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Usability of waste plastic pyrolysis liquid/oil as a flotation collector in wastewater treatment

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Pyrolysis is an important thermal waste disposal method that is more environmentally friendly than the combustion process, and almost all of its products can be converted into economic value. Specifically, the pyrolysis oils obtained are evaluated in different areas, such as the production of next-generation fuels and the recovery of valuable materials. Wastewater released during marble processing should not be discharged into the sewer without treatment, in accordance with national and international legislation, due to the high concentration of colloidal substances it contains. In the treatment of these wastewaters, conventional chemical precipitation processes and high amounts of synthetic chemicals are commonly used. Another method that can be employed for treating these wastewaters is the chemical substance-assisted flotation process, where efficiency depends on the use of oil-based chemicals. In this study, the treatment of marble processing wastewater was carried out for the first time using the flotation process, with pyrolysis oils obtained from mixed plastic waste pyrolysis as the collector material. According to the treatment experiments, the flotation collector that showed the highest suspended solid (SS) and turbidity removal efficiency was the pyrolysis oil obtained at a pyrolysis temperature of 700 °C. The flotation treatment findings were modeled using experimental design, and it was also revealed that collector dosage, mixing speed and air flow rate significantly affected the removal efficiencies.

Water impact

Chemically assisted flotation treatment of wastewater typically requires a large amount of synthetic chemicals. This study suggests that significant environmental and economic advantages can be achieved in wastewater treatment using pyrolysis oils as an alternative to these chemicals.

1. Introduction

Natural stones have been used for centuries in human settlements, structures and artistic designs, becoming a symbol of civilization. Today, with the expansion of their application areas (such as interior and exterior decoration, paving stones, and exterior cladding), the demand for natural stones has increased, making it one of the most attractive industries. In commercial terms, natural stones are rock types, such as marble, that can be extracted as blocks in economically suitable sizes, cut into desired dimensions as blocks and plates, and polished according to demand. It is estimated that the total amount of waste generated during the processing (cutting and polishing) of marble blocks and plates in Turkey is around 60–70% of the stone extracted from the quarry.[1] The amount of dust released during the processing of a 1 m^3 block (weighing approximately 3 tons) varies between 30–40% of the block's weight, depending on the thickness of the plate to be obtained from the block.[2–4] The marble processing industry is one of the sectors that consumes the most water. Therefore, it is important to purify and reuse water within the industry. Fine-sized dust wastes in marble plants are generated by block marble cutting, side cutting and head cutting machines, as well as by wiping and polishing processes.[3] The larger-sized dust particles (0.1–2 mm) settle in the channels by gravity as they flow toward the waste pool. The finer-sized particles (<0.1 mm) remain suspended in the water. These suspended fine-sized marble dusts can generally be removed in the sedimentation tank by adding flocculants, thereby producing clean water that is free of solid particles or has minimized suspended solids. This treated water can then be reused in marble processing.[3] The presence of fine-sized particles in the water reused in the marble plant can scratch the marble during the wiping and polishing stages and impair product quality. Therefore, the water to be reused in the marble plant should not contain suspended solids. In addition, flocculants used in these enterprises to precipitate colloidal substances in water are expensive chemicals.

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There are studies reported in the literature on the physicochemical treatment of natural stone and marble processing wastewater. Treatment methods such as coagulation and flocculation were mostly preferred.[5–8] In these studies, polyacrylamide-based anionic, cationic and nonionic flocculants and various coagulants were used.[5,7,9]

In a study aiming to remove suspended solids (SS) from marble processing wastewater by electrocoagulation process (EC) using aluminum and iron electrodes, the SS removal efficiency was found to be 99.8% in the EC process using parallel-serial monopolar iron electrodes.[6] As a result of flocculation studies with classical flocculants and UMA flocculants in the solid–liquid separation of travertine marble processing wastewater, it is known that UMA flocculants give better results than anionic flocculants.[8] In another study, the effect of pH and polymer charge density on the flocculation of natural stone wastewater was investigated. For the marble suspension used, the best flocculation performance was obtained with anionic polymers at 34% charge density, and for the travertine suspension, the anionic polymer was obtained at 28% charge density. At the same time, they achieved high sedimentation rate and high turbidity values at high pH.[10]

There are studies reported in the literature on the treatment of wastewater from natural stone–marble processing industries with the flotation process, but they are very limited. As it is known, the flotation method is a treatment method that allows the separation of particulate matter in the liquid medium from other substances by floating or settling in water and requires a high amount of air to be given to the system.[11,12] In this method, the hydrophilic and hydrophobic properties of the substances to be treated are important factors. In addition, the selection of chemical collectors used in the chemically supported flotation process is important. Anionic, cationic and oil-based collectors are mostly preferred in the chemical flotation method applied for wastewater treatment and enrichment of mineral ores. These can be synthetic in origin, depending on their production methods.[13] Some of the disadvantages of such collectors are that they are typically derived from petroleum derivatives and are expensive and non-renewable. The production and use of polar oil collectors can lead to various occupational hazards for humans and significant environmental risks.[14]

In the flotation of solid materials such as coal dust in liquid media, non-polar oils of hydrocarbon origin such as kerosene, diesel and fuel oil are generally used as collectors to increase the floatability of the solid material and to create stronger bubble–particle bonds. These oils cover the surface of the solid material in the form of a film and increase the adhesion force between the particle and the air bubble, thus ensuring stronger contacts. Thus, the flotation speed increases.[15,16] Since these types of oils consist of non-polar hydrocarbon chains, they cover the surfaces of solid particles and increase their natural hydrophobic properties, resulting in increased flotation success. These collectors can be commercial oils such as diesel oil and kerosene, as well as waste oils from various usage areas. In the studies reported in the literature, waste oils such as waste engine oil,[17,18] waste vegetable oil,[19] and waste cooking oil[20] have been used as collectors in the flotation process. In the flotation of fine coal, waste engine oil was used as a flotation collector and 62.51% clean coal yield and 73.77% recovery rate were obtained.[17] With the flotation process in which fine slag waste engine oil, formed from the gasification of coal, was used as a collector, 92.13% recovery efficiency was obtained.[18] Similarly, in solid material flotation, waste vegetable oil was used as a flotation collector under different temperature conditions and the coal with the highest combustion efficiency at 25 °C was recovered.[15] With waste cooking oil used for the separation of carbon ash from the fine slag formed by the coal gasification process by flotation, a product yield of 89.59–90.34% was obtained.[20] According to the results of the studies where waste oils were used as collectors, there are significant gains in terms of economy and environment by reusing waste oils instead of commercial collectors in the flotation process.

An important type of waste oil that has a heavy hydrocarbon content and is problematic to dispose of is the pyrolysis oil formed from the pyrolysis of plastic waste.[21] It may be possible to find a solution to a significant environmental problem by recovering these waste oils and evaluating them in different application areas. It has been reported by scientists that waste plastic pyrolysis oils can be evaluated in areas such as fuel and energy production and chemical substance recovery.[21–25] The use of these pyrolysis oils as flotation collectors can also be investigated.

Experimental design is a technique used to find and interpret the independent variable values affecting the uncontrollable variable by systematically changing the values of the controllable (independent) variables affecting the uncontrollable variable (dependent) in a process and for a purpose.[26] The large number of experiments can also pose significant problems, especially in processes with high part costs and experiments based on product destruction. Experimental design methods provide an easy, systematic and complete analysis opportunity compared to the classical method by reducing the number of experiments to be performed, ensuring that the experiments were carried out systematically and taking into account the interactions between the variables. The optimization of the parameters affecting the process performance can be achieved by using experimental strategies such as RSM.[27] The number of experiments to be performed and the process parameter limits to be used in this study will be determined by the experimental design method.

According to literature studies, collectors obtained from waste oils are generally used in the enrichment of coal and other mineral ores. The aim of this enrichment process is to collect mineral colloidal substances from the oil with the flotation process (recovery). In chemically supported flotation processes where waste oils are used as collectors, no study has been encountered on the removal of colloidal substances from wastewater. With such pretreatment processes, colloidal substances in the wastewater can be purified and pollution can be reduced. In this way, wastewater can be directly recovered after flotation according to the area of use or the pollution load of subsequent advanced treatment processes can be reduced. Marble processing wastewater can be purified with the flotation process due to its high colloidal mineral composition. Based on aforementioned statements, in this study, pyrolysis oils obtained from the pyrolysis of plastic wastes were used as collectors for the removal of turbidity and solid matter in the flotation of marble processing industry wastewater. This study, with this idea and method, was carried out for the first time in the scientific field and applied for wastewater treatment. In this way, pyrolysis oils will be converted into materials of economic value by finding a new evaluation area and marble processing industry wastewater will be treated with a collector material produced from waste instead of synthetic collectors.

