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ROLE OF POLYELECTROLYTES IN THE FILTRATION OF COLLOIDAL PARTICLES FROM WATER AND WASTEWATER

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ABSTRACT

An extensive review has been made of the literature in conection with the use of polyelectrolytes in the removal of colloial particles from water and wastewater by mechanisms of filtration.

Pertinent literature on the nature of colloidal materials nd current theory related to particle interactions and coagulation as been briefly reviewed. Present thought on the physical aspects nd the chemical aspects of filtration has been considered. Refernces related to the characterization and behavior of multi-media ilters as well as single media filters were included in this work. articular attention was directed to the review and evaluation of rticles related to specific applications of the use of polyelecrolytes in water treatment, and in domestic and industrial wasteater treatment.

INTRODUCTION

The problem of solid-liquid separation is basic to the reas of water purification, and to municipal and industrial wastewater treatment. Solids occurring in natural waters and various waste effluents range in size from several hundred microns for suspended material, down to a few millimicrons for materials in colloidal suspension. The separation of the larger, heavier particles may often be accomplished by the processes of sedimentation and/or filtration. Because of the surface characteristics of colloidal particles, some type of destabilization of the colloidal solution is necessary to promote the aggregation of particles into larger clumps which can be separated from solution by subsequent filtration. In recent years the use of polyelectrolytes has become increasingly important as an aid to the destabilization and clarification of various wastewater containing colloidal suspensions.

The present work effort has as its primary purpose the need to review and evaluate the literature relative to the role of polyelectrolytes in the filtration of colloidal particles from wastewaters. Also considered have been basic mechanisms related to colloidal behavior in filtration.

NATURE OF COLLOIDAL SUBSTANCES

Colloidal dispersions consist of extremely small particles (of the order of 1 to 200 millimicrons in diameter) held in suspension in a liquid medium. Because of their size and the fact that the particles often carry an electrical charge, thus repelling like particles, they may have little tendency to agglomerate and settle. Numerous examples of such stable colloidal solutions are found in nature and are often the source of color and turbidity in natural waters. Hence, much of the early work directed to understanding the nature of colloids was related to efforts to clarify water and wastewaters.

Two general types of colloids are usually recognized. Hydrophilic colloids are particles dispersed in water and owe their stability largely to a strong affinity for water. Hydrophobic colloids do not have an affinity for water and owe their stability primarily to the electrical charge that they carry. Clark, et al.[1] list soaps, soluble starch, soluble proteins and synthetic detergents as examples of hydrophilic colloids, and various metal oxides as examples of hydrophobic colloids.

Colloidal systems may also be described in terms of stability. O'Melia[2] has referred to thermodynamically stable colloidal systems as reversible, while thermodynamically unstable colloids are called irreversible. Examples of thermodynamically stable colloids include soaps and detergents, proteins and starches, while examples of thermodynamically unstable systems include clays, metal oxides and some microorganisms. In water and wastewater treatment, the primary concern is with aggregation of thermodynamically unstable colloidal systems.

In a recent review on the state of the art of coagulation[3], it was pointed out that at least two approaches have been advanced to explain the basic degree of stability of colloidal systems. The first approach, usually designated as the chemical theory, views a colloid as an aggregate of specific chemical composition which can chemically interact with various coagulating agents. The second approach emphasizes physical mechanisms. In particular, the electrical double layers surrounding colloidal particles are considered to be of prime importance in determining the degree of stability of colloids. Actually these theories are not independent but overlap at many points.

ELECTRICAL DOUBLE-LAYER THEORY

The charge on a colloid may be due to a number of factors[3,4] including the adsorptions of low molecular weight ions on the particle surface and/or the dissociation of ionizable groups associated with the colloid particle. The resulting charge on the particle will cause a repulsion of ions of like charge and an attraction of ions of opposite charge (counter ions) to the surface of the particle. The more or less compact layer of counter ions at the particle surface are often designated as the Stern layer and is attached to the particle by electrostatic and van der Waals forces. Surrounding the Stern layer is a diffuse layer in which the concentration of counter ions decreases as it extends out into the bulk of the solution (Figure 1). The diffuse layer is visualized as being the result of the tendency of counter ions to move toward the particle, and the tendency of the ions to move away from the

