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Using Ceramic Materials for Enhanced Wastewater Treatment in Industrial Applications

THE AUTHOR

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ABSTRACT

Currently, effluents generated by industry represent the major contributor to water pollution problems. This is probably due to the fact that the industry consumes a huge amount of water and simultaneously produces a huge volume of highly polluted wastewater. Coagulation-flocculation technique is one of the physical-chemical techniques widely employed to treat industrial wastewater. While implementing this method, the major concern is how to make the process more efficient in terms of economics and residual water quality and at the same time improve the produced sludge (in terms of quantity and characteristics) so that it can be easily treated or disposed off later. Floc characteristics are important in determining the efficiency of industrial wastewater treatment. This study on low-cost ceramic materials (e.g. bentonite) as coagulation aids suggests a promising alternative to the expensive polymeric coagulant aids for industrial wastewater treatment.

KEYWORDS

ceramic coagulant aids, industrial wastewater treatment, coagulation, flocculation
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1 Introduction

The best purification approaches are sought in order to fulfil the decontamination objectives required by law. There are many processes for wastewater treatment, such as coagulation, precipitation, extraction, evaporation, adsorption on activated carbon, ion exchange, oxidation and advanced oxidation, incineration, electroflotation, electrochemical treatment, biodegradation and membrane filtration [1]. However, many of the available proposed processes cannot be used on an industrial scale for technological and especially economic reasons. Complete treatment requires several steps, and it is often appropriate to combine several methods of purification towards high efficiency, knowing that each method has its advantages and its disadvantages. An industrial effluent treatment process line must also be designed according to the quality objectives: for instance, lowering the levels of pollution, reuse or recycling.

A general scheme of industrial water treatment involves three main stages [1]: a primary treatment or pre-treatment step using mechanical, physical and chemical methods; a secondary treatment or purification step using chemical or biological methods and treatment of the sludge formed (e.g. incineration). In certain cases, a tertiary treatment of the water can also be required to remove the remaining pollutants or the molecules produced during the secondary purification (e.g. the removal of salts produced by the mineralization of organic matter). Primary treatment only concerns with heterogeneous effluent (i.e. effluent containing suspended solids or immiscible liquids) and eliminates the solid particles and suspended substances (colloids or dispersions) from the effluent.

2 Coagulation and flocculation processes

Coagulation-flocculation is frequently applied to processes in the primary purification of industrial wastewater and in some cases in secondary and tertiary treatment [2]. Coagulation using chemical coagulants consists of combining insoluble particles and dissolved organic matter into large aggregates, thereby facilitating their removal in subsequent sedimentation, flotation and filtration stages. It usually involves the dispersal of one or several chemical reagents, which destabilizes the colloidal particles, leading to the formation of micro-floc. Bonding the micro-floc particles together by the addition of a flocculation additive forms larger, denser flakes that are easier to separate. A simple separation step then eliminates the floc. The coagulants and flocculants frequently used are mineral additives, including metal salts such as polyaluminium chloride and synthetic polymers such as polyacrylamide.

Using of these chemical substances may have several environmental consequences, including an increase in metal concentration in water (which may have human health implications), the production of large volumes of (toxic) sludge and the dispersion of acrylamide oligomers, which may also be a health hazard. For these reasons, alternative coagulants and flocculants have been considered for environmental applications [3]. Biopolymers may be of great interest since they are natural, low-cost products characterized by their environmentally friendly behaviour. Among these biopolymers, chitosan may be considered as one of the most promising coagulation/flocculation materials [4]. Figure 1 shows the clarification system incorporating coagulation and flocculation.

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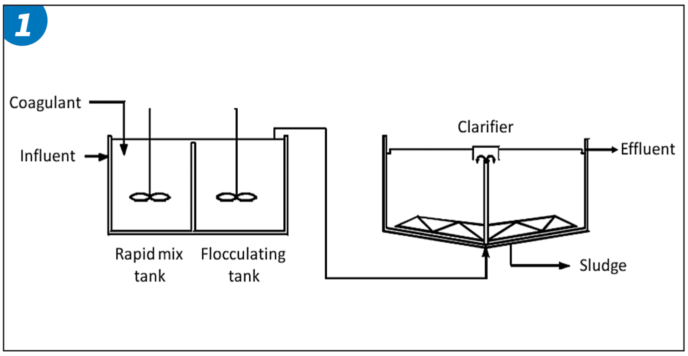