2. Materials and methods

2.1. Characterization of andesite marble processing industry wastewater (AMW)

During the cutting of andesite marble blocks, a high amount of process water is used to suppress dust and prevent the cutting devices from heating. As a result of the use of this water, wastewater with a high concentration of colloidal matter is formed. Within the scope of this study, andesite marble processing plant wastewater (AMW) to be treated with the flotation process was supplied from an andesite marble processing plant in Konya (Türkiye) province. The characteristics of this raw wastewater are given in Table 1.

2.2. Production and characterization of pyrolysis oil collectors

In the study, plastic wastes were obtained from the waste collection center and shredded to 8 mm size. Equally mixed HDPE-, LDPE-, PP-, PET- and PS-type plastic wastes were pyrolyzed on a laboratory scale, using a fixed bed pyrolysis system at a heating rate of 5 °C $\min^{-1}$ at 300 °C, 500 °C and 700 °C final temperatures (Fig. 1). Pyrolysis oils collected in the liquid holding vessels of the system were used directly as flotation collectors (POC) and were named C300, C500 and C700 depending on the pyrolysis temperature.

Table 1 Andesite marble processing plant wastewater (AMW) and particle size distribution

Parameter	Value
pH	7.7
Solid (g L^{-1})	39
Turbidity (NTU)	13 980
Conductivity (μS cm^{-1})	472
Temperature (°C)	16.5
Particle size (μm)	Amount (%)
−150 + 106	3.27
−106 + 75	3.11
−75 + 53	2.95
−53 + 38	7.05
−38 + 20	20.63
−20 + 0	62.99

A SHIMADZU brand GC-MS/FID was used to analyze the organic components contained in the pyrolysis liquids. Pyrolysis oils were extracted with *n*-hexane before being fed to the column. A column with the dimensions of 30 m × 0.25 mm × 0.25 μm was used. He was used as the carrier gas in the system. The flow pressure in the column was 90 kPa, the total flow was set as 8.3 mL $\min^{-1}$ and the column flow was set as 0.48 mL $\min^{-1}$. The extracted samples were first injected into the GC column as 1 μL at 250 °C. After the GC column, the sample was analyzed using FID and MS detectors with a parallel signal output. Fourier transform infrared (FTIR) spectroscopy was performed to determine the functional groups of the pyrolysis oils. Analyses were performed by a KBr method using a Thermo Scientific Nicolet iS5 FT-IR brand device. The organic structure of pyrolysis oil samples was investigated in detail by Nuclear Magnetic Resonance (NMR). A Bruker Avance brand 300 MHz (7 Tesla) solid and liquid NMR spectrometer was used.

2.3. Flotation experiments

For the flotation treatment of AMW, a laboratory-scale DENVER flotation apparatus with air and mixing support was used. The apparatus consists of mixing, aeration and control sections. The experimental system shown in Fig. 2 was used.

In the preliminary experiments, POC was used for doses of 0.5 mL L^{-1}, 1.5 mL L^{-1} and 2.5 mL L^{-1}. For each experiment, 30 ppm L^{-1} pine oil was used as a frother. The mixing speed was selected as 1200 rpm, 1300 rpm and 1400 rpm, and the flotation time was selected as 2 min and 4 min. First, POC was dosed to 1 L of raw wastewater and the system was mixed at the selected mixing speeds for 2 min. Afterwards, pine oil was added to the system and air was supplied at flow rates of 10 L $\min^{-1}$, 20 L $\min^{-1}$ and 30 L $\min^{-1}$ and mixing and aeration were performed for the selected flotation period. At the end of this period, the flotation sludge (concentrated upper layer-froth phase) was collected within 1 min. At the end of the experiment, samples were taken from the treated water and analyses were performed.

2.4. Treated wastewater analysis

After the treatment of AMW, turbidity and suspended solids (SS) were measured. Turbidity values were measured using a TB1 Portable VELP Scientifica brand turbidimeter. The suspended solid concentration was measured according to standard methods.[28]

2.5. Experimental design and statistical analysis

Within the scope of the study, marble processing industry wastewater obtained from pyrolysis oils was purified by

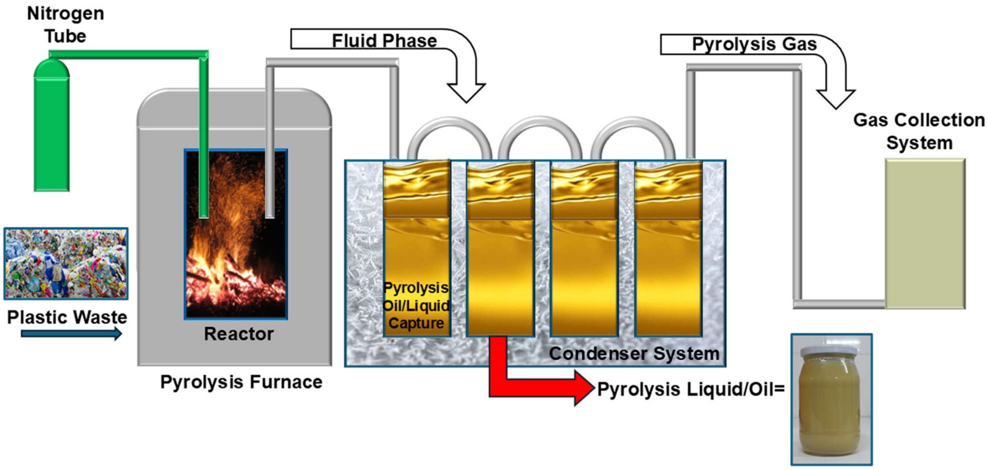

Fig. 1 Pyrolysis liquid/oil production in a pyrolysis system.

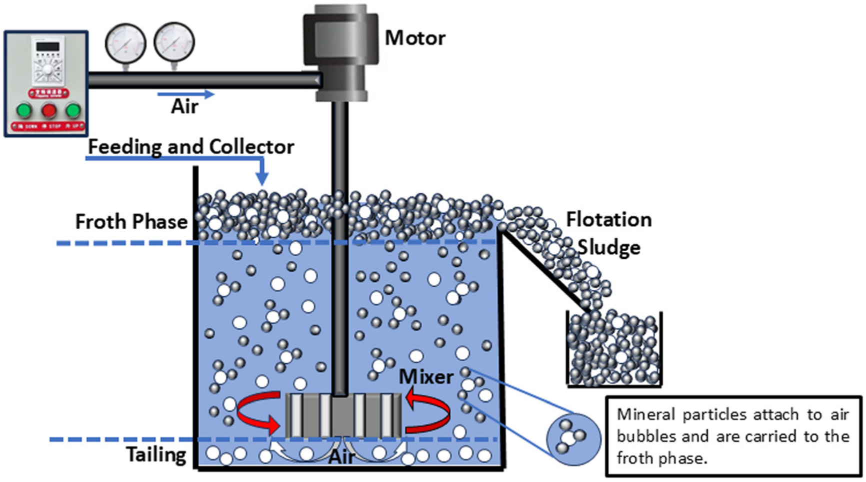

Fig. 2 Flotation experiment.

subjecting it to a flotation process with flotation collectors. Central composite design (CCD), one of the experimental design methods, is a very useful method to interpret the relationship between the selected experimental variables and the response values obtained against these variables. This study experiments were conducted in accordance with central composite design (CCD), one of the design types of response surface method (RSM), and the data were fitted to a second-order model and optimization was performed. Modeling was designed using the Design Expert (7.0) program. First, preliminary flotation experiments were conducted, and the factors and levels that were effective in turbidity and SS removal and to be used in the experimental design were determined. Then, an experimental plan consisting of 30 experiments was created for the pyrolysis oil collector that provided the highest treatment efficiency in the preliminary test results. According to the measured turbidity and SS values, the removal efficiencies were calculated and the statistical analysis of the 2-response model was performed. In addition to 24 points in CCD, there are a total of 30 experiments, 6 repetitions at the center point and 8 axis points.

