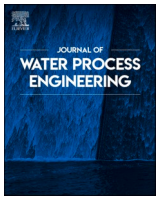
Journal of Water Process Engineering 56 (2023) 104499



Contents lists available at ScienceDirect

Journal of Water Process Engineering

journal homepage: www.elsevier.com/locate/jwpe



Investigation of starch as flocculant for removing oil from oily wastewater

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ARTICLE INFO

Keywords:
Wastewater treatment
Flocculation
Modified starch
Pregel starch
Bilgewater

ABSTRACT

The treatment of oil-containing wastewater was carried out in 3 stages coagulation, neutralization, and flocculation processes. In this study, natural flocculants that are alternatives to polyacrylamide (PAM), have been investigated, as PAM poses a danger to drinking water and aquatic organisms. Flocculant properties were given to starch by modification, pregel, and graft methods, and flocculation results were examined. Oil content and pollution removal performances from wastewater were evaluated with the flocculant effect, the effect of pH conditions, dosage amounts, and temperature parameters. Since the chemical flocculants used in the flocculation sedimentation process to treat oily wastewater cause environmental damage, a natural flocculant effect study was carried out. The effect of starch flocculants synthesized by pregel, modified, and graft techniques on the oily wastewater, bilge water, was evaluated. In this context, the interaction of the effects of PAM, Pregel starch, modified starch and starch graft acrylamide flocculants on the bilge water with different ambient pH, dosage amount and temperature are included. Impact assessment at 5.5–7-8.5 ambient pH for 4 different flocculants; The effect evaluation of 10–15–25 mL dosage amounts and the effect evaluation at 25–40–60 °C temperatures were investigated by experimental studies. Suspended solids analysis, COD, Turbidity and oil-grease determinations are the analyses made for the improvement results in water due to impact assessments. According to the results obtained, it is a flocculant-modified starch that can compete with PAM but needs further development. 98.14 % suspended solids removal, 34.30 % COD removal, 98.94 % turbidity removal and approximately 99.9 % oil removal efficiency were obtained with modified starch.

1. Introduction

Oily wastewater, also known as oil-contaminated or oil-laden wastewater, is a type of industrial wastewater that contains various types of oils, greases, and hydrocarbons. It is a common byproduct of many industrial processes, including: *(i) oil and gas production:* Wastewater generated during the extraction and refining of oil and natural gas often contains crude oil and various hydrocarbons, *(ii) manufacturing:* Industries such as metalworking, food processing, and automotive manufacturing can produce oily wastewater due to the use of cutting fluids, lubricants, and oils, *(iii) vehicle maintenance and repair:* Automotive repair shops and maintenance facilities produce oily wastewater through activities like oil changes and engine repairs, *(iv) marine operations:* Ports, shipyards, and vessels generate oily wastewater from ship bilge water and fuel transfer operations, *(v) food service:* Restaurants and commercial kitchens produce oily wastewater through the disposal of cooking oils and grease [1]. Today, due to the increase in energy demand, the processing and transportation of oil and fossil fuels indicate that oil is one of the most important wastes mixed with water [2]. When oily wastewater is discharged into the environment, it can disrupt ecological health, and affect living life [3]. Considering the scarcity of water resources and environmental pollution, the issue of how to treat and recycle oily wastewater has become an important and urgent issue in engineering fields [2]. In addition to all these pollution sources, several million tons of oil from transportation operations are mixed into the world's water resources every year [4,5].

MARPOL, which stands for the International Convention for the Prevention of Pollution from Ships, is an international treaty that aims to prevent and control pollution from ships, including the disposal of various types of waste generated on board vessels. MARPOL waste includes different categories of waste generated during the operation of ships, and the convention sets out regulations and requirements for the handling, storage, and disposal of these wastes. The six main categories of MARPOL waste are as follows: (i) oil: This category includes oil residues, bilge water, and oily mixtures. MARPOL Annex I contains regulations to prevent the discharge of oil into the sea and sets limits for oil

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https://doi.org/10.1016/j.jwpe.2023.104499
Received 3 May 2023; Received in revised form 24 October 2023; Accepted 27 October 2023
Available online 30 October 2023
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content in discharged water (ii) Noxious Liquid Substances (NLS): These are substances that, if discharged into the sea, can harm marine life or the environment. MARPOL Annex II contains regulations for the control of such substances and their handling (iii) Harmful Substances in Packaged Form: This category includes packaged goods that may be hazardous to the marine environment if not handled properly. MARPOL Annex III provides guidelines for the packaging and labeling of these substances (iv) Sewage: It includes both blackwater (from toilets) and graywater (from sinks, showers, and kitchens). MARPOL Annex IV sets out standards for the treatment and discharge of sewage from ships (v) Garbage: This category covers solid waste generated on board, such as plastics, food waste, paper, and more. MARPOL Annex V regulates the disposal of garbage to prevent pollution of the marine environment (vi) Air Emissions: While not typically referred to as "waste," air emissions from ships, including sulfur oxides (SOx), nitrogen oxides (NOx), and greenhouse gases, are also addressed under MARPOL. Annex VI focuses on reducing air pollution from ships through regulations on engine design and fuel quality.

Ships are required to manage and dispose of these wastes in accordance with MARPOL regulations to minimize their impact on the marine environment. Port facilities and authorities play a crucial role in ensuring compliance with these regulations and providing appropriate disposal and treatment facilities for MARPOL waste. Violations of MARPOL can lead to penalties and fines for shipowners and operators [6].

Coagulants/flocculants play very important roles in the field of water treatment according to their adsorbance capacities. Conventional water treatment methods used today often have only one functionality, resulting in complex devices and laborious processes [7,8]. Therefore, it is of great importance to develop coagulation/flocculation methods both in scientific research and in practical applications [9,10,32,35]. Efforts to recover and clean water from oily wastewater by coagulation/flocculation are of great economic, social, and environmental importance for the protection of the ecological system and the evolution of researchers.

The process of coagulation-flocculation has been the subject of studies by several authors for the treatment of wastewater generated in petroleum-derived wastes [11,12,34]. Removal of oil from wastewater by coagulation is a combination of physical and chemical processes. These processes include two steps: aggregation, and flocculation [13]. The main task of the coagulants in this process is to neutralize the negative charges of the oil particles and to reduce the electrostatic repulsion of the electric double layer. This incident is considered "destabilization". Then, the destabilized particles begin to develop and gradually collect into large agglomerates. Under free precipitation or air flotation, separation of the agglomerates from the water phase occurs [15].

The agglomeration process depends on the chosen flocculant. Accordingly, many researchers continue their studies on the development of new flocculants with high efficiency, low cost and environmentally friendly features [14]. Studies are in the direction of developing multifunctional flocculants such as effective removal of turbidity in water and inhibition of bacterial growth. Conventional flocculants such as inorganic metal-based and synthetic organic polymeric flocculants, which are the subject of studies, do not have significant sterilization [8,15]. In addition, the release of metal ions or harmful polymeric monomers into water is known to cause serious health problems [16,17]. The high-performance natural polymer chitosan and its derivatives [18,19] are effective both as good-performing flocculants and in improving their antibacterial properties.

Starch-based flocculants have been used in water treatment over the years due to their cheapness, biodegradability, environmental friendliness, and effectiveness in low quantities. [20–23]. Starch is a plentiful and natural resource, and the cost is much lower than agglomerates such as chitosan. It can be easily modified to meet a variety of applications by adding different functional groups to its structure because it contains a large number of hydroxyl groups in the saccharide ring. [23–26].

In this study, the pollution caused by petroleum-derived wastes in the water is discussed. The natural flocculant effect for the treatment of wastewater was investigated and a series of experiments were carried out to eliminate environmental effects and increase efficiency. The pollution left by the polyacrylamide chemical used as a flocculant on water and soil was desired to be removed, and the usability of starch, which is a natural flocculant instead of polyacrylamide, was desired to be measured with efficiency and economy evaluations. With the flocculant polyacrylamide chemical, it was desired to remove the pollution on water and soil, and besides, it was desired to measure the usability of starch, which is a natural flocculant instead of polyacrylamide, by evaluating the efficiency and economy. Four different new starch-based flocculants (PAM, modified starch, pregel starch, and starch graft acrylamide) were successfully prepared. In addition to the flocculant effect, the pH of the medium, the dosage amount, and the temperature effects were also investigated. pH, Total Suspended Solid Matter (TSSM) (mg/L), Chemical Oxygen Demand (COD) (mg/L), Turbidity (NTU), Oil Grease (mg/L) analyses were made for water. To characterize the structure of the prepared flocculants, Perkin Elmer Spectrum 100 brand -FTIR was used. Surface morphology properties were analyzed using Jeol JSM 6510-lv Brand Low Vacuum Scanning Electron Microscope -SEM.

