Chemistry for Sustainable Development **28** (2020) 388–393

UDC 628.3

DOI: 10.15372/CSD2020244

Coagulants in the Processes of Waste Water Treatment in Dairy Complex Industry

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(Received October 24, 2019; revised January 13, 2020)

Abstract

Complex coagulants comprise a developing and very promising area for the processes involved in the treatment of natural and waste waters. In spite of somewhat higher cost, complex coagulants are devoid of the disadvantages of many classic coagulants and demonstrate high efficiency in water purification from metals, fats, oil products and suspended matter; they also provide a substantial decrease in the concentrations of dissolved organic substances (chemical oxygen demand). The simplest method of manufacturing complex coagulants is the introduction of an additive composed of the products of hydrolysis of titanium-containing compounds into the classic reagents based on aluminium or iron salts. Soluble titanium salts or titanium dioxide may serve as the source of titanium compounds. The waste waters of dairy industry contain a large amount of dissolved organic substances and emulsified fat, so the purification of these waters is one of the most complicated problems. Trial coagulation treatment of model wastewater containing whey showed a high efficiency of complex titanium-containing reagents. Complex coagulants exceeded traditional reagents in efficiency by 10–15 % as average, and the rate of precipitate filtration was 1.2–1.5 times higher. The sediment had a looser structure, did not clog the pores of the filtering material, and readily gave moisture off. Tests of the best samples of complex reagents with the combined household and industrial waste waters of the dairy processing enterprises of the Moscow Region confirmed their high coagulation characteristics with respect to the most common pollutants, and the acceleration of sludge filtration processes will significantly reduce the capital costs of building local sewage treatment plants. The residual content of titanium ions in water, when using the entire line of modified coagulants, did not exceed the maximum permissible level for fishery water bodies.

Keywords: water treatment, sewage, complex coagulante

INTRODUCTION

Difficulty in the purification of waste waters from the enterprises of the food industry is due to the presence of a broad range of pollutants in these waters. As a rule, the plants of the dairy industry have several separate systems of waste water disposal. The majority of them usually include the following water disposal systems [1, 2]:

– storm-water drainage (drainage of atmospheric precipitation from the territory of the plant) is distinguished by the high content of suspended matter, and in some cases also petroleum products, surfactants and other pollutants;

– household sewage (from administrative and household buildings) is characterized by medium content of suspended matter, but it includes substantial amounts of biologically oxidizable organic compounds. This type of waste waters is usually characterized by the high chemical and biological oxygen demand (COD and BOD, respectively), and the presence of dissolved nitrogen- and phosphorus-containing compounds;

– industrial sewage, with its waste water composition depending first of all on the industrial technology at the enterprise, and parameters may vary substantially within a day. For instance, the waste waters from the works processing milk products are characterized by the high content of fat (in particular emulsified ones), suspended substances, and high COD and BOD values.

Purification of waste waters from the milk processing plants is usually carried out at the city stations of deep biological purification. However, in view of the extremely high level of pollution, these waters pass the obligatory stage of preliminary purification at local purification plants before being transported to city stations.

According to the accepted scheme, the local purification facilities include [1, 2]:

– preliminary mechanical purification (fat traps; grids; sand catchers);

– coagulation purification in combination with floatation;

– finishing mechanical purification (sand, polymer filters).

The reagents that are usually used in these processes include the solutions of lime to correct pH and to transform a part of fatty acids into insoluble form in combination with coagulation with aluminium or iron salts. Coagulants based on the indicated compounds are used in purification processes of these kinds for a long time, in spite of the fact that the efficiency of purification with their use does not exceed 30–40 %, and reagent dose may reach 1–2 g/L [3]. In addition, the use of aluminium or iron containing coagulants has a number of substantial limitations. Iron compounds may form organic complexes, and coagulant solutions possess high corrosion activity. Moreover, a large amount of difficultly filtered precipitate is formed when iron-based coagulants are used [4]. Coagulants based on aluminium compounds exhibit low efficiency in cold water, they have a narrow working pH range, and the maximum permissible concentration (MPC) of residual aluminium for the water of fishery water bodies is rather low (0.04 mg/L) [5], which greatly holds back the application of these coagulants in wastewater purification. Because of this, it seems very interesting to search for new efficient reagents with improved properties.

