

BITTERNS AS COAGULANTS FOR TREATMENT OF MUNICIPAL WASTEWATER

G. El Diwani, Sh. El Rafie

National Research Center
Chemical Engineering and Pilot Plant Lab.

ABSTRACT:

Bitterns, by products of solar salt production, are found to be enriched in magnesium. Bitterns have been found to be effective and economic coagulants for municipal wastewater. Freshly collected grab samples of municipal wastewater from Zenien municipal wastewater treatment plant, were alkalized to pH levels of 11.4 ± 0.1 by adding caustic soda and calcium hydroxide. Serial dosages of liquid bittern were added and the jar-test technique was used to determine the effect of the process on a number of determinant parameters. Liquid bittern, dried bittern and synthetic polymer (Zetag 92) were used singly as coagulating agents to determine their clean-up effect on effluent characteristics. The extent of bacterial inactivation was investigated as well. Seawater dry bittern was found to be an effective and economic source of magnesium that may be used in the treatment of municipal wastewater. Turbidity and suspended solids removal exceeded 99%. Recorded chemical oxygen demand removals reached 90%. Very limited difference in efficiency of treatment were noted between the use of caustic soda and calcium hydroxide as alkalized agents. Liquid bittern demonstrated an advantage over dry bittern in imparting the least increase in dissolved solids to treated effluent. The process is very effective in inactivating fecal bacteria. Carbonation by the addition of CO_2 in concentration ranging between 3.26 and 80 ml/L (depending on initial levels of pH, alkalinity and the nature of the alkalizing agent used) were needed to neutralize clarified supernatants to acceptable levels. Rate of settling for the precipitated hydroxide through the reaction between magnesium ion from liquid bittern or dry bittern at different concentrations with caustic soda and calcium hydroxide solutions were studied singly and compared with settling rates of synthetic polymer Zetag 92. Finally factors imparting the economic of the process are considered to estimate the cost incurred.

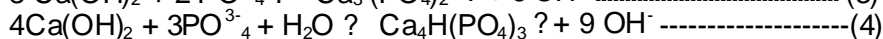
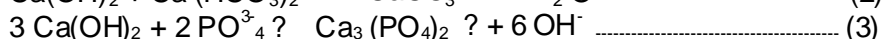
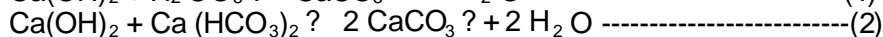
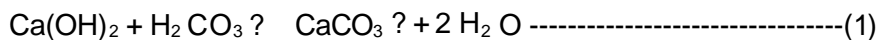
INTRODUCTION

The use of seawater bittern improves clarification of wastewater by high-pH/magnesium processes. Magnesium present in sea water can be concentrated by solar desalting. This can be achieved by inducing the depositing of CaCO_3 , calcium sulfate (CaSO_4), and sodium chloride (NaCl), thus forming a bittern (liquid bittern (LB) or dry bittern (DB) with high concentrations of magnesium salts and limited amount of potassium (K) and sodium (Na) salts. **Ayob** (1999)^[2].

The lime seawater process has been investigated by various research in the past two decades (**Dubose**, 1973)^[4], (**Ferguson**, 1984)^[9] and (**Ayoub**, 1994)^[3]. Lime effectively acts

as both a precipitant for phosphates, many trace metals, and bacteria, and as a coagulant for the removal of suspended and colloidal materials in municipal wastewater (**Grabow**, et al. 1978)^[11], (**Fujita**, et al. 1981)^[10] and (**Dziubek**, et al. 1989)^[6].

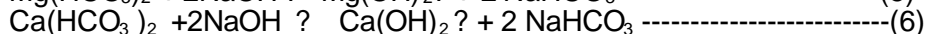
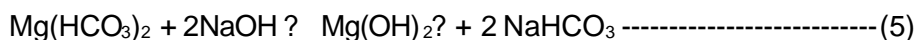
The mechanisms of chemical clarification are explained by the following reaction (**Tchobanoglous** and **Burton**. 1991)^[14]:



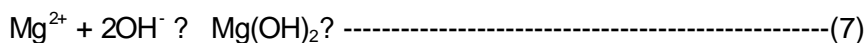
The calcium carbonate formed according to Eq.(1) and Eq.(2) precipitates out of solution at pH range of 9.1 – 9.5, and acts through the “sweep coagulation” mechanism to entrap suspended and colloidal particles. It also acts as a “weighting agent” by increasing the density of the settleable particles, thereby enhancing their settlement (**Leentvar** and **Rebhun**, 1982)^[1]. Precipitation of phosphates [Eq.(3) and Eq. (4)] occurs within the pH-range 10.5 – 11.0 (**Dziubek** and **Kowal**, 1984)^[5].

