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NEW PROCESS FOR PHYSICO-CHEMICAL PRETREATMENT OF DAIRY EFFLUENTS WITH AGRICULTURAL USE OF SLUDGE PRODUCED

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ABSTRACT

A combined physico-chemical process is suitable for the effective pretreatment of dairy effluents, achieving almost complete removal of fat, and considerable reduction of protein content. The specific cost of COD removal using the process is only half or a third of that using aerobic biological methods. Depending on the chemicals used, further treatment or, in certain cases, agricultural utilization, of the sludge is possible. In addition, the components remaining in the effluent have low molecular weights, are easily degradable, and are very favourable as nutrients in municipal aerobic post-treatment. Investigation of the sludge showed that it did not contain any pathogen organisms and therefore its application on land is recommended. Laboratory and field experiments have shown that, with agricultural use of the sludge, increased plant growth and grain production were achieved.

KEYWORDS

Physico-chemical pretreatment; dairy effluents; use of dairy sludge; soil conditioning.

INTRODUCTION

Irrespective of the individual country and its industrialisation policy, most milk processing plants are located in towns or villages. The removal of the organic components of their effluents is generally the task of the municipal wastewater treatment plants. The diary effluent usually forms only a small part of the municipal wastewater, and thus the potential treatment problems such as sludge bulking are negligible. However, in Hungary, food processing plants have to pay a relatively high penalty if their effluent contains a considerable concentration of fat (above 80 to 120 mg/litre), and this penalty decreases profits significantly. Thus, the installation of effluent pretreatment, based on phyisco-chemical processes, is very advantageous. This practice has spread in the diary and meat industries of Hungary (Kárpáti et al., 1980; Kárpáti and Szabó, 1984; Tabakov and Kárpáti, 1984).

Since 1975, the Hungarian meat industry has used the well-known metal hydroxide precipitation methods for effluent pretreatment, and since the beginning of the 1980s, these methods have also been used in the dairy industry, where several treatment facilities operate continuously. The sludge from meat industry plants is classified as hazardous waste, but diary industry sludge can be effectively treated in anaerobic digesters or used in agriculture. This was shown in experiments which indicated ways of minimizing costs and of controlling the quality and quantity of the chemicals used, and which also showed the suitability of the sludge produced for agricultural applications.

MATERIALS AND METHODS

Experiments were conducted to investigate the effectiveness of coagulation and flocculation in dairy effluents and model emulsions. Previous experience had shown that the colloidal state and properties of industrial (dairy) effluents changed rapidly. In the case examined, the length of this critical time interval ranged from 4 to 6 hours (the plant had a fat trap and an equalization basin). The diary plant supplied a town with milk, and it also produced soft cheese.

The model emulsions were prepared from commercial milk containing 2.8% fat and tap water. The $FeSO_4$ and $Al_2(SO_4)_3$ solutions used were prepared from analytical grade (p.a.) reagents. Similarly, p.a. grade sulphuric acid and sodium hydroxide were used for pH adjustment. Commercial grade sodium lignosulphonates and slaked lime were utilized (quality unknown). This was also the case for the poly-electrolytes used.

The effect of pH on the stability of the emulsions was investigated using sulphuric acid. The precipitating effect of lignosulphonates (LSAs) was studied, and the relationships between the pH and the amounts of precipitants used were investigated. In these experiments, the chemicals, followed by the necessary amount of sulphuric acid, were added to a beaker containing the emulsion. The coagulation effect of the cations (i.e., the metal hydroxides) was determined at various pH values, the pH being adjusted with NaOH and $Ca(OH)_2$. After addition of the chemicals, the solutions were mixed for 2 minutes, vigorously initially then, in the second part of the experiments, the mixing blade moved slowly. The samples were poured into Imhoff cups for settling. When the precipitations were carried out using sulphuric acid and metal hydroxides, the effect of poly-electrolytes on the separation of the precipitate was examined. Samples were taken from the clear liquid phase and the COD, TOC, and the extractable fat content (extracted using CCl_4) were determined.

Over the experimental period, the operating techniques were revised and the same qualifying characteristics were determined. The heavy metal contents of the sludges produced in different treatment plants and of liming materials used in agricultural practice were compared. The growth and grain production of various crops grown on soils to which diary sludge had been applied was compared with that of control crops grown on acidic, sandy, brown forest soil.