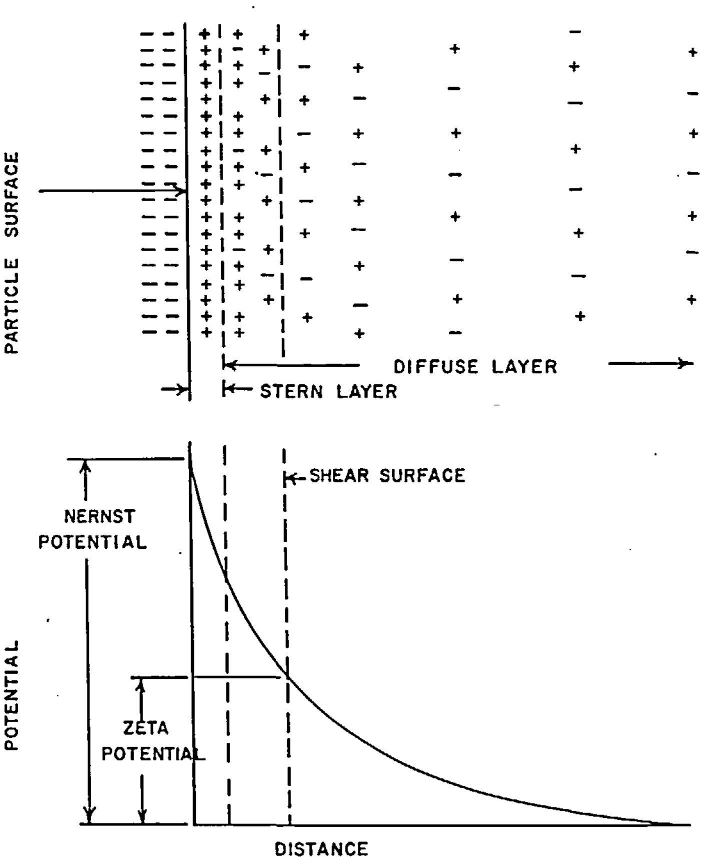


FIGURE 1

Electrical Double-Layer and Associated Potentials particle due to diffusion and shear resulting from particle motion. As seen from the diagram, potential differences are set up between the particle surface and various other parts of the system. The potential between the particle surface and the bulk of the solution is known as the Nernst potential, while the potential between the plane of shear and the bulk of the solution is known as the zeta potential.

The measurement of the zeta potential has proven useful in contributing information regarding colloid stability and the general nature of colloids. Such measurements may be made by a variety of techniques based on electrophoresis and related phenomena[4, 5,6,7,8,9,10,11]. The use of such techniques has been reviewed by Kawamura, Hannah and co-workers.[12,13] More recently, Wang and Shuster[14] have modified and improved the indirect colloid titration technique described by Kawamura and others.[12,13] Experience gained with this method has been described by Bilgen.[15]

INTERACTION OF COLLOID PARTICLES

Colloid particles of like sign tend to interact with one another under the influence of a number of forces. The particles are attracted because of van der Waals forces, but repulsed by electrostatic forces, and hence possess a resultant interaction energy. In addition, the particles posses kinetic energy due to Brownian motion of the particles in solution and under some circumstances kinetic energy due to turbulent mixing. When the kinetic energy exceeds the resultant interaction energy, coagulation of the particles may result. The relative roles of Brownian motion and turbulent mixing depends upon the particle size. With small sizes, Brownian motion provides the major part of the kinetic energy, while turbulent mixing is of major importance in the coagulation of large sizes. By combining the Smoluchowski and Levich equations, it is possible to predict the critical particle size.[3,16] Figure 2 illustrates the nature of the potential energy interactions.[3] It will be noted from the diagram that as the distance

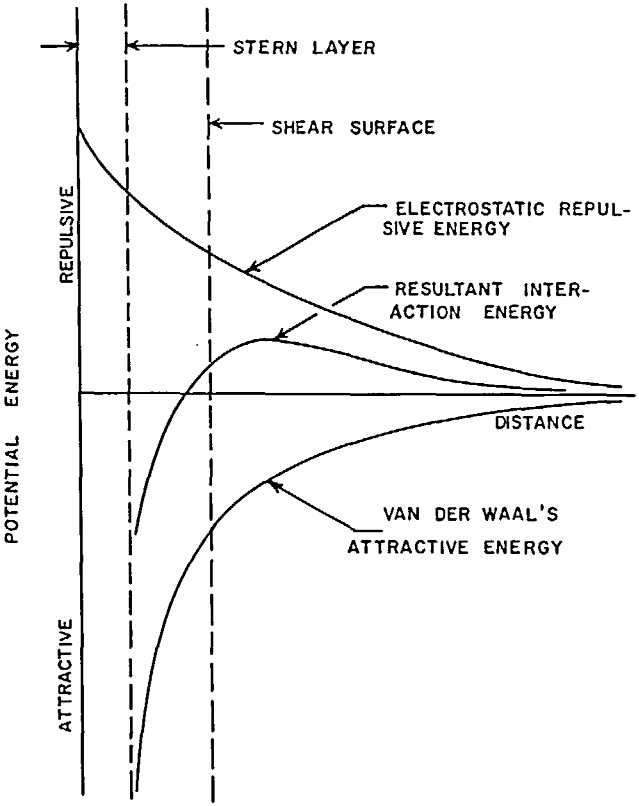


FIGURE 2

Potential Energies of Interaction of Colloidal Particles with Distance

between particles decreases, both the repulsive and the attractive forces increase, resulting in a net interaction energy. This energy level may be considered as an activation energy barrier which must be overcome for coagulation to take place. Or in terms of zeta potential, as long as the zeta potential is greater than the attractive energy, the particles will not coagulate. The zeta potential may be reduced by either (1) compression of the double-layer thickness by introducing various counter ions into the diffuse layer, or (2) by reducing the particle surface charge by promoting the adsorption of counter ions onto the particle surface. The first mechanism is often described as the double-layer interaction mechanism and is exemplified by the use of nonhydrolyzed ions such as sodium or calcium. This mechanism involves double-layer interactions.[2,17] The second mechanism has been designated as the specific surface-interaction mechanism, and involves the neutralization of surface charges through the presence of polymeric substances, such as hydrolysis products of aluminum and iron which are highly charged. Physical mechanisms of boiling and freezing have also been reported to be effective in destabilizing some types of colloids.