2. Materials and methods

2.1. Raw bilgewater characterization

Bilge water was preferred as the oily wastewater sample because it is the waste sample closest to the other water characteristics entering the wastewater treatment process. Bilgewater, which was directed to the Ship Waste Collection and Processing Facility, was taken as a sample upon request from the Shipyard in Tuzla (one of the districts of Istanbul) with "40.83457, 29.26790" coordinates. In the study, the characterization of the bilge water on the amount of oil, chemical oxygen demand, suspended solids, and turbidity was investigated. "SM 5520 D" standard method for Oil-Grease analysis, "SM 2130 B" standard method for turbidity analysis, "TS EN 872" standard method for Suspended Solids analysis were used.

After the characterization of the bilge water, the coagulation and neutralization processes, which are the pre-treatments before the flocculation process, were also applied. Polialuminiumcloride (PAC) coagulant was used in the coagulation process. The pH value of PAC used in the solution is 3.0 and was purchased from the manufacturer Akkim Kimya San ve Tic A.Ş. The lime used for neutralization was in powder form and 1 g of lime powder was mixed with 100 mL of distilled water and used as a solution.

2.2. Synthesis of flocculants

The flocculant effect was investigated with four different samples-PAM, modified starch, pregel starch, and starch graft acrylamide. The anionic PAM used in the experiments was produced by using the commercial sample that was obtained from Abacı Kimya Ltd. Şti. The starch modification was realized by the method developed by Prachayawarakorn et al. [27]. The flocculant taken in powder form was turned into a gel by adding 7 g of PAM powder to 1000 mL of water and was used in gel form in all experiments. Modified starch, pregel starch, and flocculants were prepared by grafting technique, and commercial natural corn starch was used. The properties of the corn starch used were determined as 13 % by weight of moisture and 0.5 % by protein. Pregel starch, also known as pre-gelatinized or pregelatinized modified starch, is a starch product that has been chemically or physically processed to undergo partial gelatinization. Gelatinization is the process of breaking down the crystalline structure of starch granules and swelling them by heating in the presence of water. In experimental studies examining pregel starch

Table 3.1
Characteristics of Raw Bilgewater (taken as a sample upon request from the Shipyard in Tuzla with "40.83457, 29.26790" coordinates).

Turbidity (NTU)	2875
Total suspended solids (mg/L)	2924
COD (mg/L)	2682
Oil grease (mg/L)	10,500
pH	11

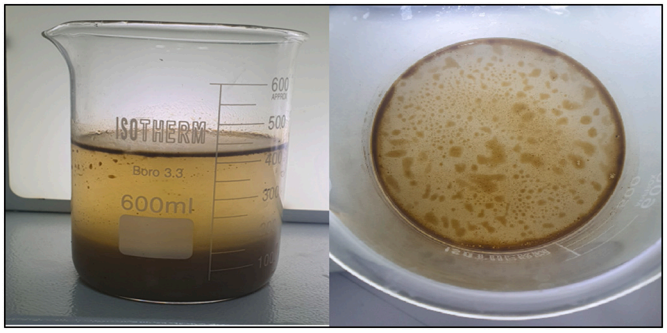


Fig. 3.1. Raw image of Bilgewater taken from Tuzla Shipyard located at coordinates "40.83457, 29.26790".

as a flocculant, the method that was developed by Teh et al. [28] was used. This method, which is the only one for the pregel process, has been preferred. The method developed by Mishra et al. [36] was used in experimental studies in which graft starch was examined as a flocculant.

For the pre-flocculation process, pH determination was made with coagulation and lime, taking commercial treatment plant studies as a guide. PAC at pH 3 was used for the coagulation process. In all experiments, 65 mL of PAC was used to reduce the pH of Bilgewater to 4 using PAC. The effect of pH environment was investigated at three different pH values (5.5–7–8.5). The amounts to be used were decided based on the aggregation state of PAM, Modified Starch, Pregel, and Starch flocculants used in the flocculation process. The amounts used for each flocculant were 15 mL PAM, 80 mL modified starch, and 120 mL pregel starch-water mixture, respectively. Powdered flocculants, PAM, were prepared by mixing 7 g of PAM powder with 1000 mL of distilled water and 50 g of Modified Starch into 250 mL of distilled water. In addition, the grafted flocculant was prepared and used by mixing 50 g of the solid vaccine in 250 mL of distilled water. On the other hand, Pregel starch was directly evaluated with the semi-gel consistency performed under the preparation conditions. It was observed that the synthesized vaccine-featured flocculant swelled, dispersed and floated in the water, similar to the adsorbent structure after it was dried and kept in water for use due to its unbreakable gel state. 40 mL was added using this form.

The flocculant effect at different doses was carried out in order to completely remove the colloidal structures in the wastewater from the wastewater. It is aimed to approach the appropriate discharge criteria values with different flocculant dosing. It is also desirable to compare the effect of flocculants used at the same dosage amount. With the TSSM, Oil-Grease, and Turbidity results obtained as a result of the examination of the pH effect, the pH 7.0 environment was preferred with the evaluation of the most efficient flocculation. The amounts of PAC and Lime are the same as those used in the pH impact analysis. The effect of flocculant dosage has been studied in 10–15- and 25-mL volumes. Also, at different ambient temperatures, the bridging bond may weaken, or the temperature may increase the bridging bond strength, forming strong bulk structures. As the most appropriate dosing condition was 25 mL flocculant as a result of the dosing effect analysis, 25 mL of each flocculant was dosed and the pH of the medium became 7.0 and the flocculation variability of the bilge water was measured at 25, 40, and 60 °C. It was desired to examine the effect of temperature change on the bridging bond that will be formed by the addition of flocculant to the

Table 3.2
Flocculation analyzes of all samples at pH 5.5, 7, and 8.5 values.

	PAM			Modified Starch			Pregel Starch			Starch Graft Acrylamide		
pH	5.5	7	8.5	5.5	7	8.5	5.5	7	8.5	5.5	7	8.5
TSS (mg/L)	298	19	157	106	54	59	1328	385	857	1578	1333	1623
COD (mg/L)	2383	1106	827	2052	1762	1221	1856	901	1006	940	1046	1163
Turbidity (NTU)	160	34	187	110	30	48	354	153	345	414	375	497
Oil Grease (mg/L)	<10	<10	140	<10	<10	<10	24 0	201	228	228	144	168

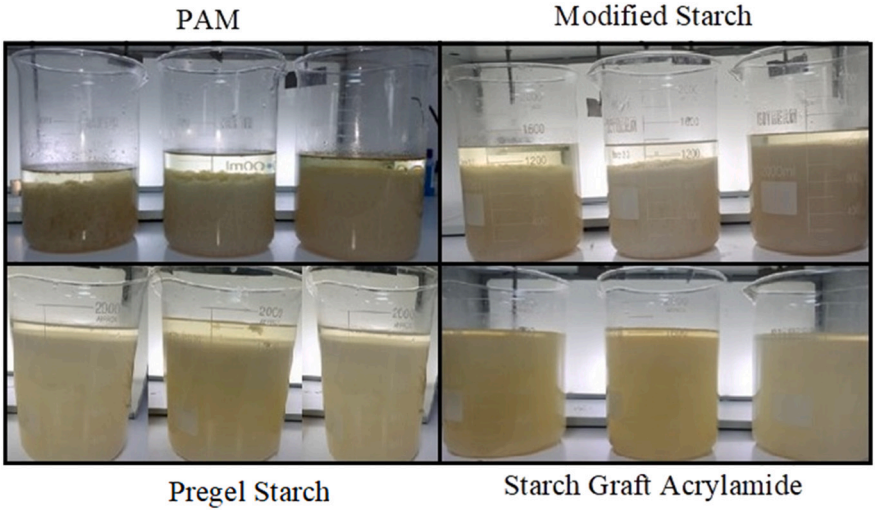


Fig. 3.2. Flocculation samples with PAM, Modified starch, pregel starch, and starch graft acrylamide at pH 5.5, 7, and 8.5 environments, respectively, after 10 min.