In this respect, alternative coagulants based on titanium and silicon compounds deserve attention. Aluminosilicic flocculant-coagulants (ASFC) obtained from the side products of apatite-nepheline floatation possess the synergic effect of aluminium salts as coagulants and active silicic acid which is responsible for flocculation properties. The efficiency of ASFC is substantially higher than that of traditional reagents, and its cost is approximately 3–4 times lower than the cost of aluminium sulphate [6–8]. In spite of this fact, the tendency of reagent solution to undergo polycondensation (gelation), the low content of the active component (less than 2 %), and the acid medium in the solution of ASFC (pH <1) bring substantial limitations of the area of its practical application. Titanium-containing reagents demonstrated high efficiency in the purification of waste waters with the high content of dissolved organics and suspended substances [9–14], but their high cost does not allow their wide application.

A solution of this problem may be the use of complex titanium-containing reagents based on traditional coagulants [15–17]. The addition of the products of hydrolysis of titanium compounds (PHTC) to aluminium- or iron-containing coagulants allows a substantial increase in the efficiency and levelling of the disadvantages of traditional reagents. In view of insignificant PHTC content (up to 10 mass % of the total dose of coagulant), the cost of complex reagents is only slightly higher than that of the coagulants based on aluminium or iron.

The goal of the present work was to evaluate the possibility to use complex titanium-containing coagulants (CC) in the purification of waste waters of the dairy industry. To achieve the formulated goal, we studied the effect of different forms and doses of PHTC on the efficiency of the purification of model waters and determined the parameters of filtration of the precipitates obtained using CC.

EXPERIMENTAL

CC samples were obtained by adding PHTC to the aqueous solutions of aluminium or iron sulphates and (oxy)chlorides (Tekh. Grade, Kemira, Finland). The fraction of PHTC in the solutions of coagulants was 10 mass %, calculated for oxides [15].

The model waste water was prepared by dispersing the wastes from dairy production (milk whey, skimmed milk) in tap water for 1 h.

Reference samples were traditional reagents – coagulants based on aluminium sulphate, aluminium oxychloride, ferric chloride, ferrous sulphate.

Modelling of coagulation purification was carried out with the help of laboratory flocculator FC4S (Velp Scientifica, Italy): the phase of rapid coagulation – 2 min (150 r.p.m.), the phase of flaking – 8 min (10 r.p.m.), sample settling time – 30 min.

Efficiency was evaluated on the basis of the changes in the water colour index in the initial and purified waste water with the help of a portable DR 2800 spectrometer (Hach Lange, USA) calibrated with respect to the chromium-cobalt scale, and on the basis of the content of suspended substances determined with the help of a portable turbidity meter HI 98307 (Hanna Instruments, Germany) through recalculation for kaolin. All measurements were carried out with the sample after its preliminary decanting.

The residual content of coagulant ions (Al, Fe, Ti) was determined with the help of atomic emission spectrometry using the microwave plasma spectrometer Spektro-Skay (GK Skaygrad, Russia).

The rate of precipitate filtration was calculated y measuring the volume of the filtrate obtained by passing the water treated with coagulants through the red ribbon filter with the pores 5–7 μm in size for 1 min.

Fat content was determined with the help of concentration meter KN-2M (PC PEP SIBEKO-PRIBOR, Russia).

The content of dissolved organic compounds was determined using the arbitrary method of COD determination according to GOST 31859–2012 "Water. Method of determination of chemical oxygen demand".

RESULTS AND DISCUSSION

At the first stage of the experiment, we determined the efficient dose of reagents allowing the most substantial decrease in the colour index and turbidity of model water. The initial content of suspended substances was 500 mg/L, and colour index was 385 degrees of the chromium-cobalt scale. The data on the efficiency of purification with the use of different coagulants are presented in Table 1.

One can see that rather high doses of coagulants are necessary to achieve a high degree of purification. Titanium (IV) chloride demonstrates the efficiency which was equivalent to traditional reagents, but its dose was approximately 1.25–1.5 times lower, which is in good agreement with the literature data [18]. Taking into account the low efficiency of ferrous sulphate, we decided to reject this reagent in further experiments.

At the second stage, we evaluated the effect of PHTC additive on the efficiency of model water purification using various traditional reagents (Fig. 1). Titanium (IV) hydroxide obtained through the hydrolysis of titanyl sulphate (TS) or titanium (IV) chloride (TC), as well as titanium dioxide in the form of rutile (TD), were used as the modifying additives.