RESULTS

The efficiency of biological and physico-chemical treatment of dairy effluents is remarkable, even after several hours of equalization, if sufficient mixing, suspended solids retention, and reverse inoculation can be guaranteed. This results in the formation of a markedly higher buffer capacity compared to model emulsions. Over a relatively narrow pH range, around pH values of 4.5 to 4.6, most of the original protein content of the milk quickly coagulates and then slowly settles or floats, thus separating from the bulk liquid. At lower pH values, the proteins redissolve and they form a stable system ('meagre milk') as a colourless solution. This coagulating or stabilizing effect of the proteins also occurs in the case of milk emulsions. The fat droplets stabilized by proteins separate or remain in emulsion depending on the stability of the proteins (especially caseins).

Figure 1 shows the effectiveness of precipitation in the vicinity of the iso-electric point, for 0.5 to 2% milk emulsions and equalized dairy effluent. It can be seen that coagulation is not so marked and separation is noticeably slower and less successful in the case of the industrial effluents. The amount of sulphuric acid necessary to reach the isoelectric point in the case of the fresh milk emulsions was only half of that needed by the equalized effluents.

When the isoelectric point was reached, settling and floating precipitates were formed in all cases. At high pH values, the amount of floating precipitates increased, while at lower pH values, the amount of settling precipitates was characteristically greater. The separation of the phases was time-consuming in all cases, and it could only be slightly enhanced by polyelectrolytes. It seems impossible to achieve fat and protein separation on a commercial scale by this method.

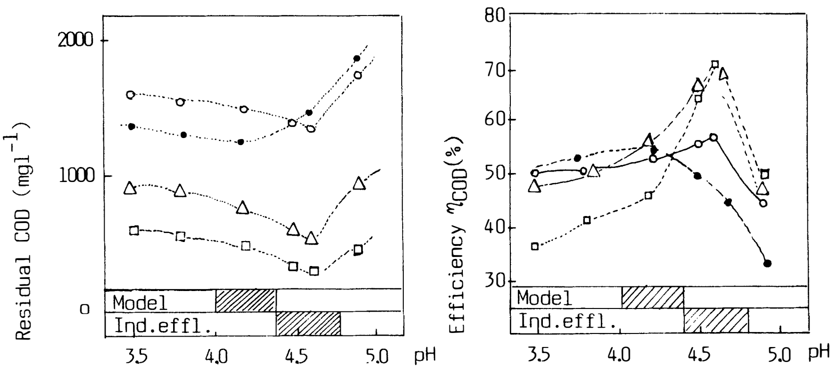


Fig. 1. Efficiency of precipitation with sulphuric acid near the isoelectric point using model emulsions and dairy effluents
□, △, ○ - 0.5, 1, and 2% concentration model emulsions prepared from milk containing 2.8% fat
● - effluent taken from the equalization basin
▨ - rapid sludge separation, settling
□ - very slow sludge separation

In the case of the lignosulphonates (LSAs), the optimum pH range was found to be 2.8 to 3. With $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$, the best phase separation occurred at pH = 7 and pH = 8, respectively. Very slow precipitate formation was found with the LSAs, whereas with $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$, precipitate formation was better with the use of greater amounts of chemicals, but the separation of the phases was not very good. Moreover, floating precipitates formed in this system. Figure 2 shows the effectiveness of effluent treatment based on analysis of the transparent liquid phase versus chemical dosage. Flocculation could be enhanced by using anion active polyelectrolytes with the metal hydroxides and, in the case of the model emulsions, quicker flotation of the precipitate could be achieved. In the case of the industrial (dairy) effluents, the majority of the precipitate floated more slowly.

When slaked lime was used for neutralization, the weight of the precipitate increased and difficulties occurred in phase separation. Although the presence of polyelectrolytes increased the flocculation rate, both floating and settling precipitates were formed. Figure 2 shows clearly that precipitation with alum followed by flotation for sludge separation can be used successfully as a commercial process. Electroflotation was used on a commercial scale at the beginning of the 1980s (Tabakov and Kárpáti, 1984), and dispersed air separation was used some years later.

It was surprising that the reactions of the fresh model emulsion and the equalized plant effluent with the slaked lime gave completely different results. The calcium ions, at the usual temperatures, had very little effect on the proteins of the fresh emulsion, while the protein of the equalized plant effluent coagulated almost completely. This difference is shown in Figs 3 and 4. Figure 3 shows the amount of settled precipitate and its fat content versus the slaked lime dosage.