Some confusion exists in distinguishing between the terms "coagulation" and "flocculation". In this work the definition used by LaMer[18] is preferred. Coagulation refers to the reduction in zeta potential of colloid particles resulting in destabilization of the particle by compression of the electrical double-layer. Flocculation is defined as the agglomeration of colloidal particles into a three-dimensional floc network by the formation of chemical bridges between particles. Coagulation is usually considered to be a rapid process while flocculation is considerably more time dependent.

It may be noted that a number of studies have been made with the objective of establishing criteria for the design of flocculation apparatus. Notable is the work of Camp,[19] TeKippe and Ham,[20] Argaman[21] and Mohtadi and Rao.[22] Attempts have been made to develop models for predicting performance but with somewhat mixed success. Pilot plant work appears to be essential for good design. As Argaman stated, "Although the use of traditional jar tests for flocculation control provides some indication of the most appropriate type and concentration of flocculent, pilot plant studies are essential if the design of new plants is to be accompanied by some assurance of success."

While information regarding the kinetics of the various physical-interaction mechanisms would be most valuable, it has been noted[3] that reliable models are generally lacking. Coagulation has been viewed as involving the following rate-determining steps: (1) the rate of distribution of counter ions into homogeneity; (2) the rate of movement of counter ions into the diffuse double-layer, or adsorption of the ions on the particle surface with subsequent zeta potential reduction; and (3) the rate at which these charge-altered particles collide. Further clarification of these steps is needed.

COAGULATION BY METAL IONS

Some salts of certain metals such as aluminum, iron, calcium and magnesium when used as coagulants, yield corresponding metal hydroxides, carbonates or more complicated hydrolysis products. These materials can be effective in the destabilization and removal of colloidal particles from solutions. Many of the hydrolysis products precipitate from solution and enmesh colloidal particles in the structure. The metal ions may also be effective in neutralizing particle charges either directly, or through a pathway involving the charge on the various hydrolysis products of the metals. Studies related to understanding the mechanisms involved, and various applications involving this type of coagulation, are extensive in the literature[18,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47]. This type of destabilization will not be considered in detail in this paper. Particularly good reviews of the chemistry involved are found in articles by Stumm and Morgan[48] and Stumm and O'Melia.[43]

USE OF POLYELECTROLYTES

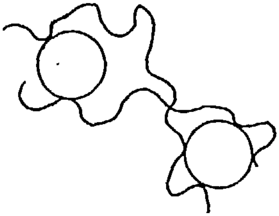
Polyelectrolytes are water-soluble, high molecular weight, synthetic organic polymers containing a series of repeating chemical units. These repeating units are characterized by having ionizable functional groups which dissociate in solution producing charged sites along the polymer chain. When the polymer produces a net positive charge, it is called a cationic polyelectrolyte; when it produces a negative charge, it is called an anionic electrolyte. Polyelectrolytes having no ionizable functional groups are called nonionic electrolytes. It may be noted that polyelectrolytes in nature have been investigated as well as those produced by man.[49]

Polyelectrolytes serve as coagulants in two broad manners. They first of all, may act as primary coagulants in neutralizing colloids directly and allowing aggregation to take place. Secondly, the polyelectrolyte acts as a coagulant through a bridging mechanism. LaMer and co-workers,[18,33] Michaels[50] and Ruehrwein and Ward[51] have been instrumental in developing an acceptable model that explains the ability of long chain polymers to destabilize colloidal suspensions. This theory postulates that a colloidal particle may attach to one or more adsorption sites on the long polymer chain (as seen in Figure 3A) with the remainder of the chain extending out into the bulk of the solution. Other particles may also become attached to the chain at other sites, and hence the polymer molecule serves as a bridge. Hence, particles may become bound into clusters or flocs and grow in size. An increase in polymer concentration in solution will promote increased bridging or flocculation up to the point that adsorption sites are no longer available and the particles become coated with polymer to the extent that the particles are prevented from coming close enough together to allow aggregation.

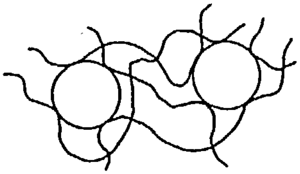
It was pointed out by LaMer and Healy[33] that the bridging mechanism is probably the controlling mechanism in floc formation, rather than the electrostatic charge effect. They have noted that negatively charged polyelectrolytes can be effective in destabilizing negatively charged particles.