Fig. 1 • Clarification system incorporating coagulation and flocculation

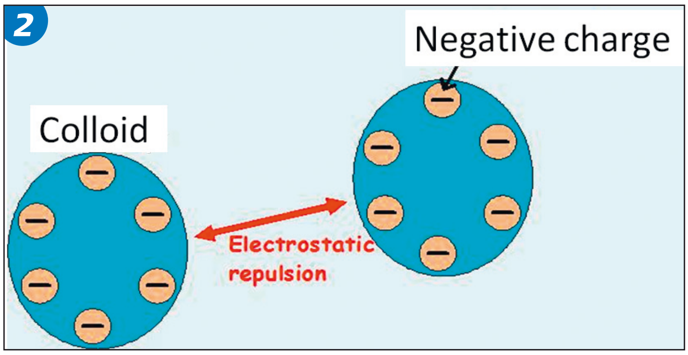

Fig. 2 • How the chemical coagulants work

3 Materials

3.1 Organic polyelectrolytes

The use of organic polyelectrolytes in water treatment was recently reviewed by Bolto and Gregory [5], with emphasis on the types of polymers commonly available and the nature of the impurities to be removed. Polyelectrolyte applications in industrial wastewater treatment have been reviewed by Bratby [6] and Türkman [7]. Examples include effluents from the dye, textile and milk industries. Figure 2 shows how the chemical coagulants works. The colloids are negatively loaded so that they repel each other and cannot make contact.

The two major classes of materials used in coagulation/flocculation processes [8] are:

(1) inorganic and organic coagulants including mineral additives (lime, calcium salts, etc.), hydrolyzing metal salts (aluminium sulphate, ferric chloride, ferric sulphate, etc.), pre-hydrolyzed metals (polyaluminium chloride, polyaluminosilicate sulphate, etc.) and polyelectrolytes (coagulant aids), and

(2) organic flocculants including cationic and anionic polyelectrolytes, non-ionic polymers, amphoteric and hydrophobically modified polymers and naturally occurring flocculants (starch derivatives, guar gums, tannins, alginates, etc.).

Examples of polymeric flocculants used in water and wastewater treatment are shown in Table 1.

Table 1 • Examples of polymeric flocculants used in water and wastewater treatment

Cationic polyelectrolytes	Anionic polyelectrolytes	Non-ionic polymers
• Poly(diallyldimethyl ammonium chloride) • Epichlorohydrin/dimethylamine polymers • Cationic polyacrylamides • Poly(alkylamines) [poly(ethyleneimine), poly(vinylamine)] • Poly(styrene) derivatives • Ionenes • Sulphonium polymers • Natural cationic polymers (chitosan, cationic starches)	• Anionic polyacrylamides • Carboxylic acid polymers • Phosphonic acid polymers • Sulphonic acid polymers • Natural anionic polymers (sulphated polysaccharides, modified lignin sulphonates)	• Polyacrylamide • Natural non-ionic polymers (starch, cellulose derivatives)

3.2 Inorganic metal salts

Coagulation is mainly induced by inorganic metal salts, e.g. aluminium and ferric sulphates and chlorides. The most common additives are aluminium sulphate (generally known as alum), ferric chloride and ferric sulphate [9]. The addition of these cations results in colloidal destabilization as they specifically interact with and neutralize the negatively charged colloids. Common inorganic coagulants are shown on Table 2. For example, once the Fe(III) coagulant has been added to the solution to be treated, the Fe(III) ions hydrolyze rapidly in an uncontrollable manner, forming a range of hydrolysis species that play an essential role in the coagulation process. Figure 3 shows the determination of optimal Fe(III) dosage.

Table 2 • Common inorganic coagulants

Name	Typical formula	Typical strength	Typical forms used in water treatment	Density / kg/m^3	Typical uses
Aluminum sulfate	$Al_2(SO_4)_3 \cdot 14\text{–}18\ H_2O$	17 % Al_2O_3	lump, granular, or powder	961.1–1121.3	primary coagulant
Alum	$KAl(SO_4)_2 \cdot 12H_2O$	8.25 % Al_2O_3	liquid	1331.4	
Aluminum chloride	$AlCl_3 \cdot 6H_2O$	35 % $AlCl_3$	liquid	1497.5	primary coagulant
Ferric sulfate	$Fe_2(SO_4)_3 \cdot 9H_2O$	68 % $Fe_2(SO_4)_3$	granular	1121.3–1153.3	primary coagulant
Ferric floc	$Fe_2(SO_4)_3 \cdot 9H_2O$	41 % $Fe_2(SO_4)_3$	solution	1472.6	primary coagulant
Ferric chloride	$FeCl_3$	60 % $FeCl_3$, 35–45 % $FeCl_3$	crystal, solution	961.1–1025.2 1342.5–1483.6	primary coagulant
Sodium aluminate	$Na_2Al_2O_4$	38–46 % $Na_2Al_2O_4$	liquid	1467–1550.1	primary coagulant; cold/hot precipitation softening