Another important aspect of lime precipitation is the appreciable degree of disinfection occurring in the process. The decreased microbial content attained in the effluent is due to the combined effect of exposure to high pH and simulating particles as 60 – 100 % of viruses in wastewater are adsorbed to particles (**Vrale**, 1978)^[18] and **degaard**, 1989)^[14].

Caustic soda of hydroxyl ions needed to raise the pH to levels at which precipitation of calcium and magnesium hydroxides are induced. The following chemical reactions take place:



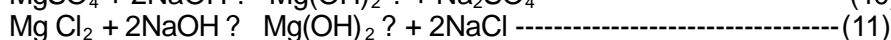
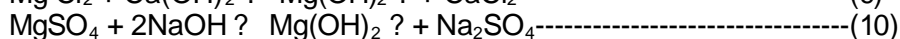
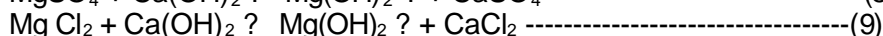
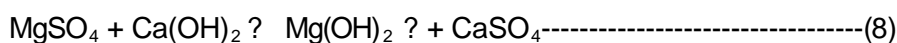
Removal of turbidity, suspended solids and organic matter using only NaOH as the alkalizing agent was reported to be comparable to that achieved when using only lime (**Merrill** and **Jordon**, 1975)^[13] and (**Ferguson** and **Vrale** 1984)^[8]. However, from the stand point of economics and efficacy of phosphate removal, the usage of lime is favored over NaOH. However, alkaline flocculation was found to be most effective in matrices containing relatively high concentration of magnesium ions (**Elmaleh et al.** 1996)^[7]. When magnesium is initially present in wastewater, an increase in pH upon alkalization will result in the precipitation of magnesium hydroxide:



Magnesium precipitation begins at approximately pH 9.5, becomes significant above pH 10.5, and is essentially complete at pH 11 – 11.5. Good clarification is usually not achieved until pH 11 – 11.5 is reached (**Dziubek** and **Kowal**, 1984)^[5]. The resulting magnesium hydroxide is a gelatinous precipitate, which was found to serve an efficient coagulant and flocculant aid (**Vrale**, 1978)^[18]. Therefore, in order for the treatment process to operate efficiently, either lime or NaOH should be used to increase the pH of the original wastewater to pH 11.0 – 11.5 (**Ayoub**, 1994)^[3] and (**Ayoub** 1999)^[2]. At such a high pH, two major reactions are effective in liquid-solid separation: CaCO_3 and Mg(OH)_2 precipitation. Both the CaCO_3 precipitate (point-of-zero-charge at approximately pH 8-9, Parks, 1967) and the primary particles are negatively charged. The formation of CaCO_3 induces a sweep coagulation process, whereby only the larger particles are entrapped. On the other hand, the Mg(OH)_2 precipitate (point-of-zero-charge of magnesium oxide is approximately at pH

12.4, (Stumm and Morgan 1981)^[16] has a large adsorptive surface area and a positive superficial charge, which attracts the negatively charged colloidal particles, including the CaCO₃ flocs, thus inducing adsorption and agglomeration. This explains the significant efficiency achieved when Mg(OH)₂ is precipitated. Several researches have investigated the effect of high-pH magnesium and calcium precipitation on coagulation using a variety of magnesium ion sources, such as magnesium chloride, magnesium carbonate, magnesium hydroxide, processed dolomite, seawater, seawater liquid bittern and marine dried

bittern. In the course of coagulation with seawater, Mg(OH)₂ precipitation may occur by any of the following chemical reactions, depending on the alkalizing agent employed:



The present study aimed investigating the efficiency of coagulation of municipal wastewater (MWW) with **LB**. A comparative evaluation of the results obtained with similar experimental results using **DB** or synthetic polymer zetag 92 as coagulating agents was conducted. Besides the investigation of the effect of the process on physicochemical characteristics the treated (MWW), the effect of high pH and coagulation-flocculation on the level of reduction in the bacterial population of fecal origin were assessed.