Numerous studies have been made to help elucidate the mechanisms involved in polymer-promoted destabilization.[52,53,54,55,56,57] Extensive tests have also been made on the health effects of various coagulant aids.[58,59,60,61,62,63,64,65,66]

A- POLYMER ADSORPTION ON COLLOID SURFACE



B- FORMATION OF FLOC



C- POLYMER OVERDOSE

FIGURE 3

Attachment of Polymer Chains to Colloidal Particles

FILTRATION PROCESSES

The removal of solid particles from water and wastewater by filtration has been extensively studied, and many applications have been reported upon. It is most important to keep in mind that filtration as a process of clarification is almost always associated with other processes such as coagulation, flocculation and sedimentation, and hence a clear understanding of filtration involves a knowledge of the overall process.[67]

Basic theories of filtration have often been classified in terms of physical and chemical theories. A number of investigators have described the removal mechanisms in terms of two steps which are: (1) the transport of particles to the filter medium surface, and (2) the attachment of the particle to the surface.[68,69] The first step involves phenomena which are primarily physical, namely straining, sedimentation, inertial impingement, interception and Brownian movement. The second step involves various electrokinetic and chemical effects. As pointed out by Wnek[10] the failure of some filter models to predict filter behavior has in many instances been due to the lack of recognition of the interaction of these mechanisms. As a convenience, however, the filtration process will be discussed in the following sections roughly in terms of physical and chemical aspects. It may be noted here that the emphasis here will be on the process of particle removal for clarification purposes, and not solids removal for solids recovery purposes as is of interest, for instance, in the chemical industry.

Types of Filter Media

Many types of granular materials are used as filter media, including natural silica sand, crushed anthracite coal, diatomaceous earth, garnet sand, perlite, powdered and granular carbon and others. Various mixtures of different media have also been used and have utility in particular situations. By far the most commonly encountered medium is graded silica sand. For a good discussion of particle size, shape and size distribution, numerous texts are available, such as Fair, Geyer and Okun.[71]

The use of multi-media granular filters has increased in recent years. In a single media sand filter, the sand particles become graded during backwash with fine material at the top and coarser material grading downward to the bottom. As a result, the filter may clog in the upper layers with material removed from solution in a relatively short time. The intent of multi-media filters is to provide coarse, low density material (such as crushed anthracite coal) at the top, progressing to fine, high density material (such as garnet sand) at the bottom. Silica sand may be used as a third medium intermediate in density and fineness. With such beds the burden of removal occurs in the coarse upper layers and the polishing occurs in lower layers. Thus the solid particles may penetrate further into the bed for the same head loss with subsequent longer filter runs. With proper selection of media size and density, the bed will remain stable under conditions of backwash. Among recent articles reviewing the mechanisms of particle removal with mixed media are those of Conley and Hsiung,[72] Craft,[26] Mohanka,[73] Rice[74] and Westerhoff.[75] Cleasby and Woods[76] have described studies made with multi-media filters. They examined the use of the Pruden model and the Camp model for predicting the degree of intermixing between media. They concluded that neither model is completely adequate for design purposes.

Physical Aspects of Filtration

One approach to describing the filtration process has been to develop expressions relating the time rate of change in particulate matter concentrations in terms of various physical parameters of the system, such as particle size, fluid velocity, bed depth and porosity. Assuming a first order relation for the rate of change in concentration, and making use of a mass balance with respect to solids entering and leaving the system, Iwasaki[77] suggested the following equations which have become the basis of most theoretical relationships:

$$\frac{-\partial C}{\partial L} = \lambda C \qquad [1]$$

$$\frac{v\partial C}{\partial L} = \frac{\partial \sigma}{\partial t} + (\varepsilon - \sigma)\frac{\partial C}{\partial t} \qquad [2]$$

where C = volumetric concentration of particles at any time or depth

L = depth of the filter bed

λ = filter coefficient (called the impediment modulus by Iwasaki)

σ = volume of retained particles per unit of filter volume

t = time of filtration

ε = filter bed porosity

The term $\partial C/\partial t$ in equation 2 is the rate of change of material within the pores and is usually negligible.

It may be noted that the first order relation of equation [1] has been verified by work of Friedlander[78] and Spurny et al.[79] Equation [2] is based on assumptions that the filtered material does not undergo chemical or biological changes nor does the density or the porosity change with time.[69]

It has been generally recognized that the filter coefficient is not truly constant but is a function of the specific deposit, σ, as well as time and bed depth. Various investigators have proposed models to show this dependency. Ives has generalized this work in the following expression:[80]

$$\lambda = \lambda o \left[1+\frac{B\sigma}{\varepsilon}\right]^{y} \left[1-\frac{\sigma}{\varepsilon}\right]^{z} \left[1-\frac{\sigma}{\sigma u}\right]^{x} \qquad [3]$$

where B = a geometrical constant related to the degree of bed packing, and equal to $(\varepsilon/1-\varepsilon)$

σu = specific deposit at saturation

x,y,z = empirical values of exponents

Ives further showed that when x, y, and z had values of 1, equation [3] reduced to a form originally proposed by him. It also predicted the form of models predicted by other investigators depending upon values of x, y, and z chosen. Combining equations [1] and [3] yields:

$$\frac{-\partial C}{\partial L} = \lambda o \left[1+\frac{B\sigma}{\varepsilon}\right]^{y} \left[1-\frac{\sigma}{\varepsilon}\right]^{z} \left[1-\frac{\sigma}{\sigma u}\right]^{x} C \qquad [4]$$

While equation [4] can be solved incrementally using a digital computer, a number of difficulties have arisen with its use. To use the equation, the constants must be evaluated empirically. In addition, the units of must be in terms of volume of material per unit volume for use in the equation. However, these values, while related to turbidity or similar terms, are not easily obtainable.