In this experiment, the suspended particles (fat, protein, and slaked lime) remaining in the treated samples were separated by precipitation in a further step by the injection of 400 mg/l $FeSO_4$. The amounts of sludge were measured and the fat extracted and determined. The results are presented in Fig. 4.

In the case of the fresh emulsions, the precipitation and settling of fat and proteins were incomplete, even if greater amounts of slaked lime were used. However, this method of treatment was successful in the case of the plant effluents, and the majority of the fat and proteins could be removed.

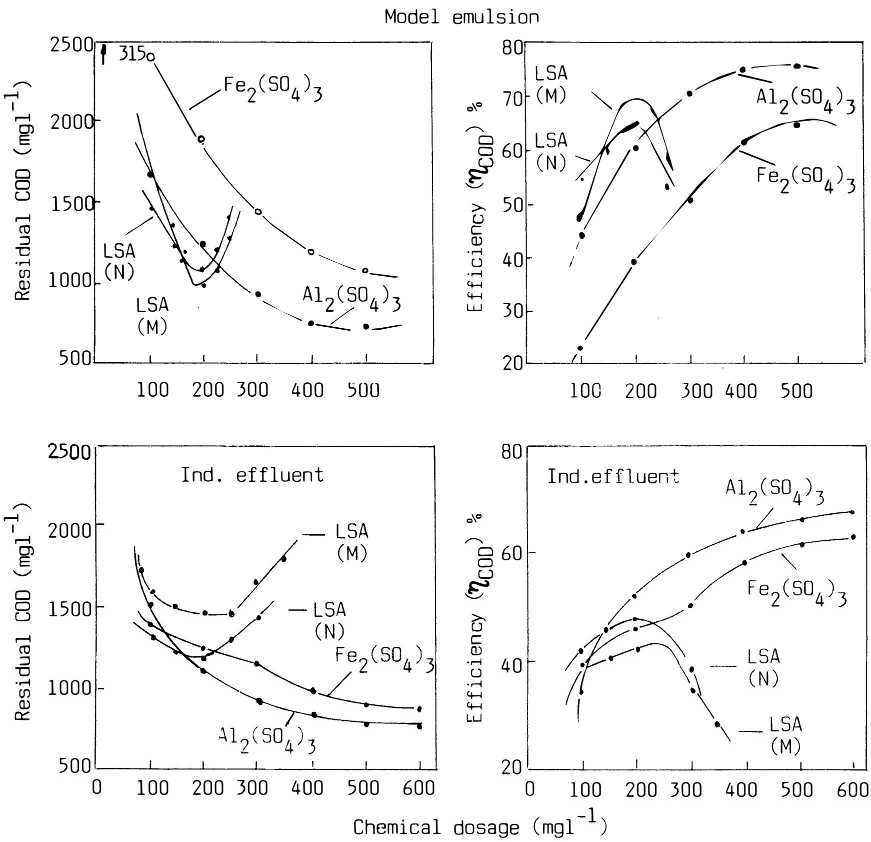


Fig. 2. Efficiency of precipitation versus chemical dosage; 2% model emulsion prepared from commercial milk with a fat content of 2.8% and tap water; LSA(N) = Norwegian lignosulphonate; LSA(M) = Hungarian lignosulphonate.

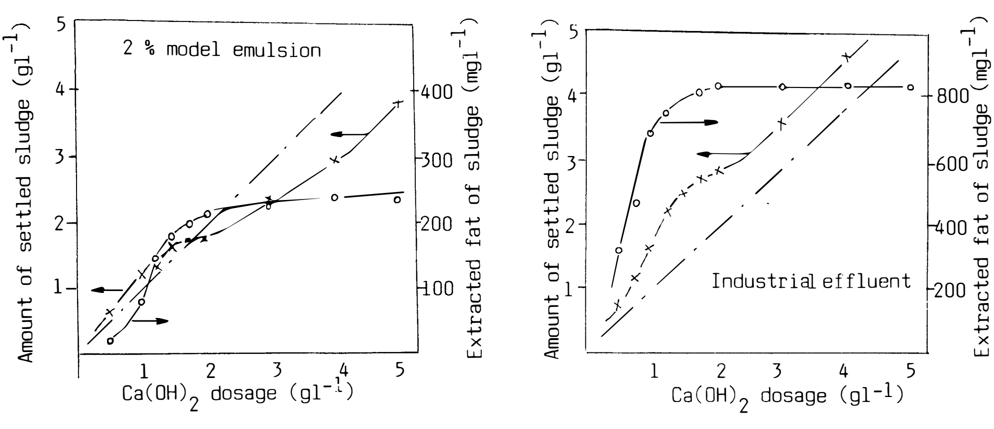


Fig. 3. Quantity of settled sludge and its extractable fat content versus slaked lime dosage