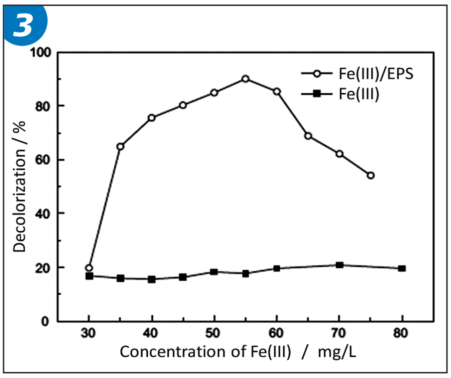

Fig. 3 • Determination of optimal Fe(III) dosage [18]

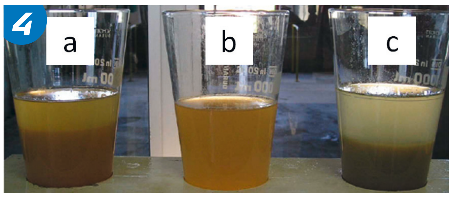

Fig. 4 • Photograph of samples analyzed – a: effluent after PAC treatment, b: raw effluent, c: effluent after chitosan-based material treatment

Metal speciation in solution has been well documented [9]. In wastewater treatment using inorganic coagulants, an optimum pH range in which metal hydroxide precipitates occur should be determined. The addition of metals depresses the wastewater pH to a lower value. In general, decreasing the pH from the alkaline levels to near neutral levels has a strong positive effect on the reduction of turbidity, suspended solids and chemical oxygen demand (COD). However, the significant disadvantage of these conventional coagulants is the inability to control the nature of the hydrolysis species formed when the coagulant is introduced in the solution [10]. As a result, their performance is dependent not only on the pH of the water and their concentration, but also on the temperature and nature of the solution. Therefore, new types of reagents have been developed [11].

3.3 Alternative coagulants

Pre-hydrolyzed forms of aluminium, such as polyaluminium chloride (PAC), and iron, such as polyferric sulphate (PFS), are more effective than traditional additives. Their significant advantage is that their hydrolysis occurs under specific experimental conditions during the preparation stage of the coagulants and not after their addition to the raw solution. It is known that PAC-based products provide better coagulation than alum at low temperatures and also produce lower volumes of sludge. Because they are already partially neutralized, they have less effect on the pH of the water and so reduce the need for pH correction. However, a detailed understanding of the flocculation mechanisms (in particular the mode of action) of these coagulants is still lacking [12].

3.4 Polymeric coagulant aids

The coagulation process is not always perfect as it may result in small flocs when coagulation takes place at low temperatures or produce fragile flocs that break up when subjected to physical forces. It is not only necessary to overcome these problems but also to improve the process to obtain good quality effluent and rapid sedimentation of the flocs formed. To do so, several products known as coagulant aids can be used to bring together and agglomerate the flocs formed by the coagulant [9]. These water-soluble polymers, regularly used in water treatment, are mainly synthetic, although a few natural products may be of interest [10]. The polymeric additives are broadly characterized by their ionic structure: cationic, anionic and non-ionic [12]. Ionic polymers or "polyelectrolytes" of various structures are usually used as coagulant aids to enhance the formation of larger floc in order to improve the rate of sedimentation [12]. Coagulant aids can act either by polymer bridging or by charge neutralization [12]. Figure 4 shows samples of (a) effluent after PAC treatment, (b) raw effluent and (c) effluent after chitosan-based material treatment. It is generally expected, and often found, that the coagulation–flocculation efficiency of chitosan is proportional to its charge, and, consequently, highly N-deacetylated samples are usually applied as coagulant and flocculant materials.