The current physical filtration theories, summarized by Ives and others,[80] appear to have severe limitations. As noted by several investigators including O'Melia and Stumm, Fox and Cleasby, Mintz, and others,[69,81,82,83] present models are not capable of predicting the performance of a filter treating a given solution without extensive laboratory testing. Ives and Sholji[49] have noted that current models are in marked disagreement when used to predict the relationship between the filter coefficient and the variables of particle size, filtration velocity and water viscosity. O'Melia and Stumm[69] conclude that current physical models are either too simple to be flexible enough to apply in practice, or too complex to be used without extensive experimentation.

Consideration of the development of head loss during filtration is important in filter design and operation. A number of relationships have been proposed to relate the parameters influencing head loss and are reviewed in numerous articles and texts.[1, 71,84,85,96,87,74,88,75]

Ives has shown that the Carmen-Kozeny equation may be modified by the addition of a term that is a function of the specific deposit.[88] He reports that a linear head loss with time curve results when the filtrate concentration is small with respect to the influent concentration. Ives and Sholji[49] have reported on findings relating the filter coefficient and various physical parameters of their experimental system.

Chemical Aspects of Filtration

As it has become increasingly apparent that purely physical models were insufficient to adequately describe filtration processes, increased attention has been focused on chemical and electrokinetic aspects of solids removal in filters. A number of investigators have suggested that sorption of suspended matter on filter media plays an important role in filtration. In this regard the work of such people as Camp,[19] Fox and Cleasby,[81] O'Melia and Crapps,[68] Ives and Gregory[85] and others has been noted and discussed by O'Melia and Stumm.[69] The latter authors have presented a filtration model suggesting that suspended particles are removed from solution in a filter bed by a two-step process:

1. Particles are transported to the filter surface.
2. Particles are attached to the surface of the filter media.

The transport process is physical-hydraulic in nature and involves such phenomena as straining, sedimentation, inertial impingement, interception and Brownian diffusion. The attachment process is primarily an electrochemical process influenced by both physical and chemical parameters. Both processes may be considered rate controlling in water filtration. Conditions under which each predominates is considered to depend largely upon particle size. The physical phenomena tend to control for large particles (diameter $> 30\mu$), while chemical effects dominate for small sizes (diameter $< 1\mu$). Both mechanisms are influential for intermediate sizes.

Yao, Habibian and O'Melia[89] have proposed that filtration and coagulation may be viewed as analogous processes, and that the similarities can be helpful in understanding filtration phenomena. They note that the coagulation process may be viewed in terms of the frequency of collision between particles by fluid motion (orthokinetic flocculation) and by Brownian diffusion (perikinetic flocculation), multiplied by a "collision efficiency factor," which reflects the ability of coagulants to destabilize colloidal particles with subsequent attachment. The authors suggest that a similar approach can be used to describe filtration processes. The basic mechanisms of transport, after Yao et al.[89] are illustrated in Figure 4. Shown here is a single piece of filter media acting as a collector. Suspended particles are shown for several cases

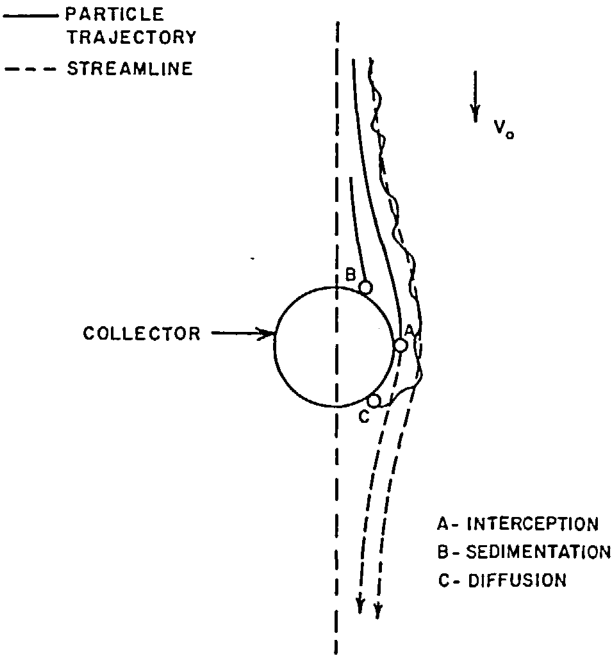


FIGURE 4

Particle Transport Mechanisms in Filtration (from Yao et.al.)

moving in streamlines in the general direction of the gravitational force. A particle may come in contact with the collector through interception, primarily because of its size (Case A). If the particle has a high density relative to the liquid medium, its trajectory will be influenced by gravity and it may contact the collector by the process of sedimentation (Case B). If the particle is subjected to random bombardment by molecules of the fluid medium (Brownian motion) it may come in contact with the collector through the process of diffusion (Case C). The transport processes are affected by such physical factors as the size of the media, the fluid flow and the temperature.