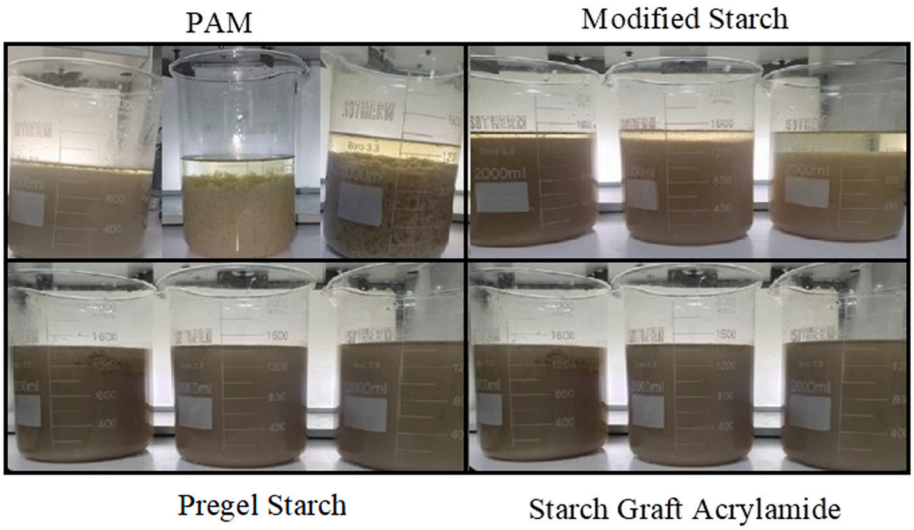


Fig. 3.3. Flocculation samples with PAM, modified starch, pregel starch, and starch graft acrylamide at different dosage amounts of 10, 15, and 25 mL, respectively after 3 min.

Table 3.3
Flocculation analyses of all samples at dosage amounts of 10, 15, 25 mL.

	PAM			Modified starch			Pregel starch			Starch graft acrylamide		
Dosage (mL)	10	15	25	10	15	25	10	15	25	10	15	25
TSSM (mg/L)	126	19	42	118	42	48	2052	1582	1378	1775	1916	1878
COD (mg/L)	1095	1106	995	1657	1558	1563	2262	2334	2134	2255	2069	1676
Turbidity (NTU)	87	34	28	124	32	26	795	702	591	894	507	444
Oil Grease (mg/L)	52	<10	<10	365	76	39	1005	996	531	1080	762	254

Table 3.4
Flocculation analyses of all samples at 25, 40, and 60 °C.

	PAM			Modified starch			Pregel starch			Starch graft acrylamide		
Temperature (°C)	25	40	60	25	40	60	25	40	60	25	40	60
TSSM (mg/L)	42	23	51	48	17	70	1378	382	42	1878	154	781
COD (mg/L)	995	512	648	1563	498	578	2134	1504	530	1676	2420	2423
Turbidity (NTU)	28	30	32	26	56	105	591	324	96	444	283	463
Oil Grease (mg/L)	<10	<10	56,2	38,8	53	117	531	408	302	254	194	228

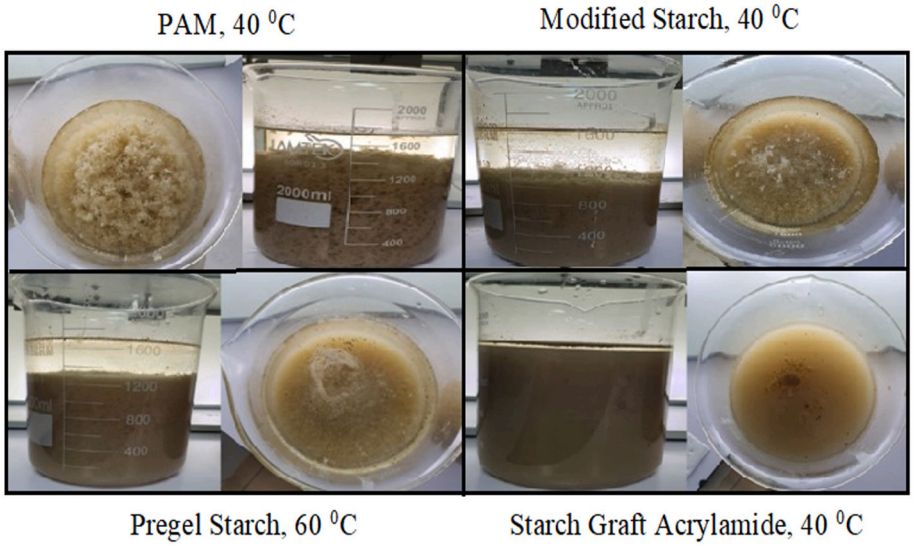


Fig. 3.4. Flocculation working with PAM (40 °C), Modified starch (40 °C), Pregel starch (60 °C), and Starch Graft Acrylamide (40 °C) after 10 min.

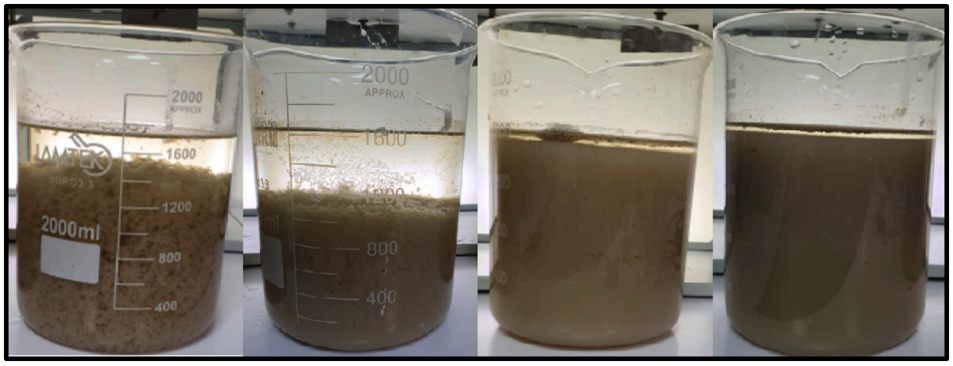


Fig. 3.5. Post-settlement effects of PAM, Modified Starch, Pregel Starch, and Starch Graft Acrylamide flocculants under the same conditions, respectively after 10 min.

Table 3.5
Flocculant effect results.

Flocculants	PAM	Modified Starch	Pregel Starch	Starch Graft Acrylamide
SS (mg/L)	23	17	382	154
COD (mg/L)	512	498	1504	2420
Turbidity (NTU)	29.8	56	324	282
Oil Grease (mg/L)	<10	53	408	194

colloidal structures formed after coagulation.

2.3. Analysis

Chemical Oxygen Demand (COD) results were measured with HACH brand LCK 1014 COD kits and HACH brand spectrophotometer. The total suspended solids (TSS) results were measured by HACH brand sample spectrophotometer. Oil and grease analyzes were measured with the SM 2130 B method, and turbidity was measured with the SM 5520 D method. Jeol JSM 6510-lv Brand Low Vacuum Scanning Electron Microscope (SEM) was used to examine the surface structures of solid samples and their photographs were taken with reduction ratios of "x35–500 μm" and "x2500–10 μm". FTIR analysis of flocculants was performed with a Perkin Elmer Spectrum 100 brand device.

3. Results and discussion

Preliminary studies were done on four different types of starches to determine the most suitable modified-unmodified starch to be used as a natural coagulant for the coagulation-flocculation of oil. Evaluation of flocculants among themselves was handled with the effects of pH, dosage amount, and temperature. The pH effect was evaluated by studies conducted in 5.5, 7, and 8.5 pH environments, the dosage effect was evaluated by the results of 10–15-25 mL flocculant dosages, and the temperature effect was evaluated by studies at 25, 40, and 60 °C.