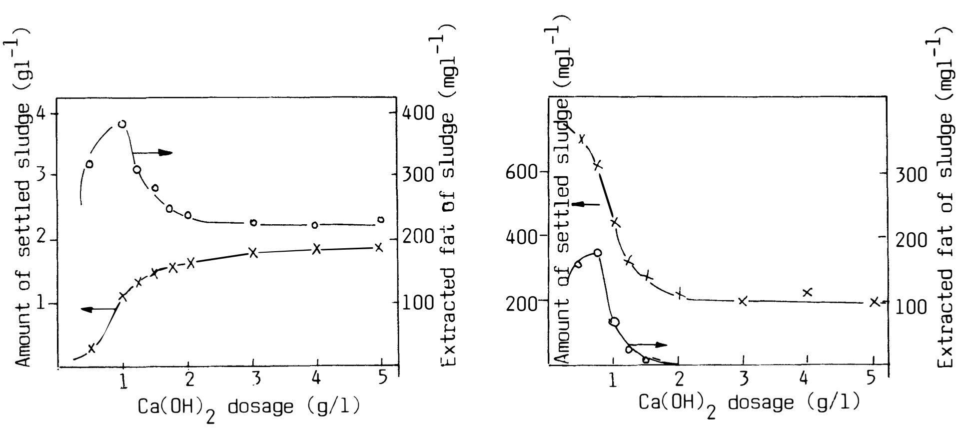


Fig. 4. Quantity of remaining SS precipitated with 400 mg/l $FeSO_4$ from the settled liquid phase and the extracted fat content (see Fig. 3)

Further experiments showed that the method and duration of equalization or of destabilization (with or without aeration) were the parameters which determined the efficiency of the pretreatment process. From the point of view of sludge settling and an alkaline medium, the settling of the sludge phase can be assured with smaller amounts of slaked lime and ferrous sulphate when the latter is added into the effluent as a second step. The presence of 100 to 150 mg/l $FeSO_4$ and a suitable alkaline pH ensure sludge stability and so-called 'sterility', and also absorb the hydrogen sulphide which forms during long storage periods or during digestion. Polyelectrolytes hinder the phase separation. This treatment process has been patented, and the first unit to be constructed, with a capacity of 50 m^3/day, began operation in 1985 (Kárpáti and Bencze, 1987). The second unit (with a capacity of 600 m^3/day) began operation at the end of 1987 (Kárpáti, 1989), and the third (150 m^3/day capacity) in July of 1989 (Kárpáti and Bencze, 1988).

The precipitation stage (used for the removal of fat and protein) enables a simple method to be used for the determination of the fat content of the dairy effluents. The fat can be extracted from the settled, filtered, and dried precipitate by Soxhlet extraction. Regarding the samples taken from a plant in operation, the fat concentration data are more reproducible and give slightly high concentration values compared to the standard method (Fülöp, 1988).

EXPERIENCES WITH COMMERCIAL PLANTS

The precipitation experiments carried out with aluminium sulphate showed that a slight acidic reaction occurs during equalization, and the resulting buffer effect lessens the demand for chemicals, compared to the situation with the model emulsions. A dose of 200 mg/l $Al_2(SO_4)_3$ is sufficient for effective coagulation without adjustment of the pH, although 1 or 2 mg/l of polyelectrolyte is necessary for complete flocculation. Phase separation can be achieved with a special dispersed air flotation process. Although a small amount of settling sludge occurs, this does not cause difficulties in plant operation. The effectiveness of effluent treatment is shown in Fig. 5A. Effluent treatment carried out with slaked lime and ferrous sulphate is more effective at plant scale than treatment with alum. This can be seen in Fig. 5B.