When particles come in contact with the collector, attachment may take place by one or more of the mechanisms of electrostatic interactions, bridging or specific adsorption, all of which are affected by chemical characteristics of the fluid medium and the filter medium, and the presence of coagulants applied in pretreatment.

Based upon the previously mentioned concepts, Yao et al.[89] have developed a model for filtration. The model is stated in terms of a single collector efficiency, η_c, defined as the ratio of the rate at which particles strike the collector, to the rate at which particles flow towards the collector. This model may be expressed as:

$$\ln \frac{C}{Co} = -\frac{3}{2}(1-\varepsilon)\alpha\eta_c\left(\frac{L}{D}\right) \qquad [5]$$

where C and Co are influent and effluent concentrations
ε = void fraction of the bed
α = collision efficiency factor (fraction of collisions which produce adhesion)
L = bed depth
D = size of filter medium

While this model requires experimental evaluation of system parameters, it is useful in describing the filtration process. It may be noted that when filtration does not yield the desired removal of particles, this model may suggest alternatives that will improve performance, such as altering the chemical pretreatment to improve the collision efficiency.

Wnek[70] has recently reported on some electrokinetic and chemical aspects of water filtration. He was primarily concerned with how charges develop on the surface of a particle and how the charge can be controlled or modified to maximize the filter removal efficiency. He concluded that surfactants, pH and ionic strength can be used to improve the efficiency by modifying charge characteristics of either the suspension, filter or both, and by making use of the bridging mechanism. He indicated that such factors as increasing the rate of deposition, extending the depth of penetration, increasing removal capacity and minimizing pressure drop were important factors.

Various investigators have presented evidence related to the influence of various chemical factors on filter performance. O'Melia and Crapps[68] have shown that the type and the concentration of anions and the pH are influential on the performance of filters. Smith[42] has shown that while coagulations and filtrations appear to be closely related, the optimum conditions for each are not necessarily the same. Moffett[90] has reported on work showing that filtration efficiency is related to particle charge, and for color and turbidity removal is optimum at zero mobility. Not all investigators agree with this conclusion.[67] Boyd and Ghosh[91] have shown a dependence of the filter coefficient on the zeta potential of the filter influent. Cleasby and co-workers[92,93] have noted that filtration removal results from a combination of mechanisms and that dominant transport and attachment mechanisms may change with time. He cites the work of Burns et al.[94] and suggests the use of a filter testing apparatus and the development of a filtrability index for evaluating filter performance. Most investigators now agree on the complexity of the filtration process and the interaction of both physical and chemical phenomena. Kawamura[95,96,97] has spoken of this in connection with design and operation of high-rate filters.

POLYELECTROLYTES AS COAGULANTS AND FILTER AIDS

Polyelectrolytes may improve the filtration process by improving the filtrability of solids suspended in solution and/or the solid floc produced by coagulation and filtration. Conley and Pitman[98] noted the improvement in the filtrability of alum floc when a polyacrylamide was added to the influent. Robeck, Dostal and Woodward[99] reported on the use of polyelectrolytes as aids to water filtration.

As discussed previously, polyelectrolytes may be effective in the destabilization of colloidal particles through charge neutralization, and/or bridging which then may permit flocculation or aggregation when contacts occur. As such they act as a primary coagulant. Polyelectrolytes may be applied in a pretreatment step to filtration where coagulation and possibly sedimentation may take place. Polyelectrolytes may also be used to pretreat the filter bed and to provide a coating on the filter media. Polyelectrolytes may also be fed directly ahead of the filter or fed directly within the bed.

Much of the basic work on the role and the characteristics of polyelectrolytes has been described in the field of colloid science. Examples of the fine work in this area includes the work of Dixon, LaMer, Gregory, and many others.[100,101,102,103,104,105] The work of Birkner and Edzwald,[106] Friend and Kitchner,[107] and Narkis and Rebhun[108] have been important in shedding light on the part played by polyelectrolytes in the flocculation process. Baumann and his co-workers[94,109,110] have done extensive work on the action of polyelectrolytes, particularly related to their action as coating materials on filter aids or filter media. They found that considerable shifts in the zeta potential were possible with a consequent change in the adsorptive ability of the filter media in many cases. Many polymer materials were evaluated for this type of application.

The work of O'Melia has been most important in helping to elucidate the part that polyelectrolytes play in the filtration process.[111] In experiments using polymers with a trickling filter effluent and also calcium phosphate solutions, he noted among his conclusions the importance of chemical pretreatment. He noted that there appears to be a particle size for which removal efficiency is a minimum which is of the order of 1μ for conventional filtration practice. He emphasized the similarity of the chemical destabilization required for filtration to that required for coagulation. He also commented on the need to design filter systems so that high performance runs are not terminated early by high head loss and suggested the use of bi- or multi-media filters, upflow filters, etc. Also noted was the possibility of overdosing with destabilizing chemicals resulting in restabilization of particles. He found that for direct filtration, precoating of filter media was essential. He felt that direct filtration was most effective for low-turbidity streams. He did not find direct filtration to be effective without chemical pretreatment, except under conditions of high cationic dosage. He found that alum and an anionic polymer used in series provided effective destabilization for the direct filtration of trickling filter effluent.