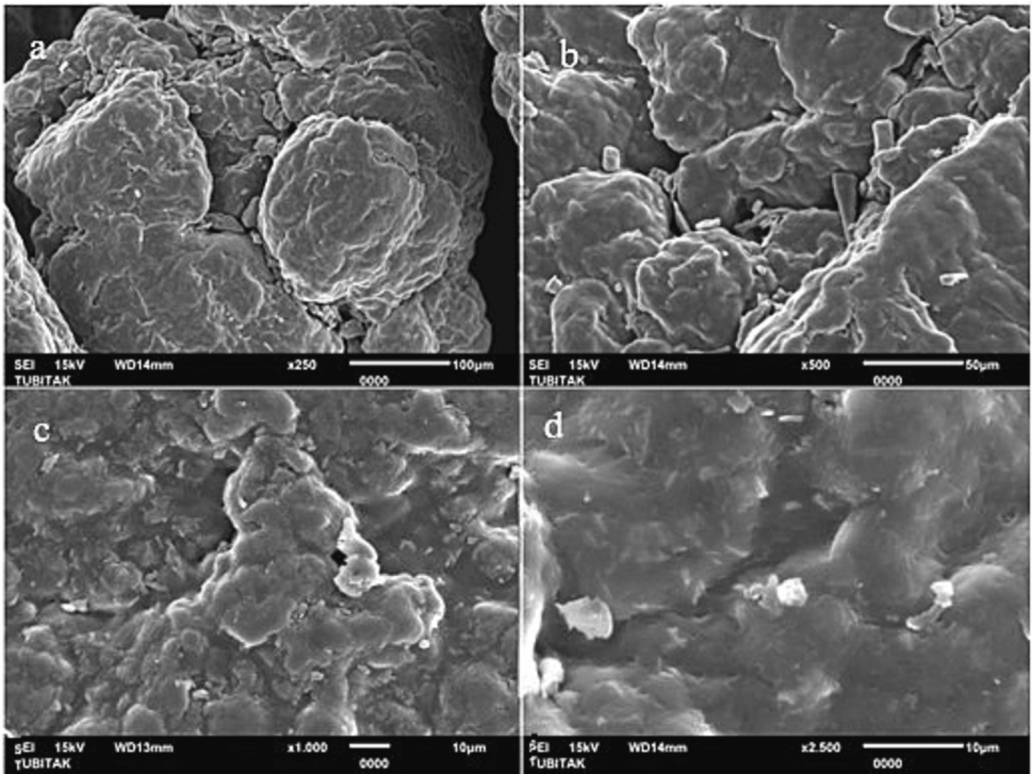


Fig. 3.6. SEM images of PAM a) 250x, b) 500 x, c) 1000 x d) 2500 x.

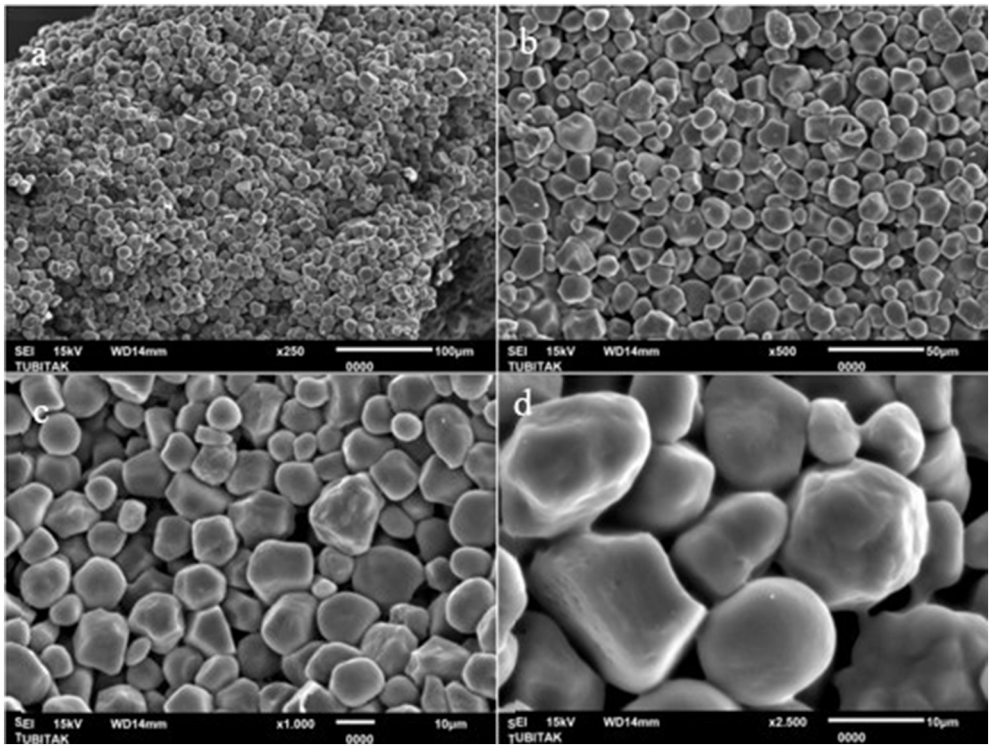


Fig. 3.7. SEM images of Modified Starch a) 250x, b) 500 x, c) 1000 x d) 2500 x.

Table 3.1 represents the characteristics of raw bilgewater, and Fig. 3.1 illustrates the image of raw bilgewater. As seen in Fig. 3.1, the oil content of bilge water is high for drainage and low for dewatering.

3.1. *Effect of pH*

Flocculation studies were carried out in 3 different pH environments (5.5, 7, 8.5) and 4 different flocculants. The results obtained are given in Table 3.2. The physical comparison of bilge water with raw water in Fig. 3.2 was observed at all pH values. It was concluded that the oil and grease analysis results comply with the discharge criteria required for full purification but are above the limit values specified in the pretreatment and deep-sea discharge criteria. In addition, it was determined that it complies with the limit values determined for the number of suspended solids and it was concluded that it is above the limit values determined for chemical oxygen demand.

The study using PAM in pH 5.5 and 7 environments obtained appropriate results according to the oil-grease and total suspended solids limit values. However, the results of chemical oxygen demand at pH 8.5 were above the criteria. In the experiments where the pH effect with PAM was examined, it was evaluated that the most effective pH value was 7. 99.35 % TSS removal in the bilge water of 15 mL PAM coagulant at pH 7; 58.76 % COD removal; Turbidity removal of 98.82 % and oil removal efficiency of approximately 99.9 % were found.

The results of the values obtained by using modified starch in all pH environments are examined, free-floating flocks' accumulation was not observed and the formed flocks collapsed for a longer time (approximately 10 min) than PAM. As the discharge criteria results of all three environments were compared, it was evaluated that Modified starch gave positive results in three different pH environments, except for chemical oxygen demand removal. It was observed that the addition of 80 mL of modified starch creates an effective flocculation result in a pH 7 environment. The effectiveness of the pH 7 medium on the bilgewater was calculated as 98.14 % SS removal, 34.30 % COD removal, 98.94 % turbidity removal, and approximately 99.9 % oil removal.

The dosage amount of Modified Starch is compared with PAM and it is concluded that modified starch is effective in removing the pollution that creates wastewater, but a high dosage amount does not create an economic result. In addition, in the studies carried out with PAM, the effect after a waiting period of approximately 1 min can only be achieved with modified starch after a waiting period of 10 min. The studies with modified starch and PAM were compared and it was seen that the results were almost close to each other, except for the study with PAM at 8.5 pH conditions.

The flock sizes obtained using Pregel Starch were smaller than the flock sizes obtained with PAM and modified starch. The resulting accumulations collapsed in about 3 min. It was observed that oil was collected on the water surface in a pH 5.5 environment. It was intended to clump the oil in water, but it did not collect on the surface and collapse. The fact that the analysis results obtained in the experiments of Pregel Starch coagulant performed in three different pH environments were higher than those of PAM and Modified Starch, shows that Pregel starch is not an alternative natural flocculant. However, it should be considered that increasing the dosage can increase the flocculation efficiency. In addition, it is thought that increasing the amount of powder Pregel used for flocculation and mixed with water can positively affect the results. As starch-grafted acrylamide was used, the flocculant swelled in water and did not disperse in water in all three pH environments. Since the collapse rate of the coagulation-like structures formed is slow, it was expected to collapse for 1 day in order to be able to analyze it. Results of grafted flocculant studies show the most effective results in the addition of 40 mL flocculant and in three different pH environments. Comparing the flocculation results with the grafted flocculant in a pH 7 environment with PAM under the same conditions, it was observed that there was a very small amount of COD values Experiments, results and observations show that the grafted flocculant cannot be an alternative for PAM under the specified conditions. As the grafted flocculant studies as re compared with the recent studies it can be seen that grafted starch can be a comparable flocculant to chitosan [19].