The specific operation costs of the effluent pretreatment methods discussed above are roughly equal. The pretreated effluents contain low molecular weight decomposed compounds and small amounts of soluble proteins. The phosphorus content is low, which is an advantage from the viewpoint of municipal sewage treatment plants. However, there is a substantial difference between the methods with respect to sludge utilization in agriculture. The application of sludge containing aluminium is not possible, because it putrifies and rapidly turns sour, making it unsuitable for soil amelioration and for compost production. However, use of the sludges containing lime has definite advantages. The only possibility of treating the aluminium-containing sludge is by anaerobic digestion, where it is combined with the sludges produced by municipal sewage treatment plants. At present, the application of lime-containing sludge is officially permitted, while that of aluminium-containing sludge is not. The investigations of the authorities showed that the sludge is non-toxic and it does not contain pathogen micro-organisms. It is not classed as a hazardous waste (Kárpáti and Bencze, 1988). The aluminium-containing sludge is presently treated in the anaerobic digester of the municipal sewage treatment plant which has a capacity of 20 000 m^3/day. The acidic dairy sludge caused small difficulties only once during the last decade (in the winter). At present, the insufficient number of anaerobic digesters in operation in Hungary is hindering the spread of the method discussed.

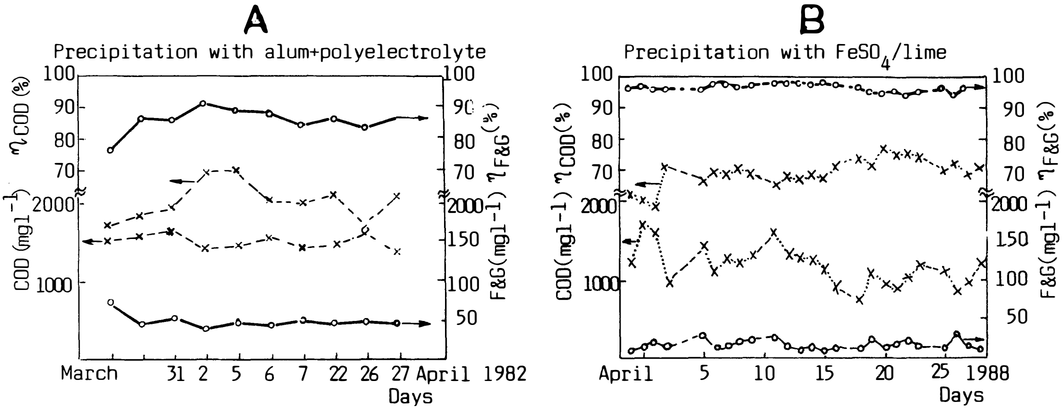


Fig. 5. Efficiencies of various precipitation methods in commercial units in the removal of fat and COD

THE USE OF DAIRY SLUDGE FOR SOIL AMELIORATION

Data on the main characteristics and various contaminants of the sludges produced by two treatment processes are given in Table 1. For comparison, the metal contents of some liming agents are also listed in the table. It can be seen that, with the exception of aluminium, the contents of metals in the sludge do not hinder its agricultural application.

TABLE 1 The Main Characteristics of Dairy Effluent Sludges and Soil Amelioration Agents

