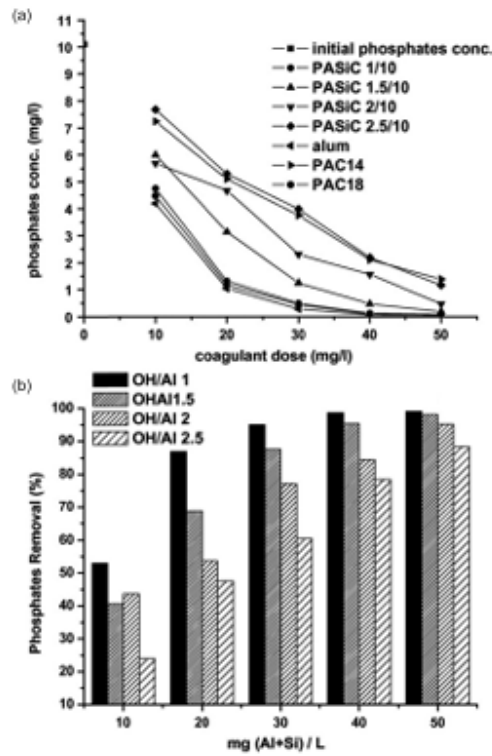
The use of alum or ferric chloride for phosphorous removal has a significant drawback, relating to the acidity of the coagulants that are being added to the wastewater. Since both aluminum sulfate and ferric chloride are acidic, they will provoke a decreased pH to both the settled solids and

the overflow water. As a result of decreasing the pH, microbial activity in the digester (aerobic or anaerobic), or in the secondary treatment process will be diminished [52].

Regarding the phosphates removal efficiency, all PASiC samples [29] with molar ratio Al/Si 10 were tested by Zouboulis and Tzoupanos and compared to the commercially available PACl-18, PACl-14 and alum coagulants. The aqueous sample to be treated was biologically pre-treated urban wastewater, collected from the exit of a full-scale wastewater treatment plant (Thessaloniki, Greece). The main characteristics were initial concentration of inorganic phosphates 10.1mg/L (measured as ortho-phosphates). Figure 2a illustrates the results of phosphates removal for initial coagulant concentrations 10-50mg/L. It can be seen that the less effective coagulant was PACl-14 (having basicity 80%, which corresponds to OH/Al ratio 2.4 and relatively high degree of polymerization), whereas the most effective were PACl-18 (having basicity 40%, corresponding to OH/Al ratio 1.2 and relatively low degree of polymerization), as well as alum and PASiC samples with OH/Al 1 and 1.5. With the latter coagulants the dose needed for limiting the concentration of phosphates under 1mg/L (according to the respective legislation limit for ecologically sensitive areas) is about 20-30mg/L, whereas with the rest coagulants the respective concentration (dose) needed is more than 40mg/L. In Fig. (2b) the percentage of phosphates removal, regarding the OH/Al ratio in the PASiC samples, is presented.

It can be noted that the removal efficiency increases as the ratio OH/Al decreases, corresponding also to the decrease of polymerization degree, unlike the aforementioned results obtained with the contaminated tap water samples and that the most efficient reagent in this case was PASiC with the least OH/Al molar ratio (i.e. OH/Al = 1). The relevant explanation relies in the respective mechanism of phosphate removal through the addition of coagulants. Jiang and Graham [58] reported that the removal of phosphates by the application of coagulation/flocculation process involves the following two major mechanisms: (a) the interaction of phosphates with the soluble aluminium forms (chemical complexation), or with the non-soluble (charge neutralization) complexes, producing compounds with generic formulae  $Al(OH)_3 \cdot x(PO_4)_y$ , which can either adsorb onto the positively charged Al(III) hydrolysis species, or may act as cores for the precipitation of Al(III) hydrolysis products; (b) The direct adsorption of phosphates onto aluminum hydrolysis products, mainly referred to precipitation with insoluble  $Al(OH)_3$  (sweep flocculation).

Based upon the obtained experimental results and the aforementioned possible mechanisms, it is suggested that the dominant mechanism during phosphates removal is sweep flocculation, as the most efficient coagulant was the PASiC with the inferior basicity. This suggestion is also supported by considering the pH values of the aqueous sample to be treated, as for the pH values higher than 7, the formation of  $Al(OH)_3$  is favored. Also, in this pH region the most dominant phosphate species are  $H_2PO_4^-$  and  $HPO_4^{2-}$ , and the latter



**Fig. (2).** Comparable evaluation of the effect of several coagulants on phosphates removal (initial concentration 10.1mg/L, pH 8); (a) Comparison of PASiC samples with Al/Si ratio 10 and OH/Al ratio 1-2.5 with alum, PACI-14 and PACI-18. Coagulant doses expressed as mg (Al + Si)/L for PASiC samples and as mg Al/L for alum and PACI, (b) % percentage removal for all PASiC samples [29].

is assumed to have higher affinity for the  $Al(OH)_3$  floc at higher pH values.

##### 5. PATENTED APPARATUS FOR C/F PROCESS

A recent patent entitled "Coagulation-sedimentation apparatus" [56] that has been published by Kosanda *et al.* in 2007, describes a flocculating device for sewage that has a separating tank in which the flow velocity of ascending flow of treated water, flowing from upper and lower chambers to their respective outlets, is equal to floc settling speed. With this design the apparatus is enabling to treat water at a higher rate.

Figure 3 shows the solid-liquid separation tank (26), according to this invention. The coagulation sedimentation apparatus includes a separation tank body (60), divided into an upper (61) and a lower chamber (62) by an appropriate

partition (64). The tank body has a raw water inlet pipe (66) that introduces raw water into the upper chamber, and a water distributing passage that introduces a part of the water from the upper chamber to the lower chamber. The upper chamber has a first treated water outlet (76), and the lower chamber has a second treated water outlet (78). The flow velocity of upwards flow of the water toward the first treated water outlet (76) in the upper chamber and the flow velocity of upwards flow of the water toward the second treated water outlet (78) in the lower chamber can be controlled so that flocs in the upwards flow can settle.