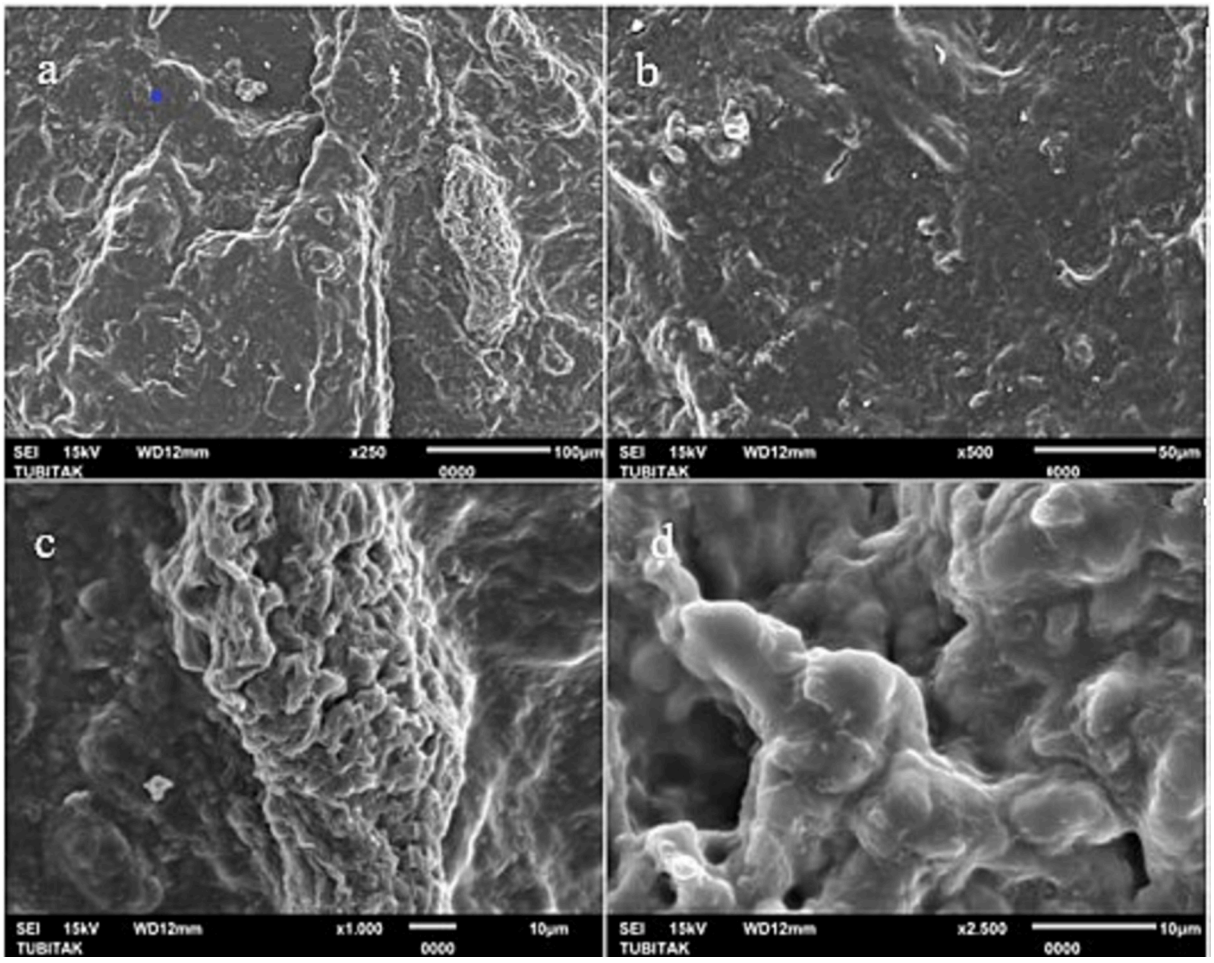


Fig. 3.8. SEM images of Pregel Starch a) 250x, b) 500 x, c) 1000 x d) 2500 x.

3.2. Effect of dosage amount

The dosage amount also effects the oily wastewater treatment of coagulation/flocculation. It has been reported that the oil removal rate has a close relationship with the coagulant/flocculant amount [15]. To examine the effect of dosage amount, the pH environment of the bilge water was prepared as 7.0 by coagulation and neutralization processes. In addition, the bilge water is at 25 °C and the flocculant dosage was studied at dosage amounts of 10, 15, and 25 mL. In the results obtained, it was seen that significant results were obtained with the use of less amount of PAM. With this observation, it was decided to continue the rest of the study with 15 mL of PAM solution.

Fig. 3.3, the phase separations due to agglomeration show that more intense aggregation occurs with an increase in the dose amount. When the analysis results in Table 3.3 are evaluated, it is seen that the results obtained by adding 25 mL of PAM are more effective. The effect on the bilge water was calculated as 98.56 % TSS removal, 62.9 % COD removal, 99.02 % turbidity removal, and >99.9 % oil removal. As a result of the dosing amount studies made with modified starch, positive results were not obtained as much as the studies with PAM. However, the modified starch flocculant was found to be at least as potent as PAM. This information obtained is important for natural flocculants that do not create an environmental load. When the results of the discharge criteria of all three environments in Table 3.3 were compared, it was determined that the most effective dosage amount was 25 mL. With the effectiveness of 25 mL Modified Starch Flocculant on the bilge water in a pH 7 environment, 98.35 % TSSM removal, 41.72 % COD removal, 99.08 % turbidity removal, and 99.63 % oil removal results were obtained.

As pregel starch was used, the phase separation resulting from agglomeration did not visually change even when the dose was increased. No effective change was observed when the dosage amount of pregel starch was decreased. While it was observed that 3 min of waiting time was sufficient when measuring pH activity, it was observed that 10 min of waiting time did not produce an effective result in this study. In studies with lower dosing, it was evaluated that lower dosing for pregel could not be an alternative to PAM. It was observed that the most effective dosage was flocculation with the addition of 25 mL. The flocculation effect of adding 25 mL of pregel to the bilge water in a pH 7 environment was found to be 52.87 % TSSM removal, 20.42 % COD removal, 79.43 % turbidity removal, and 94.94 % oil removal. Grafted starch has a slightly different structure from gel and semi-gel forms such as PAM, Modified Starch, and Pregel starch flocculants. It was evaluated that the flocculating effect of this form, which was mentioned in the pH effect analysis, could not be observed in a different pH environment for 40 mL. In this study, the 1-day waiting period applied in the pH effect study for the graft-featured flocculant was applied and analyses were made from the samples taken at the end of this period. In the dosage effect review, this was observed with minor visual differences, although not evident. In Fig. 3.3, the results of the efficiency of the graft technique are also given. Good efficacy was not observed in these results despite a 1-day waiting period. When the results in the table are evaluated, it is seen that the most effective result is achieved by adding 25 mL. The effect of 25 mL dosing results in bilge water is 35.77 % TSSM removal, 37.51 % COD removal, 84.55 % turbidity removal, and 97.58 % oil removal efficiency. When the obtained values are examined, less dose