3. Results and discussion

3.1. Characterization of pyrolysis oil collectors (POCs)

3.1.1. Physical properties. The physical properties of POCs are given in Table 2. In general, as the pyrolysis temperature increases, the density of the collector oils also increases. It can be due to the increase in the HC content of the pyrolysis oils obtained at high pyrolysis temperatures. Accordingly, the kinematic viscosity of the pyrolysis oils also increased as the temperature increased.

Table 2 Viscosity and density values of POCs

Parameter	C300	C500	C700
Viscosity (mm^2 s^{-1})	0.917	0.943	0.955
Density (g cm^{-3})	57.2	56.2	59.3

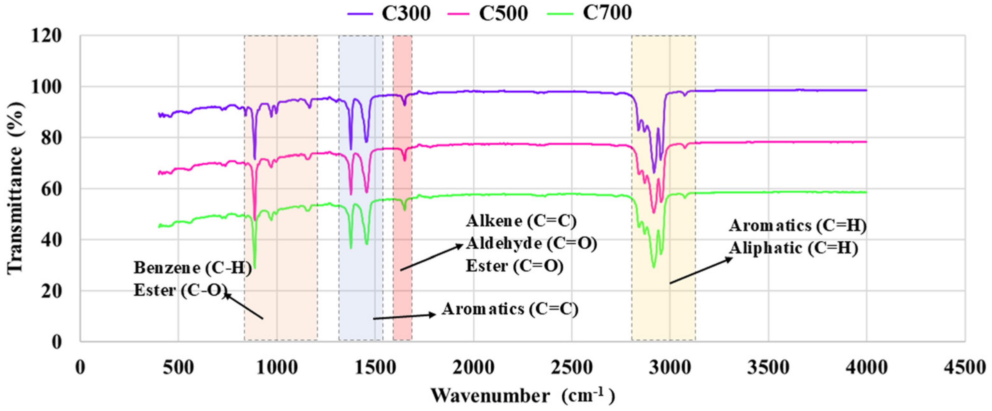

Fig. 3 FTIR spectra of POCs.

3.1.2. Chemical properties. The FTIR spectra giving the functional groups contained in the POC are displayed in Fig. 3. Small ester C═O bands were detected at 1775–1780 cm^{-1} for all collectors. The waveband at 2719–2723 cm^{-1} represents aromatic alkyl groups (C═H stretching); this can be considered as the liquid obtained from the degradation of PE containing

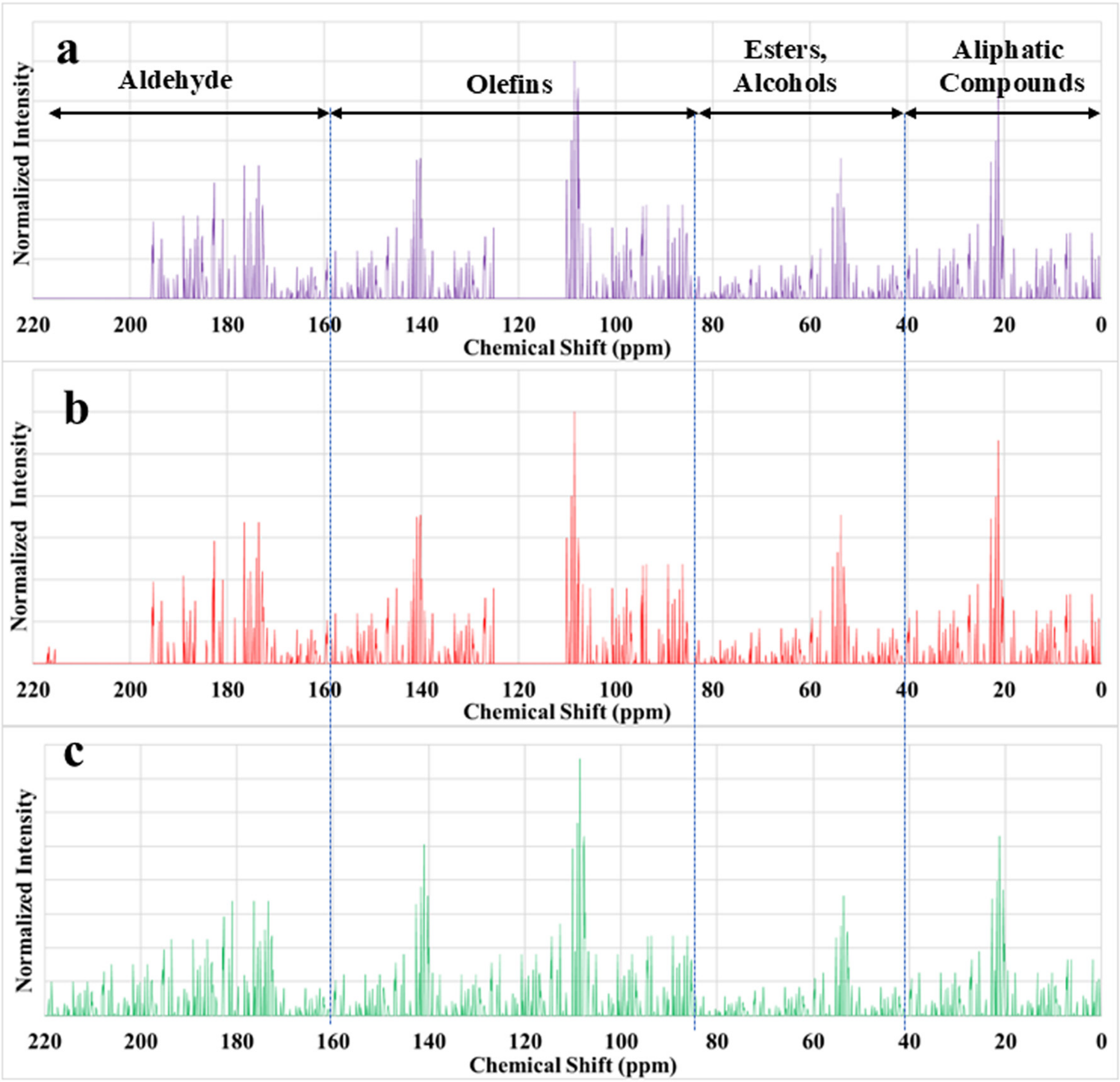

Fig. 4 NMR graphics of POCs: (a) C300, (b) C500, and (c) C700.

carbon and hydrogen having the molecular formula $[-C_3H_5-]_n$.[29] Absorption peaks corresponding to aliphatic C═H stretching vibrations were observed around 2950–2840 cm^{-1}.[30] The band at 1775–1780 cm^{-1} is the ester C═O group; the band at 1699 cm^{-1} is the aldehyde C═O group. The aromatic ring –C═C– bond or C═C band represents the alkene seen around 1648 cm^{-1}. The band in the $-CH_2$ group at 1454–1456 cm^{-1} is assigned to the aromatic C═C stretching vibration, and the C–O stretching of the ester group was seen at 1272–1277 cm^{-1}. Aromatic C–H in-plane bending was detected for *m*-disubstituted benzene at 965–968 cm^{-1}. The results show that the liquid products obtained at 300–700 °C pyrolysis temperature were predominantly paraffinic and olefinic in structure.

According to the NMR results displayed in Fig. 4, aldehyde, olefin, ester, alcohol and other aromatic groups were encountered similar to the FTIR results. The amount of aldehyde compounds observed in the range of 220–160 cm^{-1} is higher for the C700 collector than the other two collectors. The amount of olefin group and aliphatic group compounds is less for the C700 collector. As the pyrolysis temperature increased, the amount of olefins and aliphatic compounds decreased due to depolymerization and formed aldehyde group compounds.

According to the GC-MS results, the functional groups and the amounts of dominantly detected chemical compounds contained in collectors produced from pyrolysis oils are given in Fig. 5. It was observed that as the pyrolysis temperature increased, depolymerization reactions increased and polymers were broken down into long-chain hydrocarbons. As the temperature increased, alkane, alkene, alcohol and aldehyde group organic compounds in the liquid product became more dominant (Fig. 5a). As a result of the qualitative analysis, the increase in the amounts of octane, octene, decane, nonane and acetate derivative compounds as the temperature increased supports this situation (Fig. 5b).

3.2. Preliminary flotation experiments

Preliminary flotation experiments were carried out to determine the factors and levels affecting the suspended solids (SS) and turbidity removal efficiencies. The factors affecting the SS and turbidity removal efficiencies were taken into consideration as the mixing speed (1200 rpm and 1400 rpm), dose (0.5 mL L^{-1} and 2.5 mL L^{-1}), flotation time (2 min and 4 min) and air flow rate (10 L min^{-1} and 30 L min^{-1}). The SS removal efficiencies obtained according to these factors are given in Fig. 6, and the turbidity removal efficiencies are given in Table 3.