2. MATERIAL AND METHODS:

2.1 Production of Liquid Bittern LB:

The solar evaporation process was carried out at the National Research Center, Chemical Engineering and Pilot plant Lab. This involved subjecting a batch of seawater with an average density 1.234 g/ml, collected from Soda and Salt Company, Alexandria Samples were conducted to direct sunlight with aim of producing LB and DB. TABLE (I) illustrates characteristics of liquid bittern.

For this purpose, three separate metallic evaporation pans, each with a surface area of 1.0 m² and a depth of 0.15m, were installed in an adjacent open yard. Each of these three pans was filled to adjust below the rim with 125 L of SW at the start of the solar evaporation process. Such an array of pans was intended to ensure a sufficient quantity of SW for concentration by evaporation to produce an adequate quantity of LB for experimentation and subsequent production of DB. The DB was then prepared by further evaporation of a portion of the LB. When concentrates in pans reached a density of 1.297 g/ml, it was observed that most of the NaCl present in the batch of SW had crystallized and settled out of solution. The supernatant liquid was then carefully transferred by scooping to avoid disturbing the deposited NaCl. This constituted the LB, which is highly concentrated with Mg²⁺ salts and is as free as possible of any residual Na or K salts. A fraction of the LB was further exposed to solar evaporation in a separate vessel, followed by heating until a batch of white crystals settled out, which were determined to be MgCl₂ crystals. The remaining supernatant was drained and the crystals washed for use as DB. All selected physicochemical parameters were determined according to standard Methods (APHA et al., 1992)^[1].

2.2 Experimental Procedures:

Three of laboratory experiments were conducted. The first set of experiments involved two trials in which LB and DB as a source of Mg^{2+} ions and $Ca(OH)_2$ as source of OH ions was used in the treatment of samples of MWW. The second set included two trials in which NaOH was used instead of $Ca(OH)_2$ to alkalinize the wastewater. The third experiment comprised a single trial in which synthetic polymer zetag92 was added to MWW for settling.

2.3 Municipal wastewater:

The samples of MWW to be used for experimental purpose were collected from Zenien municipal wastewater treatment plant. Fresh samples were collected in the morning whenever needed and transported to the NRC for use in the experimental work. TABLE (II) illustrates characteristics of MWW.

2.4 Jar Tests:

Jar test experiments were conducted under controlled laboratory conditions using a standard jar test apparatus model [Floculator SWW₁ STURA Scientific U.K.]. This apparatus, used specifically for coagulation-flocculation tests, possess multiple stainless steel paddles.

Because all of the MWW samples needed to be alkalinized, the test procedure for each trial included placing the stock volume of MWW in 10-L glass container to which a freshly prepared 5% w/v slurry of $Ca(OH)_2$ or 4% w/v solution of NaOH was gradually added, while constantly stirring, in quantities needed to raise the pH of the MWW to 11.4 ± 0.1 .

2.5 Experimental with Liquid Bittern:

Aliquots of 500 ml of the already alkalinized MWW were transferred into each of the six jars of the apparatus, followed by the addition of LB in predetermined volumes (0, 0.3, 0.6, 0.9, 1.2 and 1.5 ml). The jar test was then conducted by operating the stirrers for flash mixing for 1 minutes. The speed of the stirrers was then reduced to impart for 20 minutes to allow coagulation-flocculation to take place. The multiple stirrers were then stopped for a 30-minute quiescent settling period, followed by carefully decanting 100 ml of clarified supernatant liquid from each of the six jars to be used for determination of the selected parameters hereunder. Settling characteristics of sludge has been investigated.

2.6 Experiments of Dry Bittern:

In this case, the amount of DB expressed in terms of volume that were added into each of the six jars containing 500 ml of alkalinized MWW were (0, 5.9, 11.8, 17.6, 23.5 and 29.4 ml). The jar test was then conducted in the same manner as in the previous case.

2.7 Experiments of zetag 92:

In this case, the amount of dry residue of the MWW content was determined as total solids. The appropriate amount of polymer was then dissolved in minimum amount of ethyl alcohol and completed up with distilled water in which each ml contains 1 mg polymer. Calculated dose 14.4 mg/l of zetag 92 based on dry solid content in blank sample was then added to MWW and introduced to jar tests. The jar test was conducted in the same manner as in the previous case with nonalkalinized MWW. Synthetic polymer (zetag 92), properties are listed in TABLE (III).