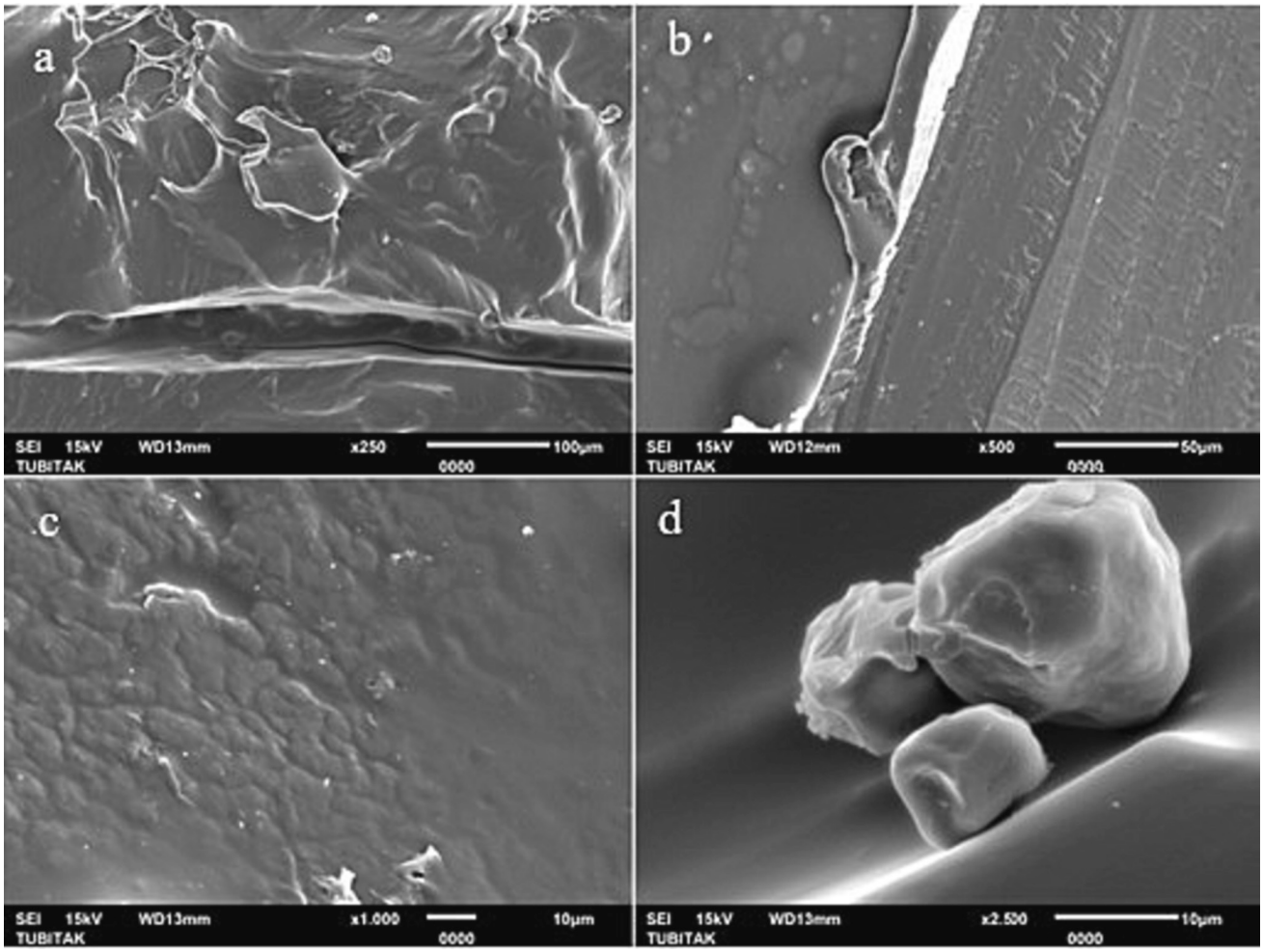


Fig. 3.9. SEM images of starch graft acrylamide a) 250x, b) 500 x, c) 1000 x d) 2500 x.

requirement for load neutralization is met as suggested in the literature [15].

3.3. *Effect of temperature*

Temperature effect studies were carried out at three different ambient temperatures and the results are given in Table 3.4. Considering that the most effective temperature environment is 40 °C with the results of the analysis, the purification effect of 25 mL PAM dosage into the bilge water in a pH 7.0 environment is 99.2 % TSSM removal, 80.9 % COD removal, 99.9 % turbidity removal, and 99.9 % turbidity removal. Approximately 99.9 % oil removal was achieved. Fig. 3.4 shows the phase separation results of the agglomeration results studied with four different flocculants.

It is shown in Table 3.4 that more effective results are obtained with modified starch in an environment where the temperature is 40 °C than in an environment of 25 °C. However, as in the temperature effect studies with PAM, it was observed that the modified starch lost its activity in ambient conditions brought to 60 °C.

The agglomeration distributions after a short waiting period are shown in Fig. 3.4. As in the results obtained when PAM is used, it was thought that the flock bonds were broken at 60 °C and that the increased steam pressure broke the weak flock channel bonds. As a result of the temperature effect parameter for modified starch, it was observed that 40 °C is the most effective temperature. Bilge water treatment efficiency was calculated as 99.4 % TSSM removal, 81.4 % COD removal, 98.0 % turbidity removal and 99.4 % oil removal efficiency. It was concluded that the most efficient temperature was obtained at 60 °C. The treatment efficiency of the Pregel Starch results on the bilge water was calculated as 98.6 % TSSM removal, 80.2 % COD removal, 96.7 % turbidity removal and 97.2 % oil removal. For starch grafted acrylamide, it can be said that flocs cannot form a strong bond in 40 °C and 60 °C temperatures, where the degreasing efficiency is highest. This situation negatively affects the treatment efficiency as well as the settling rate. The removal efficiency of grafted starch on the bilge water was calculated as 94.7 % TSSM removal, 9.8 % COD removal, 90.2 % turbidity removal and 98.2 % oil removal at 40 °C ambient conditions. It was observed that very small removal results were obtained for COD and the defouling effect decreased with increasing the temperature of the grafted flocculant. It was concluded that working in mild temperature ranges may be sufficient.

3.4. *Effect of flocculants*

After examining the pH, dosage amount and temperature parameters, the pollution removal efficiencies of the flocculants were compared among themselves. At 40 °C ambient temperature, pH 7 ambient condition, 25 mL flocculant dosage was the common evaluation parameter for each flocculant. Fig. 3.5 shows the image of PAM, modified starch, pregel starch, and starch graft acrylamide flocculants in the common evaluation parameter. It was observed that the flocculation process of PAM and Modified Starch is more effective, and the flocs formed bring the flock diameters and size of the channel structures into a suitable form for collapse. It was seen that the flocs formed after the addition of

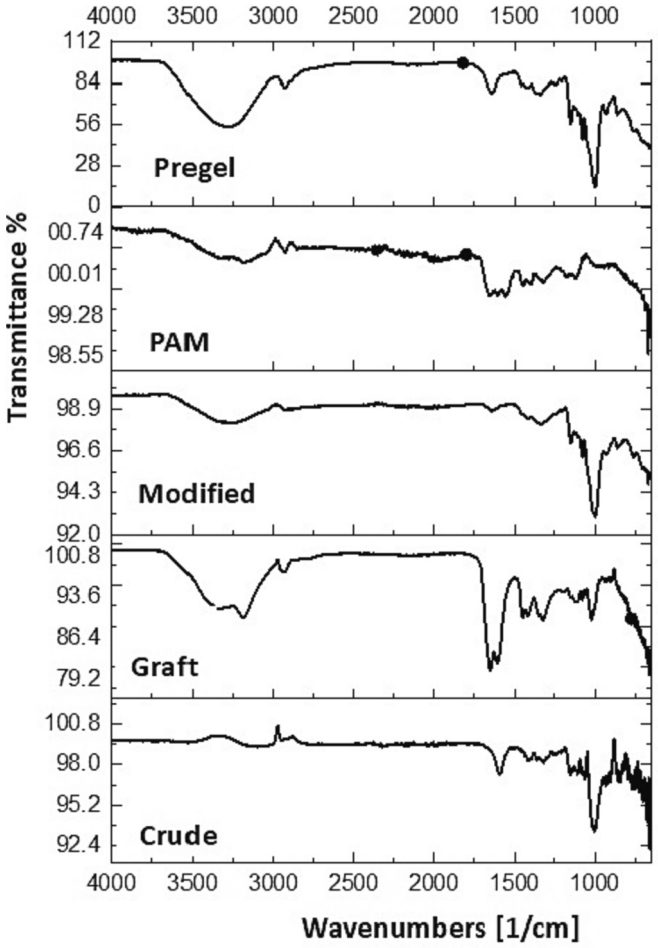


Fig. 3.10. FTIR results of Pregel Starch, PAM, Modified Starch, and Starch Graft Acrylamide flocculants, respectively.

PAM are of larger diameter. It has been evaluated that channel bonds are more flexible in flock structures formed with modified starch. It is thought that this situation will cause the flocs formed after flocculation to disperse in water.

Table 3.5. The results obtained under the same ambient conditions with different flocculants are seen. It is seen that the degreasing results obtained with the modified starch flocculant are very close to those of PAM. It is also seen that modified starch has more effective TSSM and COD removal efficiency than PAM.