In a recent article by Adin and Rebhun,[112] the authors describe a process called "contact flocculation-filtration." In this process a filter bed of relatively coarse media was used to decrease head loss, and a flocculant (alum or polyelectrolyte) was fed to the suspension immediately ahead of the filter. Flocculation occurred during contact with the filter medium. They found that a cationic polyelectrolyte was highly efficient at high hydraulic loads and that strong attachment forces resulted. This was not true with alum alone and filtering efficiency was poor. This work, in general, is in agreement with earlier studies reported by Basaran[113] and Shea et al.[114] The latter investigators emphasized the importance of properly designed multi-media filter beds progressing from coarse to fine media. Other experiences with direct filtration have been reported in the literature.[115,116,117,118].

Loganathan and Maier[119] have reported on studies made of the effects of such process variables as pH, ionic concentration and polymer dosage to the physical-chemical characteristics of solid surfaces. They noted that Ca^{++} and Mg^{++} ions enhance turbidity removal for polymer treated sand and was most effective with anionic polymers. They found that polymer pretreatment altered the zeta potential of the sand which, in turn, altered the attachment mechanism for various types of turbidity.

USE OF POLYELECTROLYTES IN WATER TREATMENT

Kleber[120] has discussed the use of polyelectrolytes in water clarification processes and has indicated advantages for their use. He further discusses requirements for feeding and mixing. Beardsley[121] has similarly indicated specific application areas of the three types of polymers. Specific problems of color removal from natural waters have been addressed by Bond and Bowie [122] and Burbank et al.[123] These studies indicated that polyelectrolytes used in conjunction with alum was effective in color removal.

A study of the use of cationic polyelectrolytes as primary coagulants for natural water treatment has been reported by Pressman.[124] For several polymers and several waters it was found that the negative charge on turbidity particles was reduced with increased dosage. Optimum flocculation occurred at a zeta potential near zero. Pressman also found that a charge reversal took place with further additions. The optimum dosage was strongly influenced by the nature of the water. Robinson[125] reported on laboratory studies and later application to Kansas River water using polyelectrolytes as primary coagulants and found them to be more effective than standard coagulants.

POLYELECTROLYTE APPLICATIONS IN DOMESTIC WASTEWATER TREATMENT

Many studies have been reported upon, relative to the use of polyelectrolytes in municipal wastewater treatment. These include use with raw sewage, treatment plant effluents, waste sludge, removal of nutrients, use with carbon, and others.

Freese and Hicks[126] described the use of polymers to flocculate raw wastewater. They used both cationic and anionic materials during primary sedimentation. They did not find a significant improvement in solids capture. Sreekantham and Sussman[127] conducted somewhat similar studies in Rhode Island and found some reduction in loads. Teot and Daniels[128] investigated the rates and degrees of flocculation after treatment with inorganic cations and anionic polyelectrolytes. It was found that anionic colloids are not flocculated significantly by anionic polyelectrolytes in the absence of multivalent cations. Both rate and degrees of flocculation of raw sewage were logarithmic functions of polyelectrolyte and multivalent cation concentrations. Wirts[129] reported on experiences with a demonstration project in Cleveland in which polymer addition was made. It was noted that significant improvements in SS and BOD removals were obtained in primary treatment. In addition, more efficient operation of the secondary treatment was obtained and sludge pumpability improved.

Kraus[130,131] has reported on the use of specially prepared membranes formed from polyelectrolytes for use with primary and secondary effluents from treatment plants. He stated that membranes formed from sewage constituents, while rejecting salts and organic materials, seemed inferior to separately formed dynamic cation exchange active membranes. Tchobanoglous[132] has reportedly shown that various cationic polyelectrolytes are effective in improving solids removal from secondary effluent. Culp and Hansen[133] have described work on polishing the effluent from an extended aeration operation using mixed media filtration. In a somewhat different application, Maher[134] used cationic polyelectrolytes in coagulation of solids and coliform in combined sewer overflows. Other similar applications have been reported.[135,136,137,138] Garland and Beebee[139] have described work related to the use of powdered activated carbon together with Purifloc polyelectrolyte in treating activated sludge plant effluent. Estimated costs for a large scale unit based on pilot plant results appear to be high. Studies by Wang[47] for determining optimum powdered carbon and polyelectrolyte dosages in military wastewater treatment has been reported.

A number of applications of polyelectrolyte use in conditioning sewage sludge have appeared in the literature.[140,141,142] Success has been mixed and attention has been directed to the variability of sludge composition and characteristics. Some improvements in filtrability have been noted.