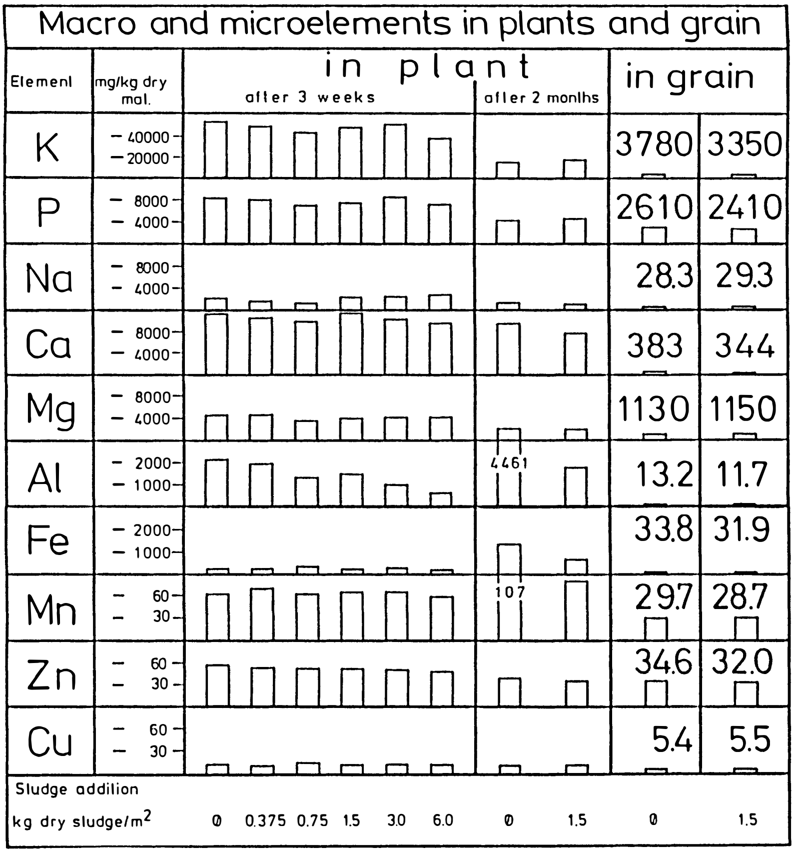
Components/contaminants of dairy sludges obtained by different precipitation methods	Precipitation agents: $FeSO_4$/lime	Precipitation agents: Alum + PE	Components/contaminants of three different agricultural liming materials used in Hungary (mg/kg dry matter)	Sample number 1	Sample number 2	Sample number 3
Dry matter (DM) content, %	7	15				
Ash, % of DM	55	12				
Fat and grease (F & G)*, % of DM	22	46	K	1830	890	5600
Nitrogen**, % of DM	1.5	1.9	Na	590	335	290
Phosphorus***, % of DM	1.1	2.9	Fe	245	360	225
Metals: K#, mg/kg DM	3200	3600	Mn	50	18	10.5
Na#, mg/kg DM	4200	5500	Cu	7.1	13.2	4.6
Mn##, mg/kg DM	155	5.5	Zn	11.8	59.6	5.4
Cu##, mg/kg DM	18	14	Pb	6.6	1.1	9.5
Zn##, mg/kg DM	130	120	Cd	<1.0	<1.0	<1.0
Pb##, mg/kg DM	15	2.3				
Cd##, mg/kg DM	0.9	0.1				

*CCl_4 extract
**Kjeldahl or CHN analysis
***Spectrophotometry
#Flame photometry
##Atomic absorption

The use of lime-containing sludge is very advantageous, especially in the case of sour soils (i.e., cold wet land). Its use increases the pH of the soil, and this hinders the uptake of heavy metals and decreases the phytotoxic effect of aluminium, but it increases the zinc concentration.

Wheat was selected as the experimental plant, and seeds were grown in culture dishes and arable land. The metal contents of plants which were three weeks and two months old and of the grain were measured. The results are presented in Table 2. It can be seen that the uptake of aluminium and manganese was markedly decreased by the addition of sludge to the soil, but a considerable increase in potassium and phosphorus was detected. The concentrations of calcium, iron, and zinc increased only slightly. The micro-element concentrations of the grain were considerably less, and the decrease in the metal concentrations was 5 to 10%.

TABLE 2 Changes in the Concentrations of Macro- and Micro-elements in Plants and Grain due to Soil Amelioration with Dairy Effluent Sludge



The properties of soil treated with sludge are favourable. The water retention capacity, morphology, and structure are changed advantageously for agriculture. Barren soils were treated with dairy sludge, at a rate of 1.5 kg/m^2, mixed into the upper soil layer (25 cm deep). In corn fields, grain production increased by between 39 to 105% (with a mean of 77%) (Czencz and Kiss, 1989).

CONCLUSIONS

Compared with various biological methods, the effective removal of fat and proteins from dairy effluents using physico-chemical pretreatment is more favourable economically. An additional advantage is that the sludge produced can be used for agricultural application.

If alum is used in the precipitation stage, then anaerobic digestion is proposed for treatment of the sludge produced. In this case, flotation with polyelectrolyte addition can be used for phase separation.

If the precipitation stage is carried out with slaked lime and ferrous sulphate, then flocculation and settling of the sludge without polyelectrolyte addition is a more favourable possibility. The heavy metal content of the sludge is low, and agricultural application of the sludge is recommended. The lime and plant nutrient (N, P, S, and organic compounds) contents mean that the sludge can be used advantageously for the amelioration of sour soils. The remaining impurities in the pretreated effluent can be decomposed easily in a municipal sewage treatment plant.

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