The flow velocity of upward flow of the water towards the first treated water outlet in the upper chamber and a flow velocity of upward flow of the water toward the second treated water outlet in the lower chamber can be controlled to appropriate velocities at which flocs in the upwards flows can still settle.

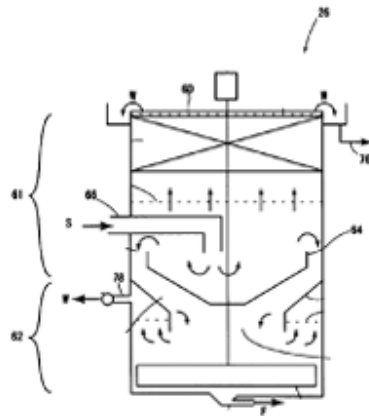


Fig. (5). An example of the solid-liquid separation tank according to Kosanda *et al.* 2007 [56].

The aim of this invention was to provide an improved coagulation sedimentation apparatus to meet the aforementioned requirements, so as to be capable of carrying out simplified treatment of polluted water, even more efficiently and at an increased speed.

Further on, by using a coagulant mixing tank having a sinuous flow path structure, the coagulants can be efficiently mixed with the water to be treated. Thus, the coagulants can be used more effectively. Additionally, during a rainfall event, an appropriate amount of coagulant can be added, according to the water quality of the raw water (untreated). In this regard also, the coagulants can be used more effectively.

The conventional apparatus, shown in Fig. (4) and the apparatus according to the invention of Kosanda's patent shown in Fig. (5) were tested by using sewage flowing in during a rainfall event as water to be treated and using ferric chloride as an inorganic coagulant and an anionic polymeric flocculant.

The ferric chloride was added in the first compartment, constituting the inorganic coagulant mixing tank (22). The anionic polymeric coagulant was added at the downstream end of the fourth compartment defining the upstream end of the organic coagulant mixing tank. A conventional solid-liquid separator was connected in the subsequent stage to carry out the respective process [56].

A more recent patent due to Bowers [3] discloses a system for continuous optimization of wastewater treatment. Specifically, is disclosed a system for controlling the injection of wastewater treatment chemicals into a wastewater treatment stream that includes a holding tank for collecting and keeping wastewater being treated, a camera positioned

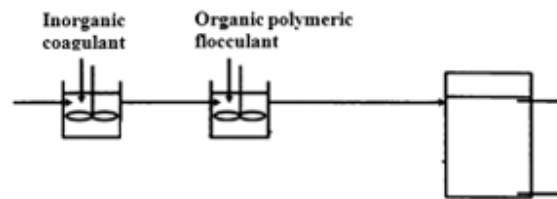


Fig. (4). Conventional coagulation-sedimentation apparatus [56].

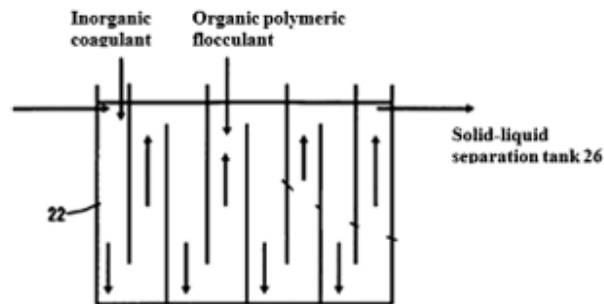


Fig. (5). Coagulation-sedimentation apparatus, according to Kosanda's patent [56].

for making images of the wastewater in the holding tank, and a computer for automatically making the images of the wastewater in the holding tank at scheduled intervals. The computer analyzes the images in order to determine the necessity for injecting wastewater treatment chemicals into the wastewater stream, by measuring the size, distribution and number of pixels of differing colors and appearances. A pump and injection port injects wastewater treatment chemicals into the wastewater stream, responding to the analysis of the images, indicating the necessity of such injection. This invention is generally directed to a system for adjusting the dosage of wastewater treatment chemicals in an automated mode, requiring limited operator oversight. More particularly, it is directed to a system in which photography, most preferably digital photography, is employed to monitor the wastewater stream [3].

#### CURRENT & FUTURE DEVELOPMENTS

There are several patents focusing on the application of C/F process for treating wastewaters. Various materials have been developed in recent years for coagulation and/or flocculation purposes. Among them is the use of inorganic-based coagulants (i.e. those based on the use of Al(III) or Fe(III) salts), of organic-based flocculants (i.e. PDMDAAC), as well as hybrid materials. In addition, there are certain patents, which are related to processes for treating wastewaters, by using clay nanoparticles (bentonite or hectorite) that comprise also an anionic coagulant, or by using tannin-based environmentally friendly polymeric coagulants. Furthermore, relevant processes, methods and systems are provided in recent patents, for lowering the concentration of phosphorus in wastewaters. The use of conventional coagulants (alum or ferric chloride for phosphorous removal has a specific drawback, relating to the acidity of the coagulants) that are being added to the wastewater. Finally, according to recent patents, it is described an apparatus for C/F process, which is enabling to treat water at a higher rate and a system for continuous optimization of wastewater treatment and of reagents addition.

#### CONFLICT OF INTEREST

This review was performed by the authors within the scope of their employment at program EPAN-II (OPC-II)/ESPA (NSRF) "SYNERGASIA II", Project (FOULMEM) – "New processes for fouling control in membrane bioreactors (11SYN-8-1084)

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