Some interesting work has been described on the removal of various nutrients and inorganic materials from wastewater. Bell et al.[143] gave details on their experience with a continuous precipitation and countercurrent filtration process for removal of phosphorus from municipal wastewater. Using alum and an anionic polyelectrolyte, they stated that total phosphate, orthophosphate and condensed phosphate could be effectively reduced over a wide range of influent concentrations. Brunner, Spiegel and Charles,[144] in describing results of a demonstration project at Fort Wayne, Indiana, stated that polyelectrolytes improved phosphorus removal in an activated sludge unit. Green et al.[145] showed that phosphorus levels could be reduced in treated wastewater using ferric chloride and a polymer flocculant to less than 1 mg/ℓ. Other similar experiences have been reported.[146,147]

APPLICATIONS OF POLYELECTROLYTES IN INDUSTRIAL WASTEWATER TREATMENT

Quite a variety of applications of polyelectrolytes to industrial waste treatment have been reported. While not all of the procedures involve filtration, the mechanisms are closely enough related to be of interest. For instance, Larson and Maulwurf[148] described work on the use of anionic polyelectrolytes with ferric chloride for the treatment of combined domestic wastewaters and meat-packing wastes. The coagulants were added in the primary sedimentation tank and promoted the formation of a settleable floc, and substantial reduction in BOD and settleable solids. No adverse effects in trickling filter operation was noted. Similarly, Lee[149] found that a combined waste from a pet food manufacturing operation and city domestic waste could be successfully treated in a secondary-tertiary treatment facility. Alum and polyelectrolyte coagulation followed by flocculation, sedimentation and mixed media filtration was used. Eye[150] found that polyelectrolyte addition to leather vegetable tannery wastes aided the clarification processes. In a report of the Armco Steel Corp.[151]

a treatment process was described for clarifying a waste stream containing 400 to 4000 PPM of emulsified oil. Alum, lime, clay and polyelectrolyte were added to the waste and a rapid mix was utilized to promote flocculation. Air flotation was then used to separate the oil. Comprehensive laboratory tests were made which included determinations of zeta potential, streaming current, and particle size distribution to evaluate the interrelationships of operating parameters. Grieves, Conger and Malone[152] found that polyelectrolytes were of help in the operation of a continuous foam clarification process used on turbid natural waters. Similarly, Michelsen and Fansler[153] reported that cationic polyelectrolytes could be used in conjunction with foam fractionation to treat textile dye wastes. Substantial reductions of COD, color and turbidity were obtained in laboratory tests. They concluded, however, that alum alone was more effective and less expensive. Sussman and Wang[154,155,156] have described on several occasions, work done on the treatment of metal plating wastes using polyelectrolytes with and without calcium ions in a flocculation process followed by filtration. When compared with a process involving ferrous sulfate and lime, they found little difference in removal rates, refiltration rate and specific resistance, but the sludge volume was considerably reduced when polyelectrolytes were used.

Lent and Ross[157,158] have conducted field studies to evaluate a wastewater treatment process utilizing powdered activated carbon and a cationic polyelectrolyte in a modified Army water purification unit. The waste stream included effluents from field military shower, laundry and kitchen units and a commercial laundromat. The removal of phosphates from industrial wastewater has been reported to be successfully accomplished by treatment with alum and polyelectrolytes.[159]

A number of articles appear in the literature in which work on the use of polyelectrolytes for treating mineral-processing solutions has been described.[156,160,161] Polyelectrolytes have been reported to be effective in this application.

In a recent report by Wang et al.[162] work on the effectiveness of organic polymers in the treatment of an industrial wastewater containing nitrocellulose was described. Cationic and nonionic polymers were found to be effective in coagulation of colloidal particles. Bentonite and lime were used as coagulant aids with the polymers. When polymers were fed to the waste stream and coagulation, flocculation and sedimentation allowed to take place, followed by filtration, excellent removal resulted. When direct addition of polymer was used in a contact coagulation-filtration process, the treatment was not successful. The very high turbidity resulted in the fast buildup of a thick layer of cake and subsequent high head loss.

MISCELLANEOUS APPLICATIONS OF POLYELECTROLYTES

A number of miscellaneous applications of polyelectrolyte use were found in the literature. While not of primary interest in this work, they were noted. For instance, Foess and Borchardt[163] have shown how the alteration of surface properties via pH can effect the degree of chemical attachment by algae. McGarry[164] has described work on the use of cationic polyelectrolytes for use with alum in the treatment of wastewater in the harvesting of algae. He reported an improvement in floc strength as the result of polymer addition.

A large number of biomedical and health-related references have been noted. Melnick[165] has reported on the use of polyelectrolytes for removal of the agent of hepatitis from blood components. Johnson[166] has reported on similar work. Melnick and co-workers[167, 168] have described methods and apparatus for concentrating viruses from large volumes of natural waters through the use of insoluble polyelectrolytes. Busch and Stumm[169] have reported on the aggregation of bacteria in waste treatment. York and Drewry[170] and Shelton and Drewry[171] have studied the relative effectiveness of several coagulants and polyelectrolytes for removing viruses and bacteria from surface waters. Brown et al.[172] noted the importance of polymer use in virus removal by diatomite filtration. Thorup et al.[173] tested a variety of polyelectrolytes as primary coagulants and coagulation aids in the removal of bacteria and viruses from artificially seeded water, cationic polymers performed most satisfactorily. Engelbrecht and his co-workers[174,175,176] have reported extensively on many aspects of the application of polymers and other coagulants to virus removal from water. Ford and Pressman[177] have reported on a field study directed towards determining the capabilities of water purification units for removing coliform organisms and viruses from a river water. It was found a prototype reverse osmosis water purification unit employing cationic polymer addition, prefiltration and hypochlorination was effective in reducing levels of coliform organisms and viruses to undetectable levels.

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