3.5 Inorganic flocculants

Flocculants are used in fast solid–liquid separations involving the aggregation of particles. Flocculating agents are classified into inorganic and polymeric materials [9]. Inorganic flocculants have almost been abandoned because they had numerous disadvantages, such as the large amounts required for efficient flocculation and subsequently the large volume of sludge produced. They are also highly sensitive to pH, inefficient towards very fine particles and applicable only to a few disperse systems [12]. Inorganic polymeric flocculants such as pre-hydrolyzed PFS or polyferric chloride (PFC) have been recently proposed. These materials contain complex polynuclear ions formed by OH bridging having high molecular weight and high cationic charge. These compounds become more effective at a comparatively lower dose than the conventionally applied reagents. They can be used over a wide range of pH and temperature due to their high level of hydrolysis. Technological progress in polymer chemistry has also improved flocculant technology to provide organic polymers and polyelectrolytes with greater purification efficiency [13].

3.6 Organic flocculants

Commercial organic flocculants are basically of two types: synthetic materials based on various monomers (acrylamide, acrylic acid, diallyldimethylammonium chloride, etc.) and natural organic materials based on polysaccharides or natural polymers (starch, cellulose, alginate, natural gums, etc.) [14]. The advantage of polymeric flocculants is their ability to produce large, dense, compact flocs that are stronger and have good settling characteristics compared to those obtained by coagulation. Polymeric flocculants are easy to handle and immediately soluble in aqueous systems. They can also reduce the sludge volume. Because cationic polymeric flocculants destabilize particles and colouring matter through the compression of electrical double layers, charge neutralization, adsorption and subsequent formation of particle–polymer–particle bridges, high removal efficiency can be achieved even with a small amount of flocculant, which generates a small volume of sludge [11].
Furthermore, the polymer performance is less dependent on pH (for example, polyamines are effective over a wide range of pH). There are no residuals or metals added, such as Al(III) and Fe(III), and the alkalinity is maintained. The flocculation performance primarily depends on the type of flocculant used, how much is used, its molecular weight, its ionic nature, the type of material in suspension wastewater and the type of wastewater [15]. Poly(acrylamide) (PAM) is a commonly used organic polymeric flocculant. It is possible to synthesize polymers with various functions (positive, negative or neutral charge) that can be used to produce a good settling performance at relatively low cost. Figure 5 shows the effect of time on water recovered during flocculation. Although extensive work has been done, future research needs to look into how molecular weight and charge density distribution affect the flocculation performance to produce a better choice of flocculants for specific industrial applications [16]. Table 2 shows a list of coagulants and coagulant aids/flocculants.

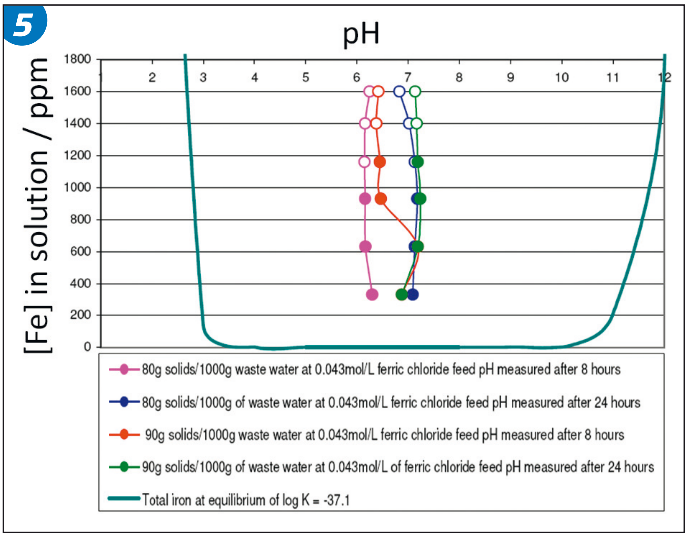

Fig. 5 • The effect of time on water recovered during flocculation [18]

3.7 Drawbacks and need for low-cost, efficient alternatives

As previously reported, the inorganic salt aluminium sulphate (alum) is one of the most widely used coagulants in conventional water and wastewater treatments. The performance of alum no longer needs to be proved, and it is appreciated for its low cost, ease of use and availability. However, it produces abundant sludge that is difficult to dehydrate, and its efficiency is entirely dependent on pH. In addition, when formed in cold water, alum flocs are not very mechanically resistant. The use of alum is a source of concern, and the debate about its possible toxicity is still open. Since high aluminium concentrations in water may have human health implications, environmentally friendly coagulants will present an interesting alternative for the purification of wastewaters [17].