In all collector types, as the mixing speed and air flow rate increased, the removal efficiency of SS and turbidity also increased (Fig. 6 and Table 3). It can be concluded that as the amount of air supplied to the system increases, the microbubbles in the system also increase and play a positive role in the adhesion of mineral particles to carrier bubbles. These microbubbles significantly affect the bonding process between mineral particles and carrier bubbles through the bridging effect.[31–33] Moreover, surface microbubbles can improve the probability of fine particles colliding on carrier bubbles through the pre-formation of agglomerates.[32,34] As the mixing speed and air flow rate increased in the flotation process, the air intake into the system also increased. Thus, the possibility of mineral particles and bubbles meeting, sticking and being carried into the foam zone (concentrate layer) increases.[35,36]

For the same mixing speed, flotation time and air flow conditions, as the collector dose increased, the SS and turbidity removal efficiency increased for all pyrolysis temperatures. SS removal efficiencies varied between 9% and 85%, 17% and 88% and 25% and 92% for C300, C500 and C700, respectively. Froth flotation is the most effective technology for separating mineral particles from wastewater based on the difference in the physicochemical properties of minerals for most mineral particles. Collectors are usually used to improve the hydrophobicity of minerals, thereby

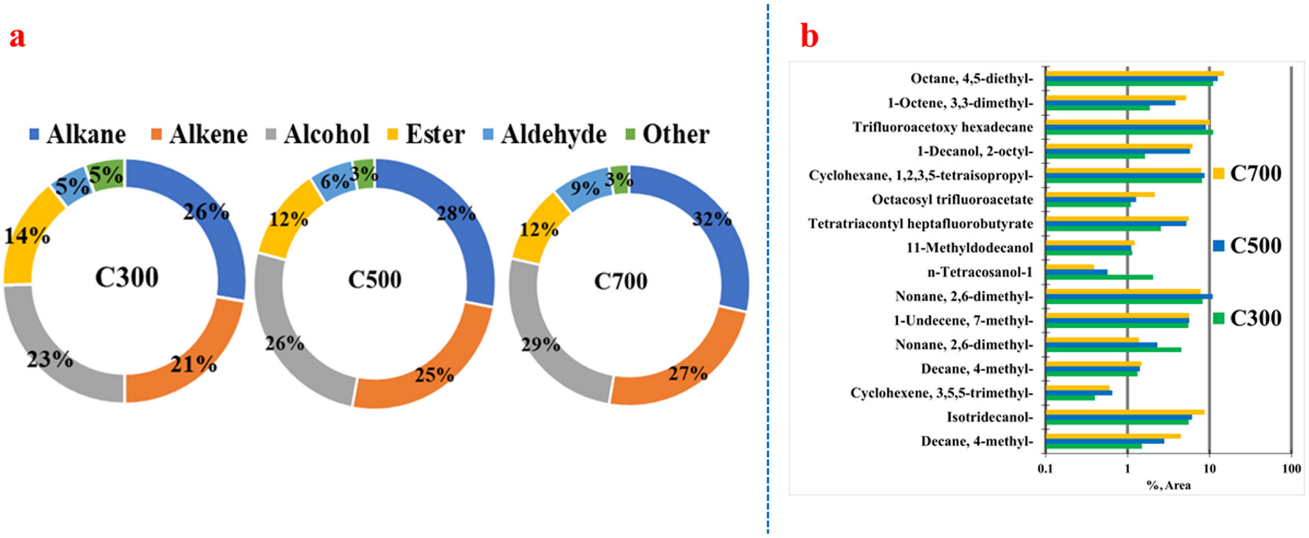

Fig. 5 Chemical group (a) and compound amounts (b) determined by GC-MS analysis for POCs.

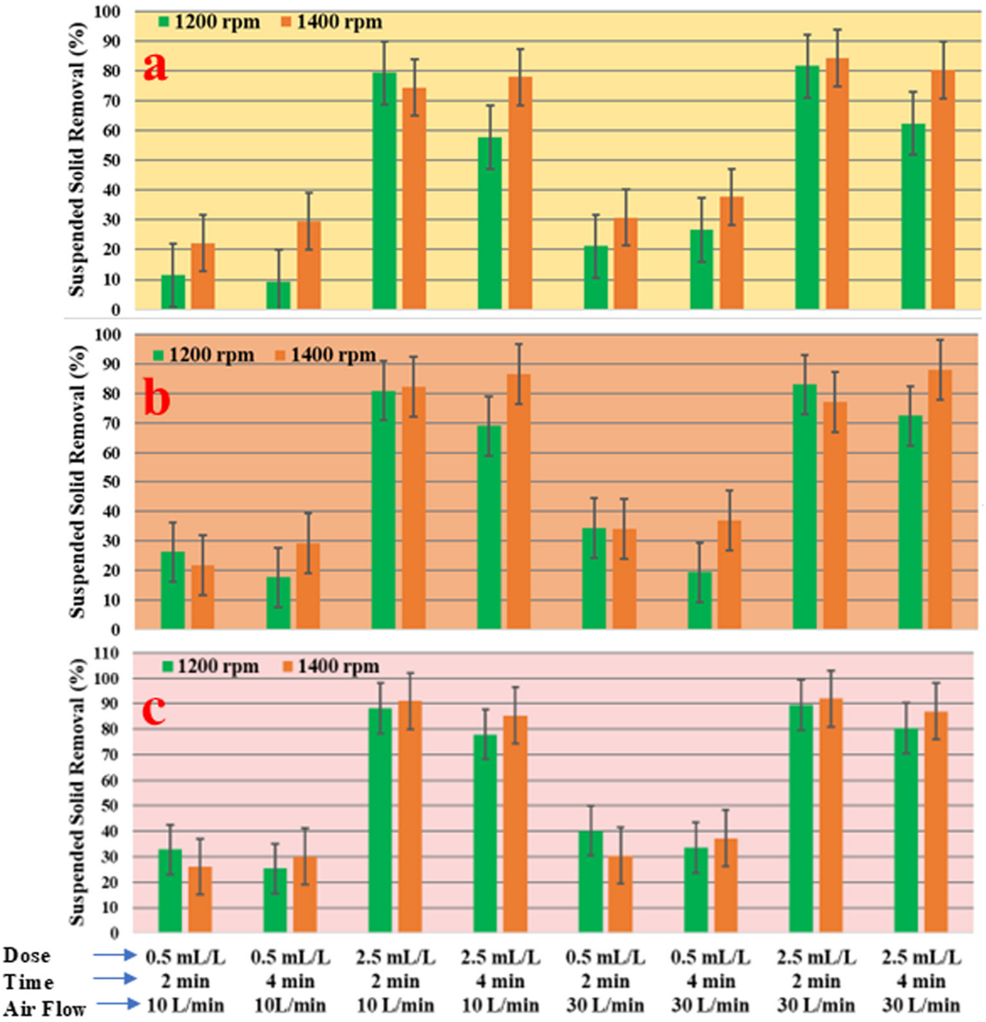

Fig. 6 Variation in suspended solid (SS) removal as a function of mixing speed, dosage, flotation time, and air flow rate: (a) C300, (b) C500, and (c) C700.

widening the gap between mineral surfaces to improve the flotation efficiency. The adsorption of collectors can reduce the repulsive hydration forces by increasing the hydrophobicity of particle surfaces, which can simultaneously

Table 3 Turbidity removal efficiencies as a function of mixing speed, dosage, flotation time and air flow rate (%)

