Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.749190

51 (2013) 3353–3360
April

Taylor & Francis
Taylor & Francis Group

Performance enhancement of dissolved air flotation column in removing low concentrations of heavy fuel oil by adding powdered activated carbon

Hossein Hosseinzadeh[a], Jalal Shayegan[a,*], Morteza Jalali[b]

[a]*Chemical and Petroleum Engineering Department, Sharif University of Technology, Tehran, Iran*
Tel. +98 21 66165420; Fax: +98 21 66022751; email: shayegan@sharif.edu
[b]*Energy & Environment Research Center, Niroo Research Institute, Tehran, Iran*

Received 18 December 2011; Accepted 9 October 2012

ABSTRACT

In this study, the effect of adding walnut shell-based powdered activated carbon (WS) to a bench-scale dissolved air flotation (DAF) column on oil removal was investigated. All experiments were conducted using synthetically prepared wastewater containing low but stable concentrations of heavy fuel oil. After comparing the effect of different WS doses from 0 (blank) to 40 mg/L at the saturator pressure of 5 bar and 10 min flotation time, 20 mg/L WS was chosen as the optimal concentration. In order to find the best flotation time for efficient use of WS capacity, experiments were repeated with and without 20 mg/L WS at longer flotation times. According to the obtained results, by adding WS, the removal efficiencies of oil and grease (O&G) and total petroleum hydrocarbons (TPH) after 60 min flotation time and without adding any coagulant, increased from 57.6 and 63.4% to 78.1 and 86.8%, respectively. By analyzing the samples taken at the flotation times of 10, 30, and 60 min, it was found that the most adsorbed TPH or nonpolar extractable hydrocarbons during the 60 min flotation time were removed during the first 10 min. Also, the TPH/O&G ratio was decreased, by increasing the flotation time.

Keywords: Dissolved air flotation; Heavy fuel oil; Adsorption; Activated carbon; Walnut shell

1. Introduction

Some of the thermal power plants use heavy fuel oil as an alternative for natural gas. In these power plants, in order to reduce fuel viscosity for handling and proper atomization, the fuel oil heats up to 320–370 K, along the path from the fuel storage tank to the boiler burner [1]. The heating process takes place by heat exchange with returned steam from the turbine, which can lead to fuel leakage into the condensate. This contamination is in addition to the contamination that would result from leaking seals on steam driven equipment, such as pumps and turbine. After removing the free oil from the condensate, the remaining oil and grease (O&G) concentration will usually decrease to less than the allowable environmental discharge limits (10–15 mg/L [2]). But these values are still much greater than the maximum allowable O&G concentration for use in high pressure boilers (0.2 mg/L), according to ASME standard. Reusing this contaminated condensate as boiler feed water can lead to coking of hydrocarbons and deposition of a hard scale on boiler tube walls. Consequently, reduction of heat transfer caused by scales will lead to higher fuel costs and rupturing of the tubes at excessively high metal

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*Corresponding author.

temperatures. Due to the high cost of producing deionized water by ion exchange and reverse osmosis, the reuse of the condensate after oil removal is required.

The most widely used oily wastewater treatment processes consist of a series of physical and chemical steps, namely, free oil removal, chemical destabilization of oil emulsions, flotation, and filtration [3]. Oil in water can be divided into four categories: free oil, mechanically emulsified oil, chemically emulsified oil, and dissolved oil [4]. A gravity separation process such as American Petroleum Institute separator is effective for the removal of free oil, but not for removing smaller oil droplets and emulsions [2,5]. The flotation process is another commonly used method due to its high oil removal efficiency and its low capital and operational costs [6]. Dissolved air flotation (DAF), dispersed or induced air flotation (IAF), and electroflotation (EF) are the main bubble generation techniques. Among the above mentioned flotation techniques, IAF and EF are less frequently used for oil removal [7]. DAF is a process in which microbubbles (30–100 μm) are formed when air-saturated water at high pressure, is released to atmospheric pressure in the flotation cell. Increasing particle buoyancy, caused by adhering to the formed microbubbles, allows them to rise to the surface [8,9]. Separation of emulsified oils with a small mean droplet size and also chemically stabilized oil emulsions using only DAF process would be difficult [10]. Therefore, in order to enhance removal efficiencies and to meet required effluent standards, adding one or more processes such as chemical destabilization, electrocoagulation, and ultrafiltration is necessary [11]. These processes have little or no effect on the removal of soluble oils. Adsorption process using activated carbon is one of the most effective techniques for the removal of soluble hydrocarbons [12]. Due to the high capital and operating costs of using granular activated carbon columns, the combination of adsorption process with other treatment processes by adding powdered activated carbon (PAC), can be considered as a cheaper alternative [13]. Hami et al. investigated the effects of adding 50, 100, and 150 mg/L PAC on the performance of a pilot DAF unit in the removal of biological oxygen demand (BOD) and chemical oxygen demand (COD), in which PAC, Alum, and polyelectrolyte were fed into the rapid-mixing tank. The results indicated that the BOD and COD removal efficiencies can be considerably improved in the presence of PAC [14].