2.8 Carbonation:

Carbonation of clarified supernatant liquids was performed to neutralize alkalinity and lower the pH of the effluent to an acceptable level. This was carried out by injecting CO_2 to aliquots of clarified supernatant liquids until acceptable pH levels. This was carried out by injecting

CO₂ to aliquots of clarified supernatant liquids until acceptable pH levels of 7 to 8 were achieved. The CO₂ was supplied by gas flow using a calibrated flow meter.

2.9 Determination of Parameters:

Values of pH, total alkalinity, conductivity, turbidity, COD, total suspended solids (TSS), total dissolved solids (TDS), Ca²⁺, Mg²⁺, Cl⁻, total coliform (TC), and fecal coliform (FC) were determined according to standard methods (APHA et al. 1998)^[1].

2.10 Bacteriological Examination of MWW Samples:

Three different ten fold decimal dilutions were prepared from each sample of raw and treated wastewater before inumeration most propable number (MPN) method was used for determination of total and fecal coliform, according to APHA (1998)^[1].

RESULTS AND DISCUSSION

The effect of Mg²⁺ dose to alkalized MWW with Ca (OH)₂ or Na OH on settling rate are shown in Fig.1 (a, b, c and d). Results illuatrated in TABLE (IV)of the tests obtained for characheristics of the clarified effluent represents percent removal in TSS Fig. 2(a and b), Turbidity Fig.3(a and b) as well as the percent increase in TDS Fig.4 (a and b) and on addition of Ca (OH)₂ or Na OH and Mg²⁺. Changes in concentration of these values served as criteria for the selection of the “ most effective “ concentration of Mg²⁺ that was shown to yield , under experimental conditions of the coagulation assy, a high degree of clarified supernatant liquid, indicated by the high removal values obtained for turbidity, TSS and corresponding low levels of residual ionizable salts indicated by values of TDS, conductivity Fig.5 (a and b) and residual chlorine Fig. 6(a and b). The percent removal of COD, Tc and Fc at most effective Mg²⁺ dose are illustrated in Fig.(7) and (8).

Effect on the clarified effluent

The effect of process on MWW Settling rates: Settling characteristics of blank Zenien MWW has been investigated. Results of gravity settling of alkalized MWW and LB, DB and zetag 92 treated MWW are summerized in Fig (1). Also settling rate of the above treatment , by Mg²⁺ ion in LB Fig 1(a and b) or DB Fig.1 (c and d), illustrated that in case of Ca(OH)₂ alkalization and after 5 minutes settling there is no big difference by changing Mg²⁺ ion concentration. While in case of NaOH we noticed that there is a big difference between the sample with no Mg²⁺ ion addition dose and other samples with added Mg²⁺ ion doses Fig.1 (a, b, c and d). The synthetic polymer (zetag 92) graphically showed 15% increase in settling rate of MWW.

Most effective magnesium ion concentration: It is deduced from TABLE (IV) that Mg²⁺ concentrations at which the highest percentage removal in turbidity, COD and TSS and the lowest percent increase in TDS and conductivity was achieved approximatly 24.304 or 24.33 mg/l (initial concentration 24.25 mg/L plus the added LB dose of 0.05414 or 0.08122 mg/L) and 25.2 or 85.83 mg/L (initial concentration of 81.12 mg/L plus the added DB dose of 0.957 or 4.705 mg/L) for Ca(OH)₂ alkalization and NaOH alkalization samples respectively.

Total suspendedsolids, Turbidity and chemical oxygen demand: Removal percent of these parametrs as a function of Mg²⁺ concentrations are illustrated in Fig(2), Fig (3) and Fig(7). The reduction in these parameters are shown in TABLE (IV). Almost the same percent removals were achieved by coagulating wastewater alkalized with Ca(OH)₂ or NaOH at the “most effective” Mg²⁺ concentrations. In all test cases where DB or LB was used

as coagulating agents, removals were in the order of (90 to 99 %) or for TSS, (60 to 88 %) for COD and (90 to 96%) or (89 to 99%) for turbidity. The effective clarification that was achieved simply by the addition of alkalinizing agents is attributed to the presence of Mg^{2+} ions at pH rang of 11.0 to 11.5, positively charged $Mg(OH)_2$ flocs are formed. **Ferguson** 1984^[8] used lime with seawater to improve clarification of wastewater by improving TSS and phosphate removal to give an effluent suitable for marine discharge. **(Ferguson and Vrale** 1984)^[8] added that moderate amounts of seawater can reduce the lime dosage needed to remove TSS and phosphates at wastewater treatment plants.