It follows from the presented data that the introduction of PHTC into traditional coagulants allows a substantial enhancement of purification efficiency. This may be due to polycondensation and flocculation on the surface of titanium compounds [19], and also due to nucleation on the negative charged PHTC surface [4, 5].

At the third stage of the experiment, we evaluated the effect of titanium compounds on the rate of filtration of the obtained precipitates (Table 2).

One can see that the addition of PHTC to CC allows a substantial intensification of precipitate filtration. This phenomenon may be explained by the formation of large flakes of the precipitate with lower moisture content.

At the final stage of the investigation, we compared the efficiency of complex reagents in the purification of waste waters (household and industrial waste waters together) from the milk

TABLE 1

Efficiency of model water purification using different coagulants

Coagulant	Coagulant dose calculated for the sum of oxides (Me_xO_y), mg/L	Maximal efficiency of purification, %	
		Suspended substances	Colour index
Aluminium oxychloride	140	95.2	94.1
Aluminium sulphate	128	99.2	98.9
Ferric chloride	143	98.4	98.1
Ferrous sulphate	200	47.1	37.3
Titanyl sulphate	176	93.3	92.4
Titanium (IV) chloride	96	97.1	94.5

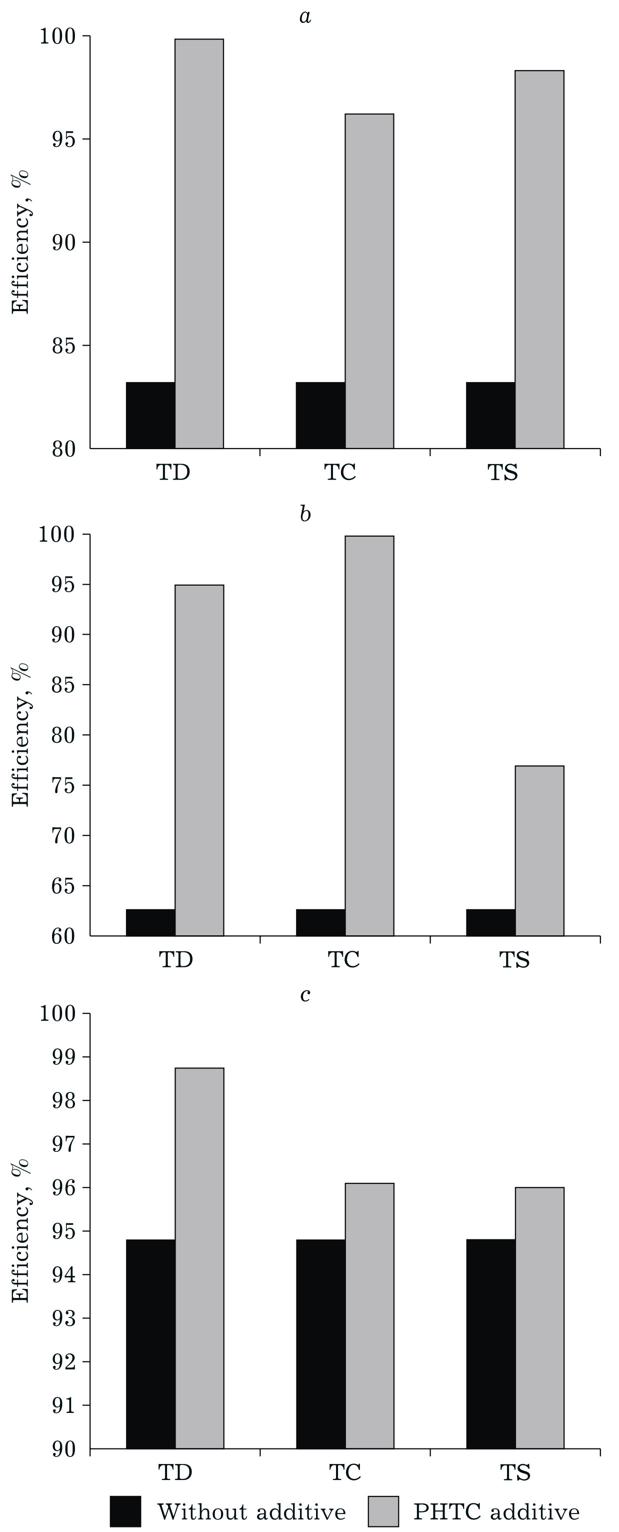

Fig. 1. Effect of the modifying additive PHTC on the efficiency of model water purification by aluminium oxychloride (*a*), aluminium sulphate (*b*) and ferric chloride (*c*).

processing plant in the Moscow Region. The composition of waste water after the stage of preliminary purification in a radial fat trap is presented in Table 3.