Starch and modified starch samples were preferred because they have natural flocculant properties, are easily available due to geographical conditions, and are economical. It has been evaluated that the modified starch has less oil removal efficiency due to the flexibility of the flock bonds.

3.5. *Characterization of flocculants*

Characterization of four flocculants used in the flocculation studies was performed by SEM and images of PAM are given in Fig. 3.6. PAM, which has a porous surface structure, has a few crystalline nanotubes on its surface. It is evaluated by Wu et al. [29] that the porous surface structure creates a bridging bond when it increases the probability of collision between pollutants in the wastewater. It has been evaluated that a PAM structure with a similar porous structure is important in terms of flocculation performance.

In the SEM images of the Modified Starch in Fig. 3.7, it was concluded that the granular structures of the modified starch and the native starch are very similar. It is evaluated that it has a porous structure as well as a granular structure, and therefore it provides flock formation between colloids. In addition, it was explained by Prachayawarakorn and Kansanthia [27] that hydroxyl groups are converted into carboxyl and carbonyl groups by the modification method carried out by the oxidation of starch, thereby gaining hydrophobic properties. For this reason, it is thought that a granular structure connected to each other is formed.

As a result of SEM analysis of Pregel Starch in Fig. 3.8, it is seen that it has a porous structure. However, it is considered that there is integration in the surface structure and this integrated structure creates fewer effective results in forming bridging bonds between colloids. In addition, the pregel sample was evaluated with the result in the most probable drying conditions for the SEM results. Due to the moisture content, SEM results have partial differences from the results in the literature. Since the pregel starch flocculant was diluted and used in the study, this situation is thought to not affect the result. The pollution removal efficiency also increases with the increase in the ambient temperature of the pregel starch flocculant. Fig. 3.8 shows the granular swelling of pregel starch. Starch granules appear to be irregular and polyhedral in shape, like images observed by Xu et al. [30].

From the SEM results of the starch graft acrylamide flocculant in Fig. 3.9, it was evaluated that the grafting process, in which the granular structure of the starch was lost, was successful. However, its transformation from a granular structure to a crystal structure did not increase the efficiency of wastewater treatment. This is an unexpected performance from grafted flocculants.

In Fig. 3.10, the FTIR results of the flocculants for pregel starch, PAM, modified starch, and starch graft acrylamide flocculants are given, respectively. Pregel starch formed a lower peak at wavelengths of 3500–3000 cm^{-1}. The peak curve formed at these wavelengths shows the O—H stretch in the carboxylic acid structure and the presence of protein in starch. The lower peak at 2930 cm^{-1} wavelength is considered to indicate C—H tension and the formation of fatty acids and lipids. At 1000 cm^{-1} wavelength, it is seen that the transmittance reaches the lowest level and forms a peak at the lower peak. This is attributed to the C-OH and C—O bonds of carbohydrates [31].

It has been evaluated by the results of Ma et al. [32] that the downward peak diffraction experienced between 3250 and 3000 cm^{-1} wavelengths in Fig. 3.10 from the ready-made PAM flocculant is dependent on the -NH_2. The downward diffraction experienced at wavelengths between 3000 and 2750 cm^{-1} is attributed to CH_3 vibrations. The tension between C═O, which is the down-diffraction carbonyl bond, is experienced at wavelengths between 1750 and 1500 cm^{-1}; The downward diffraction C—N bond is experienced at wavelengths between 1500 and 1250 cm^{-1}; The diffraction experienced at a wavelength of about 1000 cm^{-1} was evaluated as the C-O-C bonds. It is thought that the downward diffraction observed between 3500 and 3000 cm^{-1} wavelengths in pregel starch in the FTIR results of modified starch is due to the O—H stretching in the carboxylic acid structure and is due to the presence of protein in the starch. However, the fact that this diffraction is higher in pregel starch, that is, lower permeability, has been evaluated because of the presence of protein and less tension in O—H bonds. The tension in the C-OH and C—O bonds is thought to occur at a wavelength of about 1000 cm^{-1}.

The voltage of the diffraction of the starch graft acrylamide in the wavelength range of 3250–3000 cm^{-1} belonging to the -NH_2 group of acrylamides; down-diffraction from a wavelength of about 900 cm^{-1} is attributed to the C—N group of acrylamides [33]. It is a successful grafting technique. This is evaluated by comparing the results of Chen et al. and attributing the upward peak at a wavelength of about 900 cm^{-1} to the voltage formed by the N-(CH_3) bond. This result indicates that acrylamide was grafted onto the starch backbone.

4. Conclusions

Studies have shown that the most effective flocculant for oil removal

is PAM. However, it is seen that the efficiencies of the natural flocculants are related to the amount of starch and the oil and pollution. So the removal efficiency of PAM can be increased by using higher amounts. In addition to the quantitative parameter evaluation, it was observed that the flocculant prepared by the grafting technique could not reach the expected effectiveness. It is thought that when it is dried and thrown back into the water for use, it has a more adsorbent effect rather than the flocculant effect, which provides swelling. Although the results obtained with the modified starch closest to the structure provided in the PAM images, the fact that the flocs formed with pregel starch have a higher density than the dense and modified starch leads the studies to pregel starch when an alternative to PAM is considered.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Meltem YILDIZ reports financial support was provided by Kocaeli University.

Data availability

No data was used for the research described in the article.

Acknowledgements

Financial support is provided by Kocaeli University through Project FYL-2022-2765.