The use of inorganic polymeric coagulants has been also questioned. Increasing use is also being made of synthetic coagulants of organic polymeric origin. Commercial synthetic polymers have been utilized in coagulation/flocculation processes for water purification for at least four decades [17]. In comparison with alum, some of the advantages of these polymers are lower coagulant dose requirements, increases in the rate of separating the solid and water phases arising from larger agglomerate sizes, efficiency at low temperatures (hydrolyzing metal coagulants perform less well at low temperatures), a smaller volume of sludge, a smaller increase in the ionic load of the treated water, a less pH-dependent process and a reduced level of aluminium in the treated water. Polymer-based products also improve settleability and increase the floc toughness. However, although synthetic water-soluble polymers find a wide range of applications as coagulants and flocculants, the potential problems associated with their use are high cost, lack of biodegradability and polymer toxicity.

It is important to note that the use of polyelectrolytes is also a source of debate. Contaminants of synthetic polymers used in water and wastewater treatment generally arise from residual unreacted monomers (such as acrylamide, ethyleneimine and trimethylolmelamine), unreacted chemicals used to produce the monomer units (such as epichlorohydrine, formaldehyde and dimethylamine) and reaction by-products of the polymers in water [16]. For example, acrylamide is extremely toxic, producing severe neurotoxic effects [17]. Commercial forms of synthetic organic flocculants may also contain toxic products from the additives. Bolto and Gregory [16] reported that the normally used anionic and non-ionic polymers are generally of low toxicity, but cationic polyelectrolytes are more toxic, especially to aquatic organisms. The majority of commercial polymers are also derived from petroleum-based raw materials using processing chemistry that is not always safe or environmentally friendly.

Today, there is growing interest in developing natural, low-cost alternatives to synthetic polyelectrolytes [18]. Numerous biological products have recently been proposed and studied as effective coagulants and flocculants for replacing conventional materials [19]. Some of the reported products named “bioflocculants” include biopolymers (starches, chitosan, alginates) and microbial materials produced by micro-organisms, including bacteria, fungi and yeast [20]. Compared with conventional chemical flocculants, bioflocculants are safe and biodegradable polymers and produce no secondary pollution [21]. They may potentially be applied not only in food and fermentation processes and downstream processing, but also in water and wastewater treatment.

Because of the above concerns of polyelectrolyte toxicity, it is believed that the use of bioflocculants will increase [20]. Over the usual range of water pH 5–9, particles nearly always carry a negative surface charge, and because of this, they are often colloidally stable and resistant to aggregation. Coagulants are then needed to destabilize the particles. Destabilization can be brought about by either increasing the ionic strength (giving some reduction in the zeta potential and a decreased thickness of the diffuse part of the electrical double layer) or specifically adsorbing counterions to neutralize the particle charge. It is well known that bioflocculants can play these roles because they have particular macromolecular structures with a variety of functional groups that can interact with contaminants [17]. Bioflocculation is a novel approach that is effective and competitive. In particular, chitosan is a promising bioflocculant for environmental and purification purposes, as reported in recent patents [20].

3.8 Ceramic material as promising, low-cost alternative

Bentonite is an absorbent aluminium phyllosilicate, generally an impure clay consisting mostly of montmorillonite. There are different types of bentonites, and their names depend on the dominant elements, such as potassium (K), sodium (Na), calcium (Ca) and aluminium (Al). As noted in several places in the geologic literature, there are some nomenclatorial problems with the classification of bentonite clays. Bentonite usually forms from the weathering of volcanic ash, most often in the presence of water. However, the term bentonite, as well as similar clay called tonstein, has been used for clay beds of uncertain origin. For industrial purposes, two main classes of bentonite exist: sodium and calcium bentonite. In stratigraphy and tephrochronology, completely devitrified (weathered volcanic glass) ash-fall beds are commonly referred to as K-bentonites when the dominant clay species is illite. Other common, and sometimes dominant, clay species are montmorillonite and kaolinite. Kaolinite-dominated clays are commonly referred to as tonsteins and are typically associated with coal.

Bentonite clay is used as the weighting agent in water that is high in colour but low in turbidity and mineral content. This type of water usually would not form floc large enough to settle down. Thus, the bentonite clay plays its role in dye removal employing coagulation and flocculation, joining the small floc quickly [21].