Dose→	0.5 mL L^{-1}	2.5 mL L^{-1}	0.5 mL L^{-1}	2.5 mL L^{-1}	0.5 mL L^{-1}	2.5 mL L^{-1}	0.5 mL L^{-1}	2.5 mL L^{-1}
Time→	2 min	2 min	4 min	4 min	2 min	2 min	4 min	4 min
Mixing speed→	1200 rpm	1200 rpm	1200 rpm	1200 rpm	1400 rpm	1400 rpm	1400 rpm	1400 rpm
Air flow→	10 L min^{-1}	10 L min^{-1}	10 L min^{-1}	10 L min^{-1}	10 L min^{-1}	10 L min^{-1}	10 L min^{-1}	10 L min^{-1}
C300	2.06	71.37	11.52	76.23	14.37	71.03	21	82.26
C500	13.34	92.03	13.13	73.35	5.53	80.51	23.87	87.89
C700	19.41	92.59	25.74	83.33	27.45	87.60	23.48	89.95
Dose→	0.5 mL L^{-1}	2.5 mL L^{-1}	0.5 mL L^{-1}	2.5 mL L^{-1}	0.5 mL L^{-1}	2.5 mL L^{-1}	0.5 mL L^{-1}	2.5 mL L^{-1}
Time→	2 min	2 min	4 min	4 min	2 min	2 min	4 min	4 min
Mixing speed→	1200 rpm	1200 rpm	1200 rpm	1200 rpm	1400 rpm	1400 rpm	1400 rpm	1400 rpm
Air flow→	30 L min^{-1}	30 L min^{-1}	30 L min^{-1}	30 L min^{-1}	30 L min^{-1}	30 L min^{-1}	30 L min^{-1}	30 L min^{-1}
C300	10.29	73.78	18.96	78.23	21.57	73.46	27.65	83.76
C500	20.63	92.70	20.44	75.59	13.48	82.15	30.27	88.91
C700	26.19	93.21	31.99	84.73	33.55	88.64	29.92	90.8

increase the interparticle hydrophobic attraction. Oil-based collectors usually increase such hydrophobic clusters and increase the apparent particle size of fine minerals, significantly improving the collision and binding probability compared to individual fine particles.[37,38] It was observed that as the pyrolysis temperature at which the collectors were obtained increased, the removal efficiencies also increased (Fig. 6 and Table 3). As the temperature increased, the long-chain organic compounds in the pyrolysis oil gradually increased. When this pyrolysis product enters the water environment, it is adsorbed at the solid–liquid interface. This improves the hydrophobicity of the mineral particles, reduces the energy of the system and increases the flotation ability of the collector.[39] According to the GC-MS results, the increase in the amount of long-chain components such as decane-4-methyl, 11-methyldodecanol, 1-octene 3,3-dimethyl, and isotridecanol also supports this situation (Fig. 5b). The dominance of alkane, alkene, alcohol, and aldehyde groups as the pyrolysis temperature increases (Fig. 5a) also shows that collectors obtained at high pyrolysis temperatures are more effective on the SS and turbidity treatment efficiency (Fig. 6 and Table 3).

As the pyrolysis temperature increased due to depolymerization reactions, the diversity of aldehyde, olefin, ester, alcohol, and aliphatic group organic compounds in the pyrolysis liquid product also increased (Fig. 3). Accordingly, the hydrophobicity of mineral particles also increased. As the flotation time increased for each collector type, the contact between mineral particles and air bubbles increased and the adhesion of these particles to the concentrated layer increased. The highest removal efficiencies were achieved for all three collector types at 1400 rpm stirring speed, 2.5 mL L^{-1} collector dose, and 30 mL min^{-1} air flow rate. The most successful collector was C700 pyrolysis oil, which achieved 91.99% SS and 90.8% turbidity removal efficiencies (Fig. 6 and Table 3).

3.3. Central composite design (CCD)

For 2-level k factors in CCD, $2k$ axial or star points were required. In addition, center points were also included in the design. In this case, 2 × 4 = 8 axial points were needed for the 24 factorial experiments used in the study. In the second-order model to be created, main effects and first-order interactions were obtained from 24 experiments. In this study, in addition to the 24 points in the central composite design (CDC), there were 6 repetitions at the center point and 8 axial points, a total of 30 experiments. The obtained response values were fitted to a quadratic model as in the equation (eqn (1)).

$$Y_i = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n} \beta_{ij} x_i x_j \qquad (1)$$

This quadratic model takes into account the linear effects of n variables, their quadratic effects and their interactions. In this model, the β_i parameter showed the main effects of the factors. The β_{ii} parameter also indicated the shape of the curve (square effect). Finally, β_{ij} describes the interaction effect between the variables i and j. The regression equation was created by estimating the coefficients in the second-degree model with the least-squares method and regression analysis. With the help of the equation created, the estimation results for the responses were obtained, and the accuracy of the estimations and the adequacy of the model in estimation were checked.

Table 4 Factors and levels used in the experimental design

Factor	Low level	High level	Medium level
Dose (mL L^{-1})	0.5	2.5	1.5
Stirrer speed (rpm)	1200	1400	1300
Flotation time (min)	2	4	3
Air flow (L min^{-1})	10	30	20

Before starting the experimental design, the factors and levels effective in turbidity and SS removal were determined, as given in Table 4, as a result of the findings obtained from the preliminary experiments. Then, first, a full experimental plan consisting of a total of 30 experiments with 2 levels, 4 factors and 6 center points was created and the experiments were conducted in accordance with this plan. The

Table 5 Experimental plan and response values

	Factor 1	Factor 2	Factor 3	Factor 4	Response 1	Response 2
	A: dose	B: stirrer speed	C: flotation time	D: air flow	Suspended solid removal	Turbidity removal
Run	mL L^{-1}	rpm	min	L min^{-1}	%	%
1	2.5	1200	4	10	68.98	83.33
2	1.5	1300	3	20	58.42	59.13
3	0.5	1200	2	30	34.35	26.19
4	0.5	1400	4	10	29.53	23.48
5	0.5	1400	4	30	37.28	29.92
6	1.5	1300	1	20	62.05	61.13
7	2.5	1200	2	10	80.97	92.59
8	2.5	1400	2	10	84.38	93.52
9	3.5	1300	3	20	76.12	88.67
10	1.5	1300	3	20	57.15	58.89
11	0.5	1400	2	30	40.44	33.55
12	0.5	1200	4	10	25.29	25.74
13	2.5	1400	4	10	77.89	89.95
14	2.5	1200	2	30	83.06	93.21
15	2.5	1400	4	30	80.32	90.8
16	0.5	1200	2	10	26.24	19.41
17	1.5	1100	3	20	58.65	57.44
18	1.5	1300	3	20	57.01	58.1
19	0.5	1200	4	30	33.5	31.99
20	1.5	1300	3	20	56	57.39
21	1.5	1300	5	20	52.12	54.01
22	1.5	1300	3	20	58.9	59.37
23	0.5	1400	2	10	28.84	27.45
24	2.5	1400	2	30	87	94.15
25	1.5	1300	3	40	62.33	64.9
26	1.5	1500	3	20	66.07	61.13
27	1.5	1300	3	20	58.23	59
28	2.5	1200	4	30	79.5	91.39

Table 6 Model selection for SS and turbidity removal response variables

Response 1: suspended solid removal

Source	Sequential p-Value	Lack of fit p-Value	Adjusted R^2	Predicted R^2	
Linear	3.17195×10^{-12}	0.0004	0.9051	0.8676	
2FI	0.9642	0.0002	0.8809	0.8096	
Quadratic	***8.71043×10^{-05}***	***0.0049***	***0.9722***	***0.8531***	***Suggested***
Cubic	0.0019	0.3304	0.9968		Aliased

Response 2: turbidity removal

Source	Sequential p-Value	Lack of fit p-Value	Adjusted R^2	Predicted R^2	
Linear	***9.79575×10^{-14}***	***3.3245×10^{-05}***	***0.9300***	***0.9015***	***Suggested***
2FI	0.9713	1.57358×10^{-05}	0.9116	0.8454	
Quadratic	***0.0041***	***0.0001***	***0.9616***	***0.7849***	***Suggested***
Cubic	0.0001	0.0431	0.9982		Aliased

experimental design was carried out for the C700 collector, which was found to be the most successful in the preliminary flotation experiments.

The experimental plan and response values obtained using Design Expert for the C700 collector are given in Table 5.

For both answers, the quadratic model with high R^2 and low standard deviation values was selected as suggested by the program (Table 6).

The ANOVA calculations were carried out according to the square model and the results are given in Tables 7 and 8.

The F value of the model applied for SS removal was 68.40 and Prob > F value was < 0.05, indicating that the model is significant. When the p values for the model terms were examined, it was observed that all factors were less than 0.05. In the event that there are many insignificant terms in the model, the program recommends the model to be reduced. However, according to Table 7, the factors A, B, C, D, AC, AD, A^2, and B^2 are critical. Here, the main effects of A, B, C, and D, the interaction effect of the terms AC, AD, A, C and D, and the terms A^2 and B^2 showed the square effects of the terms A and B. As a result of the insufficiency of fit test performed for the model, the insufficiency of fit was found to be significant. According to Table 8, the F value of the model applied for blur removal was 49.32 and Prob > F value is < 0.05, indicating that the model is significant. The factors A, B, C, D, AC, AD, BC, A^2, B^2, C^2, and D^2 are critical. The lack of fit was considered significant (Table 8).