At pH 9.5, the slightly negatively charged $CaCO_3$ is formed by the reaction of carbonate ions present in the wastewater with the added $Ca(OH)_2$. As a result, $Mg(OH)_2$ flocs and, to much lesser extent the $CaCO_3$, tends to remove most of the suspended particulate material found in the wastewater, thus resulting in a highly clarified effluent.

Adsorption of dissolved and organic matter onto the $Mg(OH)_2$ and $CaCO_3$ flocs seems to be the governing factor in the removal of COD from wastewater according to **Wang and Chem** 1984^[19]. **(Dziubek and Kowal** 1989)^[6]. The percent removal of COD attained at the "most effective" Mg^{2+} concentration and alkalinized with $Ca(OH)_2$ were very similar using DB or LB as cogulants 86 and 88% removal respectively. While the alkainized MWW samples with NaOH treated in LB or DB showed variation in COD % removal 58 and 81%. Whereas zetag 92 achived 95.71 % removal for TSS.

Total Dissolved Solids and Conductivity: Fig.4(a and b) and TABLE (IV) and TABLE (V) show the variations and percent increase, respectively, in TDS and conductivity of the clarified effluent. As these two parameters, for all partical purposes, represent the same chemical indicator, the discussion presented hereafter will only relate to TDS. For reference purpose, experimental data for both parameters will be shown in the figures. In the tow modes of alkalinization, the addition of $Ca(OH)_2$ resulted in a lower percent increase in TDS. This is attributed to the fact that, when $Ca(OH)_2$ is added to raise the pH, $Mg(OH)_2$ and $CaCO_3$ are precipitated out of soluble sodium carbonate (Na_2CO_3) are formed. The latter remains dissolved as Na^+ and CO_3^{2-} in the clarified liquid and results in an increase in TDS. Moreover, the addition of the "most effective" Mg^{2+} dose of LB or DB to the wastewater alkalinized with $Ca(OH)_2$ tends to lower the percent rise in TDS by 28.22% or 87.5% respectively compared to the values obtained when NaOH alone is added to the original wastewater sample. The removal of turbidity and TSS were nearly high for the two modes of alkalinization. Percent removal values obtained were greater than 98% for turbidity and TSS. However, the percent increase in TDS when $Ca(OH)_2$ was used either in LB or in DB was lower by 42.25% or 79.7% respectively compared to the value obtained for NaOH Our results are nearly to that of **(Ayob etal.** 1999)^[2]. Whereas zetag 92 showed 27.87% removal for TDS and 94.74% removal for turbidity.

Effect of the process on Bacterial Suppression: Total and fecal coliform counts before and after the application of coagulation of the "most effective" dose to $Ca(OH)_2$ or NaOH alkalinized wastewater showed effective reduction in the viable bacterial population TABLE (VI) and Fig.(8). These observations recurred in both wastewater test samples. In the LB "most Mg^{2+} effective dose" for instance, total and fecal coliform counts dropped from 9.0×10^{12} and 3.4×10^{11} cfu/ml, respectively, to 6.0×10^3 and 2.0×10^3 after $\frac{1}{2}$ hr on alkalinization with $Ca(OH)_2$. In the second "most Mg^{2+} effective LB dose", counts dropped from 9.0×10^{12} and 3.4×10^{11} to 5.0×10^4 and 1.7×10^4 cfu/ml respectively after $\frac{1}{2}$ hr on alkalinization with NaOH. With respect to DB coagulation tests, the drop was from 9.0×10^{12} and 3.4×10^{11} cfu/ml to 4.0×10^3 and 2.0×10^3 cfu/ml, respectively, by $Ca(OH)_2$, and to 9.0×10^5 and 2.8×10^5 cfu/ml, respectively, by NaOH. This corroborates reported results **(Grabow etal.** 1978)^[11]

and (Ayoub 1999)^[2], which indicates that complete destruction of bacteria is achieved by raising the pH of wastewater to 11.2 or 11.5.