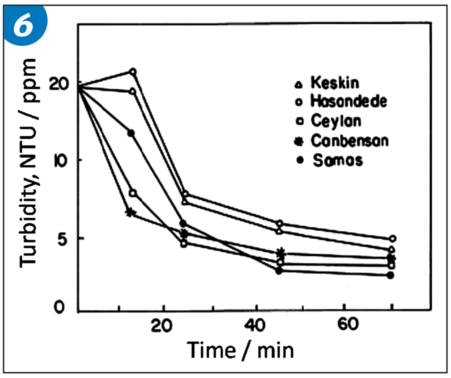

Fig. 6 • Change in turbidity of wastewater treated with CaO and different clays as a function of time [21]

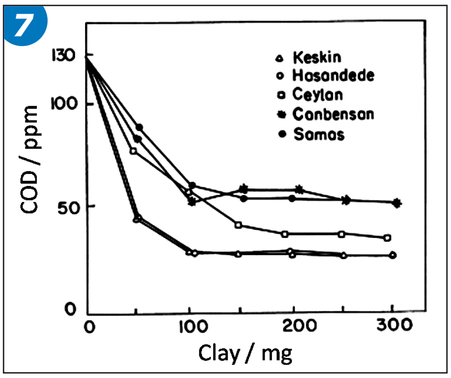

Fig. 7 • Change in COD of wastewater treated with $Al_2(SO_4)_3$ and different amounts of different clays [21]

Table 3 • Mineral analysis of bentonite (in mass-%)

SiO_2	Al_2O_3	MgO	Fe_2O_3	Na_2O	CaO	K_2O	TiO_2	other
65	16.28	3.98	3.75	1.75	0.75	0.29	0.27	0.09

3.9 Bentonite clay as ceramic coagulant aid

Materials commonly known as clays (due to their particle size), such as bentonite, have the potential to act as alternative low-cost adsorbents because they are naturally available and possess unique physiochemical properties. Bentonite consists of layers of two tetrahedral silica sheets sandwiching one octahedral alumina sheet. A mineral analysis of bentonite (in % by mass) is shown in Table 3. Due to the isomorphous substitution of the silicon ions by aluminium or ferric cations in the tetrahedral sheets, and the aluminium ions by magnesium or ferrous cations in the octahedral sheets, bentonite has net negative charges on its layer lattice. To maintain the electrical neutrality, other cations external to the lattice, like sodium or calcium ions, are commonly present in the interlayer region. When clay is in contact with water, these charge-compensating cations can be exchanged or replaced by others present in the bulk of the suspension [19]. Figure 6 shows the change in turbidity of wastewater treated with CaO and different clays as a function of time [21].

The application of bentonite as an adsorbent is largely based on its ability to exchange cations. Previous studies show that the modified bentonite obtained by replacing the inherent clay inorganic cations with suitable quaternary amine cations or surfactant to remove organic contaminants from aqueous solution can affect the capacity of the bentonite to exchange [20]. Ca-montmorillonite possesses larger adsorption capacity than Ti-montmorillonite because Ca^{2+} is easier to displace by ion exchange. The removal of acid dyes was promoted using sulphuric acid-activated bentonite compared with untreated bentonite. Bouberka et al. used pillared and surfactant-activated bentonite for treating effluent containing acid dye; they reported that the modified clays displayed higher adsorption capacity than the original clay toward the anionic dye in an acidic environment [21]. Figure 7 shows the Change in COD of wastewater treated with $Al_2(SO_4)_3$ and different amounts of different clays. The many uses of bentonite clay range from coagulant to filter aid. It is a highly effective chemical, in granular form, for the purification of wastewater and sludge dewatering. It is composed of inorganic minerals and other proprietary compounds specially produced to absorb a wide variety of contaminants. It also can encapsulate suspended solids, many organic compounds and toxicants. Bentonite clay can be dispersed into the treatment tank manually with a measuring scoop or continuously with a dry feed system, providing easy-to-use, one-step chemistry.

4 Conclusions

Coagulant aids such as activated silica, clay and polyelectrolytes are used in coagulation/flocculation processes, usually to obtain higher efficiency, to reduce the amount of required coagulant and to form stronger and more settleable flocs. In this step, the effect of bentonite as a natural coagulant aid can be observed at different dosage levels for different coagulants, with different concentrations of the coagulant aid. Bentonite is a type of clay used as a weighting agent in water high in colour and low in turbidity and mineral content. The bentonite joins with the small floc, making the floc heavier and thus making it settle more quickly. By adding bentonite to the coagulation/flocculation process, dye removal efficiencies increased by 18–60 %. If pH adjustment with lime is not needed, bentonite clay or activated silica can be used as a coagulant aid.

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