The R^2 values of the model are given in Table 9. The fact that the R^2 values are close to 1 for both response variables shows the accuracy of the applied model.

The regression equation for the SS removal response is shown in eqn (2).

Table 7 ANOVA results for SS removal

Source	Sum of squares	df	Mean square	F-Value	p-Value	
Model	10 138.18	14	724.16	68.40	7.90772×10^{-10}	Significant
A-Dose	9409.48	1	9409.48	888.80	2.35388×10^{-13}	
B-Stirrer speed	98.54	1	98.54	9.31	0.0093	
C-Flotation time	116.38	1	116.38	10.99	0.0056	
D-Air flow	126.83	1	126.83	11.98	0.0042	
AB	0.0086	1	0.0086	0.0008	0.9778	
AC	37.36	1	37.36	3.53	0.0829	
AD	20.27	1	20.27	1.91	0.1897	
BC	0.1828	1	0.1828	0.0173	0.8975	
BD	1.28	1	1.28	0.1211	0.7334	
CD	1.26	1	1.26	0.1190	0.7356	
A^2	532.20	1	532.20	50.27	8.16946×10^{-06}	
B^2	83.18	1	83.18	7.86	0.0149	
C^2	5.63	1	5.63	0.5317	0.4788	
D^2	15.08	1	15.08	1.42	0.2540	
Residual	137.63	13	10.59			
Lack of fit	131.76	8	16.47	14.03	0.0049	Significant
Pure error	5.87	5	1.17			
Cor total	10 275.81	27				

Table 8 ANOVA results for turbidity removal

Source	Sum of squares	df	Mean square	*F*-Value	*p*-Value	
Model	17 157.22	14	1225.52	49.32	6.23802×10^{-09}	Significant
A-Dose	16 269.17	1	16 269.17	654.76	1.66311×10^{-12}	
B-Stirrer speed	28.93	1	28.93	1.16	0.3002	
C-Flotation time	31.99	1	31.99	1.29	0.2770	
D-Air flow	27.40	1	27.40	1.10	0.3128	
AB	0.6281	1	0.6281	0.0253	0.8761	
AC	31.73	1	31.73	1.28	0.2789	
AD	14.84	1	14.84	0.5973	0.4534	
BC	15.15	1	15.15	0.6098	0.4489	
BD	3.70	1	3.70	0.1487	0.7060	
CD	3.49	1	3.49	0.1404	0.7140	
A^2	550.51	1	550.51	22.16	0.0004	
B^2	32.90	1	32.90	1.32	0.2706	
C^2	12.55	1	12.55	0.5049	0.4899	
D^2	121.54	1	121.54	4.89	0.0.455	
Residual	323.02	13	24.85			
Lack of fit	320.20	8	40.02	70.99	0.0001	Significant
Pure error	2.82	5	0.5638			
Cor total	17 480.24	27				

$$\begin{aligned}\text{SS Removal} = {} & 281.74 + (47.99 \times \text{Dose}) - (0.44 \times \text{Stirrer Speed}) \\ & - (4.64 \times \text{Flotation Time}) + (0.32 \times \text{Air Flow}) \\ & - (1.52 \times \text{Dose} \times \text{Flotation Time}) - (0.112 \\ & \times \text{Dose} \times \text{Air Flow}) - (5.96 \times \text{Dose}^2) + (0.000178 \\ & \times \text{Stirrer Speed}^2)\end{aligned} \tag{2}$$

All effects of the interaction effects of the factors included in the model on the SS removal response variable were examined with the help of graphics (Fig. 7). Among these, it is known that *A*–*C* and *A*–*D* interactions are significant according to the *p* values. As the collector dose and mixing speed increased, the SS removal also increased (Fig. 7a). However, according to the ANOVA results, this situation was not significant. When the *A*–*C* interaction was examined, the SS removal efficiency increased as the dose increased and the flotation time decreased (Fig. 7b). This situation is significant according to ANOVA. Similarly, according to the *A*–*D* interactions, the SS removal efficiency increased as the air flow rate and dose increased (Fig. 7c). According to *B*–*C*, *B*–*D* and *C*–*D* interactions, it was observed that the effect of these parameters on SS removal at the same time was not significant and these interactions were at a weak level (Fig. 7d–f).

The regression equation for the turbidity removal response is shown in eqn (3).

Table 9 R^2 values of SS removal and turbidity removal responses

	SS removal	Turbidity removal
Std. dev.	3.25	4.98
Mean	57.88	60.21
C.V.%	5.62	8.28
R^2	0.9866	0.9815
Adjusted R^2	0.9722	0.9616
Predicted R^2	0.8531	0.7849
Adeq. precision	25.6410	20.5231

$$\begin{aligned}\text{Turbidity Removal} = {} & 131.5 + (57.91 \times \text{Dose}) - (0.23 \times \text{Stirrer} \\ & \text{Speed}) + (8.52 \times \text{Flotation Time}) - (0.38 \\ & \times \text{Air Flow}) - (1.4 \times \text{Dose} \times \text{Flotation} \\ & \text{Time}) - (0.096 \times \text{Dose} \times \text{Air Flow}) \\ & - (0.009 \times \text{Stirrer Speed} \times \text{Flotation} \\ & \text{Time}) - (6.06 \times \text{Dose}^2) + (0.0001 \\ & \times \text{Stirrer Speed}^2) + (0.69 \times \text{Flotation} \\ & \text{Time}^2) + (0.028 \times \text{Air Flow}^2)\end{aligned} \tag{3}$$

All the interaction effects of the factors included in the model on the turbidity removal response variable were examined with the help of graphics (Fig. 8). According to the *p* values, *A*–*C*, *A*–*D* and *B*–*C* interactions were significant. Turbidity removal also increased as the collector dose and mixing speed increased (Fig. 8a). However, according to the ANOVA results, this situation was not significant. When the *A*–*C* interaction was examined, the turbidity removal efficiency increased as the dose increased and the flotation time decreased (Fig. 8b). According to the *A*–*D* interaction, the turbidity removal efficiency increased as the air flow rate and dose increased (Fig. 8c). According to the *B*–*C* interaction, while the turbidity removal decreased as the flotation time increased, this efficiency value increased as the mixing speed increased. According to ANOVA, this situation is also significant. According to the *B*–*D* and *C*–*D* interactions, it was observed that the effect of these parameters on turbidity removal at the same time was not significant and these interactions were at a weak level (Fig. 8e and f).

4. Conclusions

Marble processing industry wastewater is one of the wastewaters suitable for treatment by physicochemical methods such as chemical substance-supported flotation process due to its colloidal composition. The supporting chemicals for this process are generally oil-based. Pyrolysis