Perliminary economic evaluation study:

A preliminary cost estimation was calculated according to the prices of used raw material necessary for the treatment of 1 m³ municipal wastewater. The costs are illustrated in TABLE (VI). Treatment of 1m³ MWW using LB or DB added to Ca(OH)₂ dose cost 0.0075 £ showing highest clean up. While using NaOH with LB or DB costs 0.0042 £ but showing less clarity. Zetag 92 coagulation treatment optimum dose cost 0.36 £. The lime LB or DB process introduces appreciable saving in chemical costs, especially since lime is readily available in most countries and LB or DB can be easily obtained in coastal regions. Additional savings resulting from lime LB or DB treatment include the costs associated with disinfection. The high pH of the process induces almost complete disinfection. Thus, eliminating the need for a separate disinfection process in the treatment system (Ayoub et al. 1999)^[2]. However, when discharging to sea, the high effluent pH does not pose any adverse effect, since it will be rapidly neutralized when discharged through an efficient outfall diffuser (Ferguson and Vrale, 1984)^[8] (Odegaard, 1989)^[14]. The main disadvantage presented by the lime-magnesium process remains the large amounts of sludge generated compared to the amounts produced in conventional secondary chemical processes employing alum or ferric chloride as coagulants. Fortunately, sludges resulting from lime treatment possess superior thickening and dewatering characteristics and are suitable for filter pressing at lower cost than sludges generated from ferric chloride or alum (Forestner and Van Leirde, 1981)^[9]. Another advantageous characteristic of the sludge produced is that it can be efficiently dewatered without the addition of polymers or more lime, which are necessary for the conditioning of sludges produced from ferric chloride or alum coagulation processes. Because of its high lime content and high pH, the sludge produced is chemically "Stabilized" dose not decompose rapidly, and causes few odor problems (Odegaard, 1989)^[14]. In addition, a fraction of the sludge produced may be recirculated back into the system in a controlled way, since it has a high pH and a great coagulating capacity (Odegaard, 1989)^[14]. Sludge recirculation in actual lime-seawater wastewater treatment plants optimized the lime use, reduced effluent turbidity and phosphate levels, and improved the process performance during transiant failuers of seawater or lime dosing (Ferguson and Vrale, 1984)^[8].

Finally, sludge recycling into economically viable products, such as cement or other cementitious material, may also help in minimizing the impact of increased sludge production.

CONCLUSION

The results of the present study demonstrate that the chemical treatment of MWW by coagulation with magnesium salts is an effective and inexpensive method. Magnesium salts present in the LB and DB proved to be good coagulants for the treatment of MWW when applied in doses ranging from 0.027 to 0.135 mg/L for LB and ranging 0.957 to 4.7 mg/L for DB after alkalization with Ca(OH)₂ or NaOH to pH of 11.5. The process was highly efficient for the removal of turbidity and TSS(>98 %). TSS, TDS, and COD removal are quite satisfactory (86% on average). Although DB was shown to be more effective in removing impurities compared to LB. Also LB results in an appreciably lower increase in TDS in clarified effluent. The use of Ca(OH)₂ and LB or DB in chemical treatment of MWW should be a highly feasible process as both materials are inexpensive and available. LB is a reject waste emanating from salt-manufacturing processes using solar evaporation of seawater. LB produced in costal areas is also amenable for transportation to inland areas because of its reduced bulk compared to that of seawater. Bacterial population can be achieved as a result of high pH maintained onto Mg(OH)₂ flocs.

The combination of alkaline effluent resulting from the coagulation of MWW with Ca(OH)_2 or NaOH and magnesium salts is needed if effluent discharge standards on pH are to be maintained. The concentration of CO_2 needed to neutralize the selected lime alkalinized MWW after coagulation with the optimum dose, Mg^{2+} doses varied between 3.26 and 80 ml/L of wastewater depending on the alkalinizing agent and the pH and alkalinity before carbonation.

The disadvantage of the treatment process on water quality is minimal. The increase in TDS for some of the test samples as a result of the addition of LB or DB amounted to 28 or 87 % an increase respectively. These values are acceptable for most applications. The bittern coagulation method at high pH is a new technology and is an environmentally friendly and green treatment method.

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