References

[1] K. Abuhasel, M. Kchaou, M. Alquraish, Y. Munusamy, Y.T. Jeng, Oily wastewater treatment: overview of conventional and modern methods, challenges, and future opportunities, Water 13 (2021) 980, https://doi.org/10.3390/w13070980.
[2] C. An, G. Huang, Y. Yao, S. Zhao, Emerging usage of electrocoagulation technology for oil removal from wastewater: a review, Sci. Total Environ. 579 (2017) 537–556, https://doi.org/10.1016/j.scitotenv.2016.11.062.
[3] C.H. Fox, P.D. O'Hara, S. Bertazzone, K. Morgand, F.E. Underwoode, P.C. Paquet, A preliminary spatial assessment of risk: marine birds and chronic oil pollution on Canada's Pacific coast, Sci. Total Environ. 573 (2016) 799–809, https://doi.org/10.1016/j.scitotenv.2016.08.145.
[4] M.K.M. Ilias, M.S. Hossein, R. Ngteni, A. Al-Gheethi, H. Ahmad, F.M. Omar, M. Naushad, S. Pandey, Environmental remediation potential of ferrous sulfate waste as an eco-friendly coagulant for the removal of NH_3-N and COD from the rubber processing effluent, Int. J. Environ. Res. Public Health 18 (2021) 12427, https://doi.org/10.3390/ijerph182312427.
[5] N.C. Kothiyal, V. Kumar, N. Kumar, Pandey S. Saruchi, S. Ansar, Reduction of carcinogenic PAHs from petrodiesel engine exhaust by blending of green diesel (a new development in renewable fuels) with different biodiesel fuels, Environ. Technol. Innov. 25 (2022), 102089, https://doi.org/10.1016/j.eti.2021.102089.
[6] Y. Yau, V. Rudolph, K. Ho, C.C. Lo, K. Wu, Evaluation of different demulsifiers for Marpol oil waste recovery, J. Water Process Eng. 17 (201) (2017) 40–49, https://doi.org/10.1016/j.jwpe.2017.02.013.
[7] A.D.M.d. Medeiros, C.J.G.d. Silva Junior, J.D.P.d. Amorim, I.J.B. Durval, A.F.d. S. Costa, L.A. Sarubbo, Oily wastewater treatment: methods, challenges, and trends, Processes 10 (2022) 743, https://doi.org/10.3390/pr10040743.
[8] S. Pandey, E. Makhado, S. Kim, M. Kang, Recent developments of polysaccharide based superabsorbent nanocomposite for organic dye contamination removal from wastewater-a review, Environ. Res. 217 (2023), 114909, https://doi.org/10.1016/j.envres.2022.114909.
[9] Y. Sun, C. Zhu, H. Zheng, W. Sun, Y. Xu, X. Xiao, Z. You, C. Liu, Characterization and coagulation behavior of polymeric aluminum ferric silicate for high-concentration oily wastewater treatment, Chem. Eng. Res. Des. 119 (2017) 23–32, https://doi.org/10.1016/j.cherd.2017.01.009.
[10] M.H.M. Noor, M.F.Z.M. Azli, N. Ngadi, I.M. Inuwa, L.A. Opotu, M. Mohamed, Optimization of sonication-assisted synthesis of magnetic Moringa oleifera as an efficient coagulant for palm oil wastewater treatment, Environ. Technol. Innov. 25 (2022), 102191, https://doi.org/10.1016/j.eti.2021.102191.
[11] H.M. Kalibbala, P.W. Olupot, O.M. Ambani, Synthesis and efficacy of cactus-banana peels composite as a natural coagulant for water treatment, Results Eng. 17 (2023), 100945, https://doi.org/10.1016/j.rineng.2023.100945.
[12] E. Lester-Card, G. Smith, G. Lloyd, C. Tizaoui, A green approach for the treatment of oily steelworks wastewater using natural coagulant of Moringa oleifera seed, Bioresour. Technol. Rep. 22 (2023), 101393, https://doi.org/10.1016/j.biteb.2023.101393.
[13] X. Wen, C. Du, G. Zeng, D. Huang, J. Zhang, L. Yin, S. Tan, L. Huang, H. Chen, G. Yu, X. Hu, C. Lai, P. Xu, J. Wan, A novel biosorbent prepared by immobilized bacillus licheniformis for lead removal from wastewater, Chemosphere 200 (2018) 173–179, https://doi.org/10.1016/j.chemosphere.2018.02.078.
[14] M. Huang, Z. Liu, A. Li, H. Yang, Dual functionality of a graft starch flocculant: flocculation and antibacterial performance, J. Environ. Manag. 196 (2017) 63–71, https://doi.org/10.1016/j.jenvman.2017.02.078.
[15] C. Zhao, J. Zhou, Y. Yan, L. Yang, G. Xing, H. Li, P. Wu, M. Wang, H. Zheng, Application of coagulation/flocculation in oily wastewater treatment: a review, Sci. Total Environ. 765 (2021), 142795, https://doi.org/10.1016/j.scitotenv.2020.142795.
[16] B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, Water Res. 41 (11) (2007) 2301–2324, https://doi.org/10.1016/j.watres.2007.03.012.
[17] J.A. Ippolito, K.A. Barbarick, H.A. Elliott, Drinking water treatment residuals: a review of recent uses, J. Environ. Qual. 40 (1) (2011) 1–12, https://doi.org/10.2134/jeq2010.0242.
[18] M. Rinaudo, Chitin and chitosan: properties and applications, Prog. Polym. Sci. 31 (7) (2006) 603–632, https://doi.org/10.1016/j.progpolymsci.2006.06.001.
[19] R. Yang, H.J. Li, M. Huang, H. Yang, A.M. Li, A review on chitosan-based flocculants and their applications in water treatment, Water Res. 95 (2016) 59–89, https://doi.org/10.1016/j.watres.2016.02.068.
[20] D.O. Krentz, C. Lohmann, S. Schwarz, S. Bratskaya, T. Liebert, J. Laube, T. Heinze, W.M. Kulicke, Properties and flocculation efficiency of highly cationized starch derivatives, Starch-Starke 58 (3–4) (2006) 161–169, https://doi.org/10.1002/star.200500431.
[21] S. Pal, T. Nasim, A. Patra, S. Ghosh, A.B. Panda, Microwave-assisted synthesis of polyacrylamide grafted dextrin (Dxt-g-PAM): development and application of a novel polymeric flocculant, Int. J. Biol. Macromol. 47 (2010) 623–631, https://doi.org/10.1016/j.ijbiomac.2010.08.009.
[22] G. Sen, R. Kumar, S. Ghosh, S. Pal, A novel polymeric flocculant based on polyacrylamide grafted carboxymethylstarch, Carbohydr. Polym. 77 (4) (2009) 822–831, https://doi.org/10.1016/j.carbpol.2009.03.007.
[23] Z. Yang, J.R. Degorce-Dumas, H. Yang, E. Guibal, A.M. Li, R.S. Cheng, Flocculation of Escherichia coli using a quaternary ammonium salt grafted carboxymethyl chitosan flocculant, Environ. Sci. Technol. 48 (12) (2014) 6867–6873, https://doi.org/10.1021/es500415v.
[24] R.C. Goy, D.D. Britto, O.B. Assis, A review of the antimicrobial activity of chitosan, Polímeros 19 (3) (2009) 241–247.
[25] E. Guibal, M. Van Vooren, B.A. Dempsey, J. Roussy, A review of the use of chitosan for the removal of particulate and dissolved contaminants, Sep. Sci. Technol. 41 (11) (2006) 2487–2514, https://doi.org/10.1080/01496390607428072487.
[26] F. Renault, B. Sancey, P.M. Badot, G. Crini, Chitosan for coagulation/flocculation processes e an eco-friendly approach, Eur. Polym. J. 45 (5) (2009) 1337–1348, https://doi.org/10.1016/j.eurpolymj.2008.12.027.
[27] J. Prachayawarakorn, P. Kansanthia, Characterization and properties of singly and dually modified hydrogen peroxide oxidized and glutaraldehyde crosslinked biodegradable starch films, Int. J. Biol. Macromol. 194 (2022) 331–337, https://doi.org/10.1016/j.ijbiomac.2021.11.150.
[28] C.Y. Teh, T.Y. Wua, J.C. Juan, Potential use of rice starch in coagulation-flocculation process of agro-industrial wastewater: treatment performance and flocs characterization, Ecol. Eng. 71 (2014) 509–519, https://doi.org/10.1016/j.ecoleng.2014.07. 005.
[29] Y. Wu, X. Jiang, J. Anne, J. Wen, S. Liu, H. Liu, H. Zheng, Low-pressure UV-initiated synthesis of cationic starch-based flocculant with high flocculation performance, Carbohydr. Polym. 273 (2021), 118379, https://doi.org/10.1016/j.carbpol.2021.118379.
[30] J. Xu, H. Zhang, X. Guo, H. Qian, The impact of germination on the characteristics of brown rice flour and starch, J. Sci. Food Agric. 2012 (92) (2012) 380–387.
[31] D. Hamidi, M.B. Fard, K. Yetilmezsoy, J. Alavi, H. Zarei, Application of Orchis mascula tuber starch as a natural coagulant for oily-saline wastewater treatment: modeling and optimization by multivariate adaptive regression splines method and response surface methodology, J. Environ. Chem. Eng. 9 (2021), 104745, https://doi.org/10.1016/j.jece.2020.104745.
[32] J. Ma, J. Shi, L. Ding, H. Zhang, S. Zhou, Q. Wang, X. Fu, L. Jiang, K. Fuc, Removal of emulsified oil from water using hydrophobic modified cationic polyacrylamide flocculants synthesized from low-pressure UV initiation, Sep. Purif. Technol. 197 (2018) 407–417, https://doi.org/10.1016/j.seppur.2018.01.036.
[33] Y. Chen, G. Tian, B. Zhai, H. Zhang, Y. Liang, H. Liang, Cationic starch-grafted-cationic polyacrylamide-based graphene oxide ternary composite flocculant for the enhanced flocculation of oil sludge suspension, Compos. Part B Eng. 177 (2019), 107416, https://doi.org/10.1016/j.compositesb.2019.107416.
[34] Kumar V. Saruchi, A.A. Ghfar, S. Pandey, Oil spill remediation by grafted natural polysaccharide gum tragacanth: its kinetics and isotherms studies, Biomass Convers. Biorefin. 13 (2023) 383–392, https://doi.org/10.1007/s13399-022-02665-0.
[35] X. Liu, Q. Guo, S. Ren, J. Guo, C. Wei, J. Chang, B. Shen, Synthesis of starch-based flocculant by multi-component grafting copolymerization and its application in oily wastewater treatment, J. Appl. Polym. Sci. 140 (2023) 1–14, https://doi.org/10.1002/app.53356.
[36] S. Mishra, A. Mukul, G. Sen, U. Jha, Microwave-assisted synthesis of polyacrylamide grafted starch (St-g-PAM) and its applicability as flocculant for water treatment, Int. J. Biol. Macromol. 48 (2014) 106–111, https://doi.org/10.1016/j.ijbiomac.2010.10.004.