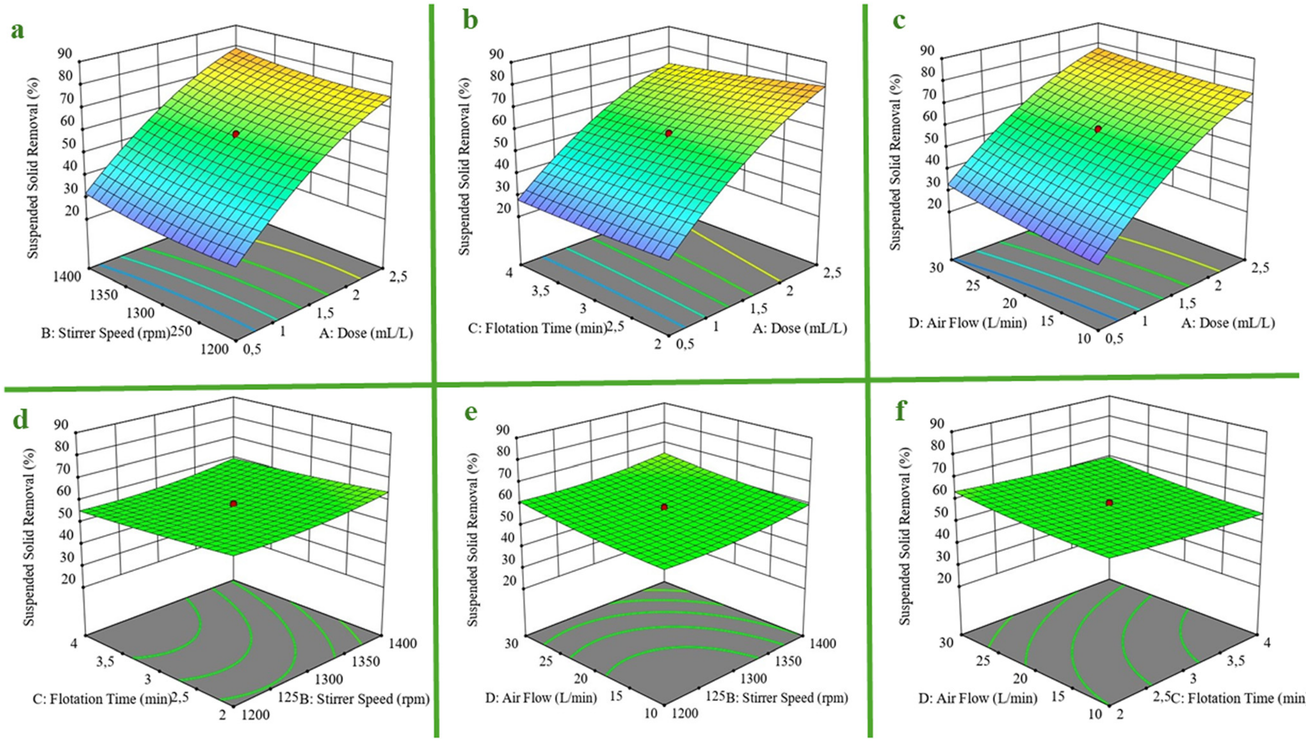

Fig. 7 Effect of factor interactions on SS removal response: (a) *A–B* interaction, (b) *A–C* interaction, (c) *A–D* interaction, (d) *B–C* interaction, (e) *B–D* interaction, and (f) *C–D* interaction.

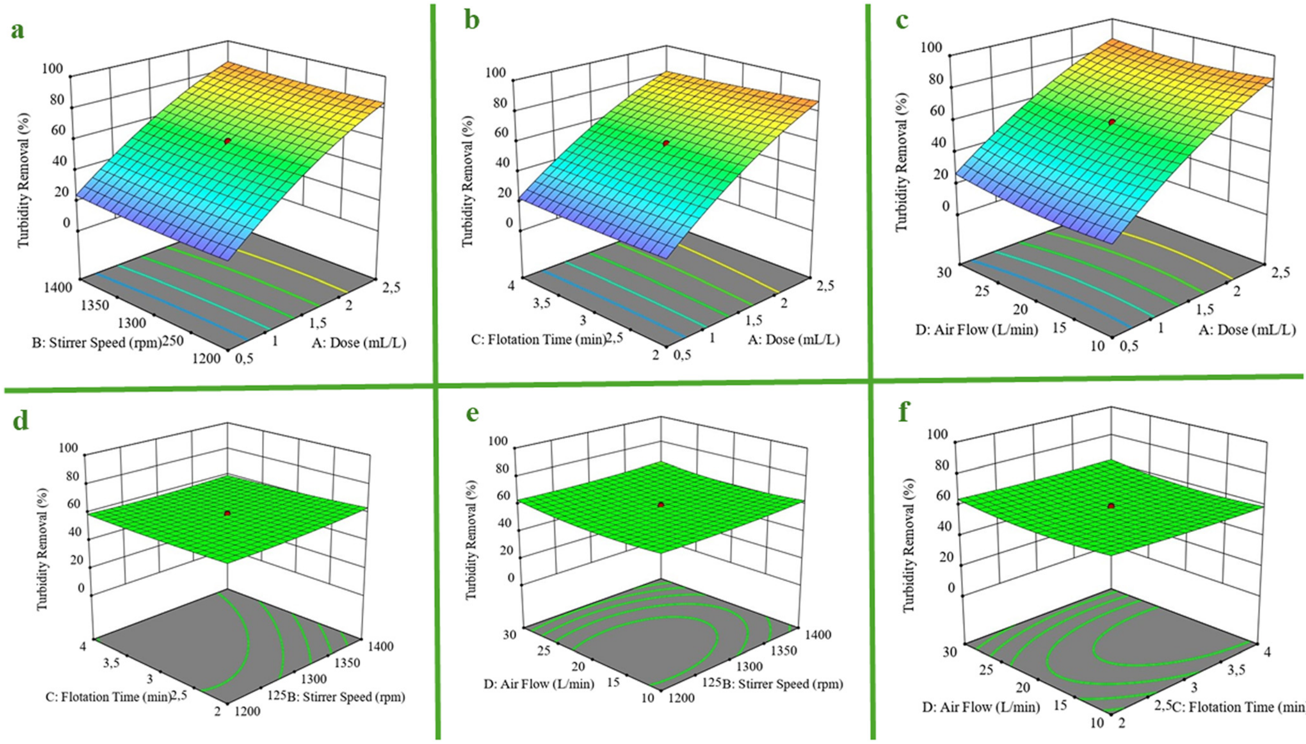

Fig. 8 Effect of factor interactions on turbidity removal response: (a) *A–B* interaction, (b) *A–C* interaction, (c) *A–D* interaction, (d) *B–C* interaction, (e) *B–D* interaction, and (f) *C–D* interaction.

oils are pyrolysis products that are suitable for evaluation in different areas and can create an economic value due to the oil fractions they contain. In this study, pyrolysis oils obtained from the pyrolysis of a mix of HDPE-, LDPE-, PP-, PET- and PS-type plastic wastes at different temperatures were used as collectors in the flotation of andesite marble processing industry wastewater (AMW) for turbidity and solid matter removal. According to the findings of this study,

- As the pyrolysis temperature increases, the density of collector oils also increases. It can be said that this situation is due to the increase in the HC content of pyrolysis oils obtained at high pyrolysis temperatures. Accordingly, the kinematic viscosity of pyrolysis oils also increased as the temperature increased. In this case, it shows that if these oils are used as collectors in the flotation process, their distribution in water will be quite easy. The liquid products obtained at a pyrolysis temperature of 300–700 °C are predominantly paraffinic and olefinic. According to NMR results, aldehyde, olefin, ester, alcohol and other aromatic groups were encountered. As the pyrolysis temperature increased, the amount of olefins and aliphatic compounds decreased due to depolymerization, and aldehyde group compounds were formed.
- For the same mixing speed and air flow conditions, as the collector dose increased, the AKM and turbidity removal efficiencies increased for all pyrolysis temperatures. AKM removal efficiencies increased up to 85%, 88%, and 92% for C300, C500, and C700, respectively. It was observed that as the pyrolysis temperature at which the collectors were obtained increased, the removal efficiencies also increased. The dominance of alkane, alkene, alcohol, and aldehyde groups as the pyrolysis temperature increased showed that collectors obtained at high pyrolysis temperatures were more effective on the treatment efficiency. The highest removal efficiencies were obtained for C300, C500, and C700 types under the conditions of 1400 rpm mixing speed, 2.5 mL L^{-1} collector dose, and 30 mL min^{-1} air flow rate. The most successful collector was C700 pyrolysis oil, which obtained 91.99% AKM and 90.8% turbidity removal efficiencies.
- In the experimental design study, it was determined that the collector dosage, mixing speed and air flow values were effective on SS and turbidity removal efficiencies for this study.
- According to the study findings, in the flotation process where pyrolysis oils are used, colloidal material removal from AMW has been achieved with high efficiency. With such pretreatment processes, colloidal materials in wastewater can be purified and pollution can be reduced. In this way, wastewater can be directly recycled after flotation depending on the area of use or the load of subsequent advanced treatment processes can be reduced. In addition, the other pollutant parameter values of the marble processing wastewater can be measured. Particulate matter of this wastewater largely treated by the aforementioned method can be reused as recycled water in the marble processing industry. With this study, the pyrolysis oils obtained as a result of the disposal of plastic wastes by pyrolysis have found a new area of evaluation in wastewater treatment for the first time, which can turn these oils into materials of economic value and minimize environmental damage.

Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

Author contributions

Merve Kalem: methodology, investigation, formal analysis, visualization, data curation, supervision, project administration, writing – original draft.

Conflicts of interest

There are no conflicts to declare.