TABLE 2

Effect of the modifying additive on the rate of precipitate filtration

Reagent	Filtration rate, mL/min			
	Without additive	Modifying additive		
		TD	TC	TS
Aluminium oxychloride	70	105	120	90
Aluminium sulphate	70	110	80	110
Ferric chloride	60	100	150	95

The average effective dose of coagulants was 100 mg/L with respect to the sum of metal oxides. The data on the chemical composition of purified water are presented in Table 3.

Analysing the obtained results, we may conclude that the samples of modified reagents surpass traditional reagents in the efficiency by approximately 10–12 %, and the rate of precipitate filtration increased by a factor of 1.2–1.5 when complex reagents were used. Increased efficiency of coagulants modified with TD as the most probable PHTC is explained by the developed surface of TiO_2 particles able to adsorb pollutants. In addition, these particles bear a negative charge on their surface and act as nucleating agents. Coagulants modified with TC turned out to be more active than TS, which may be caused by the specific mechanism of hydrolysis of chloride and sulphate salts [11, 12].

CONCLUSION

It may be concluded on the basis of the data obtained in the present work that the use of PHTC as an additive to traditional reagents (complex titanium-containing coagulants) allows one to intensify the purification of waste waters from dairy production. The addition of titanium compounds in the amount of 2.5–7.5 mass % of the mass of the reagent to be modified allows one to enhance the efficiency by 10–12 %.

For the maximal increase in the efficiency of purification, it is recommended to use PHTC formed through the hydrolysis of titanium (IV) chloride directly during coagulation. The introduction of titanium dioxide, which was obtained by calcination of titanium (IV) hydroxide, into the product also promotes a substantial enhancement of purification efficiency and water filtration rate.

TABLE 3

Efficiency of the purification of united household and industrial waste waters from Milk-processing plant

Reagent	COD, mg O/L	Suspended susbtances, mg/L	Fat, mg/L	pH	Al, mg/L	Fe, mg/L	Ti, mg/L	Filtration rate, mL/min
Initial water	1065	175.4	17.2	6.54	0.001	0.17	0.001	48
Aluminium oxychloride	525	0.23	4.2	6.49	0.21	0.11	0.001	68
The same + TC	458	0.11	3.1	6.22	0.04	0.05	0.03	117
The same + TS	441	0.15	4.1	6.35	0.05	0.09	0.07	92
The same + TD	401	0.12	2.7	6.48	0.04	0.07	0.01	110
Aluminium sulphate	559	0.31	6.3	6.40	0.33	0.12	0.001	62
The same + TC	486	0.21	3.6	6.09	0.11	0.06	0.05	83
The same + TS	502	0.21	4.3	6.29	0.06	0.10	0.09	101
The same + TD	425	0.14	2.9	6.38	0.06	0.07	0.01	117
Ferric chloride	574	0.33	6.9	6.33	0.001	0.35	0.001	65
The same + TC	499	0.29	3.9	6.01	0.001	0.21	0.09	126
The same + TS	528	0.24	4.6	6.38	0.001	0.28	0.11	96
The same + TD	433	0.16	3.3	6.35	0.001	0.18	0.02	106

Note. COD – chemical oxygen demand, TS – titanyl sulphate, TC – titanium (IV) chloride, TD – titanium dioxide.

The tests of the obtained samples with real waste water confirmed their increased efficiency with respect to traditional reagents. In addition to the mentioned advantages, we also detected a decrease in the volume of the formed precipitate and an increase in the rate of its filtration.

The samples of complex coagulants may be obtained directly at the plants by mixing titanium salts with the salts of aluminium/iron, and also as a result of processing the industrial titanium-containing wastes on the basis of the existing technologies [20, 21].

Acknowledgements

The work was carried out within the Programme of Support for young scientists teaching at the D. Mendeleev University of Chemical Technology of Russia (Claim No. Z-2020-013).

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