References

1 D. Kocadağ, Marble ındustry and evoluation of marble wastes in the context of sustainable mining, in *Environmental Approaches in Marble Mining (978-605-4839-14-8)*, ed. T. Güler and E. Polat, Muğla Metropolitan Municipality, Muğla, 2018, pp. 51–92.
2 S. Kulaksız, *Natural Stone (Marble) Mining and Operation Technology*, Ankara, 2005, pp. 10–12.
3 B. Ersoy, Description of flocculants used in marble processing plant waste water treatment, in *IV. Türkiye, Marble Symposium (MERSEM'2003) Proceedings Book*, TMMOB Chamber of Mining Engineers, Afyon, 2003, pp. 449–462.
4 A. O. Yılmaz, İ. Çavuşoğlu, İ. Alp, R. Kaya and M. Vıcıl, Problems related to natural stone potential and operation of the eastern black sea region, in *IV. Türkiye Marble Symposium (MERSEM'2003) Proceedings Book*, Afyon, 2003, pp. 435–448.
5 A. M. Alptekin, Purification of natural stone wastewaters with flocculation/coagulation method, *Master Science*, Afyon Kocatepe University, Institute of Natural and Applied Sciences, 2006.
6 M. Solak, Treatment of marble wastewater with electrocoagulation process, *Master Science*, Süleyman Demirel University, Institute of Natural and Applied Sciences, 1983.
7 K. Oğul, Coagulation and flocculation of fine marble tailings, *Master Science*, Eskişehir Osmangazi University, Fen Bilimleri Enstitüsü, 2005.
8 E. Sabah and C. Aciksoz, Flocculation performance of fine particles in travertine slime suspension, *Physicochem. Probl. Miner. Process.*, 2012, **48**, 555–566.
9 T. Taşdemir and A. Taşdemir, Optimization of floc-flotation process in the removal of suspended particles from wastewater in a Jameson cell using central composite design, *J. Water Process Eng.*, 2023, **52**, 103552.
10 B. Ersoy, Description of flocculants used in marble processing plant waste water treatment, in *IV. Türkiye, Marble Symposium*, 2005, pp. 449–462.
11 B. Bayraktaroğlu, Flotation performance analysis of n1-phenylehydrazine-1,2-bis (carbothiamide) derivatives in the

seperation of chalcopyrite, *Master Science*, Kastamonu University, Graduate School of Natural and Applied Sciences, 2019.

12 J. J. Da Rosa and J. Rubio, The FF (flocculation-flotation) process, *Miner. Eng.*, 2005, **18**, 701–707.

13 M. Y. Ethem, Basic information on reagents, *Scientific Mining Journal*, 1974, **4**, 20–34.

14 Q. Yi, W. Li, X. Zhang, J. Feng, J. Zhang and J. Wu, Tech-economic evaluation of waste cooking oil to bio-flotation agent technology in the coal flotation industry, *J. Cleaner Prod.*, 2015, **95**, 131–141.

15 H. Hacıfazlıoğlu, Y. Eker and A. V. Korkmaz, Clean fuel production from coal washery plant wastes with soybean oil, *Academic Platform Journal of Engineering and Science*, 2019, **7**(2), 200–204.

16 E. C. Çilek, *Flotation of Mineral*, Suleyman Demirel University, Isparta, 2006.

17 H. Duan, H. Chang, L. Gao, K. Gai, Y. Yu, X. Lyu and X. Zhu, Preparation of renewable collector from waste engine oil for clean flotation of fine coal with different oxidation degree, *Fuel*, 2023, **335**, 127003.

18 G. Fan, M. Zhang, W. Peng, G. Zhou, L. Deng, L. Chang, Y. Cao and P. Li, Clean products from coal gasification waste by flotation using waste engine oil as collector: Synergetic cleaner disposal of wastes, *J. Cleaner Prod.*, 2021, **286**, 124943.

19 H. Hacifazlioglu, Effect of temperature on coal flotation with waste vegetable oil as collector, *Int. J. Coal Prep. Util.*, 2018, **38**, 163–169.

20 M. Li, P. Li, J. Wu, D. Teng, G. Zhou, Y. Cao and G. Fan, Directly application of waste cooking oil on the flotation of coal gasification fine slag, *Fuel*, 2023, **331**, 125666.

21 M. Sogancioglu Kalem, The using of distillation fractions of pyrolytic oil obtained from waste plastic pyrolysis as different fuel types. TUBITAK Project Report, 2020.

22 B. Samal, K. R. Vanapalli, B. K. Dubey, J. Bhattacharya, S. Chandra and I. Medha, Influence of process parameters on thermal characteristics of char from co-pyrolysis of eucalyptus biomass and polystyrene: Its prospects as a solid fuel, *Energy*, 2021, **232**, 121050.

23 T. Maqsood, J. Dai, Y. Zhang, M. Guang and B. Li, Pyrolysis of plastic species: A review of resources and products, *J. Anal. Appl. Pyrolysis*, 2021, **159**, 105295.

24 A. W. Gin, H. Hassan, M. A. Ahmad, B. H. Hameed and A. T. Mohd Din, Recent progress on catalytic co-pyrolysis of plastic waste and lignocellulosic biomass to liquid fuel: The influence of technical and reaction kinetic parameters, *Arabian J. Chem.*, 2021, **14**, 103035.

25 S. Kartik, H. K. Balsora, M. Sharma, A. Saptoro, R. K. Jain, J. B. Joshi and A. Sharma, Valorization of plastic wastes for production of fuels and value-added chemicals through pyrolysis – A review, *Therm. Sci. Eng. Prog.*, 2022, **32**, 101316.

26 C. S. D. Rodrigues, L. M. Madeira and R. A. R. Boaventura, Optimization of the azo dye Procion Red H-EXL degradation by Fenton's reagent using experimental design, *J. Hazard. Mater.*, 2009, **164**, 987–994.

27 U. Akay, Optimization of color and cod removal from textile industry waste water using response surface methodology, *Master Science*, Eskişehir Osmangazi University, Institute of Natural and Applied Sciences, 2013.

28 SM 2540 D, *SM 2540 D - Standard Methods for the Examination of Water and Wastewater*, 20th edn, 1998.

29 I. G. Hakeem, F. Aberuagba and U. Musa, Catalytic pyrolysis of waste polypropylene using Ahoko kaolin from Nigeria, *Appl. Petrochem. Res.*, 2018, **8**, 203–210.

30 I. Ahmad, M. Ismail Khan, M. Ishaq, H. Khan, K. Gul and W. Ahmad, Catalytic efficiency of some novel nanostructured heterogeneous solid catalysts in pyrolysis of HDPE, *Polym. Degrad. Stab.*, 2013, **98**, 2512–2519.

31 M. Eriksson, M. Tuominen, M. Järn, P. M. Claesson, V. Wallqvist, H. J. Butt, D. Vollmer, M. Kappl, J. Schoelkopf, P. A. C. Gane, H. Teisala and A. Swerin, Direct observation of gas meniscus formation on a superhydrophobic surface, *ACS Nano*, 2019, **13**, 2246–2252.

32 Z. Zhang, L. Ren and Y. Zhang, Role of nanobubbles in the flotation of fine rutile particles, *Miner. Eng.*, 2021, **172**, 107140.

33 M. A. Hampton and A. V. Nguyen, Nanobubbles and the nanobubble bridging capillary force, *Adv. Colloid Interface Sci.*, 2010, **154**, 30–55.

34 P. Knüpfer, L. Ditscherlein and U. A. Peuker, Nanobubble enhanced agglomeration of hydrophobic powders, *Colloids Surf., A*, 2017, **530**, 117–123.

35 R.-H. Yoon, The role of hydrodynamic and surface forces in bubble-particle interaction, *Int. J. Miner. Process.*, 2000, **58**, 129–143.

36 N. Arbiter, Hydrodynamics of Flotation Cells, in *AIME Transactions*, 1969, pp. 134–148.

37 Z. Shen and Q. Zhang, Hydrophobic agglomeration behavior of rhodochrosite fines Co-induced by oleic acid and shearing, *Sep. Purif. Technol.*, 2022, **282**, 120115.

38 G. Sahasrabudhe, G. DeIuliis and K. P. Galvin, Hydrophobization of minerals by sorbitan mono oleate (Span® 80): Selectivity of a novel agglomeration process, *Colloids Surf., A*, 2021, **630**, 127460.

39 L. Shen, F. Min, L. Liu, J. Zhu, C. Xue, C. Cai, W. Zhou and C. Wang, Application of gaseous pyrolysis products of the waste cooking oil as coal flotation collector, *Fuel*, 2019, **239**, 446–451.