Water solubilities of heavy fuel oils are low and can vary from refinery to refinery, depending on their composition. Since these low solubilities are greater than the maximum allowable O&G concentration for use in high pressure boilers, soluble oil removal is required. On the other hand, since the measured O&G concentration in the contaminated condensate, after removing the free oil is still much greater than the water solubilities of heavy fuel oils, using only granular activated carbon columns is not effective enough to meet the boiler feed water limits. Considering the low solubility of heavy fuel oils in water, a large part of the oil content in water is in the form of emulsified oil. Therefore, the use of a modified DAF unit by adding PAC can be considered as a replacement for using two sequential treatment processes (granular activated carbon columns following a DAF unit), individually.

The main aim of this study was to investigate the effect of a modified bench-scale DAF column by adding walnut shell-based powdered activated carbon (WS) on oil removal from synthetically prepared wastewater, which contains about 13 mg/L O&G. This concentration is approximately equal to the reported effluent oil concentrations, which were obtained following DAF [15]. For these low concentrations, using membrane processes such as ultrafiltration seems to be more efficient compared to DAF. But in this study, due to the problems related to clogging and fouling of the membrane, the effect of a combined PAC adsorption and DAF process on the removal of water soluble and emulsified oil was investigated. In order to examine the effect of the adsorption process at longer flotation times, the bench-scale DAF column was designed as a batch process, in which all treated effluent after air saturation returns into the flotation column through the sparger. This design could lead to break up of flocs generated using the coagulation and flocculation process. Therefore, in the present work, the effect of PAC without adding any coagulant on the DAF performance was studied.

2. Materials and methods

2.1. Materials

Heavy fuel oil, which was used in the preparation of the synthetic oily wastewater, was supplied from the Besat power plant in the south of Tehran. Walnut

Table 1
Characteristics of the walnut shell-based activated carbon [16]

Characteristics	Walnut shell
Iodine number (DIN 53582)	737 mg/g
BET surface area	780 m^2/g
Pore volume	0.426 cm^3/g
Bulk density	0.45 g/cm^3

shell-based activated carbon was prepared by Zabihi et al. [16]. Its characteristics are summarized in Table 1. Before using the activated carbon in these experiments, it was powdered, sieved (with sizes between 170 and 325 mesh, which is equivalent to 44–88 μm) and washed by distilled water and then was completely dried in an oven at 110℃.

2.2. Synthetic wastewater preparation

In order to compare the effect of each parameter accurately, large amounts of the stock oil–water emulsion with low and uniform concentrations are required. A 60-L plastic barrel, which was equipped with a ball valve, a 2000 W heater, and a centrifugal pump (connected to the ball valve) in the bottom, was used for preparing stock oil–water emulsion. For wastewater preparation, approximately 50 L of distilled water and 1 L of heavy fuel oil (much more than the theoretically required oil), without adding any emulsifier, were poured into the barrel in which heavy fuel oil had formed a thin layer on the surface of the water. After reaching a temperature of about 70℃, the centrifugal pump was turned on and the water from the bottom of the barrel was recirculated up to the surface as a high pressure jet for 30 min. This mixing method was more convenient than using a mixer to produce synthetic oily wastewater, due to the high viscosity and stickiness of the fuel oil.

2.3. Apparatus

The bench-scale batch DAF column consists of a cylindrical flotation column with two diameters, in which a glass column with a 90 cm height and 8 cm inner diameter (ID) was placed on the top of a plexiglass column with a 10 cm height and 15 cm ID. Initially, effluent water from the bottom of the column is transferred into a stainless steel saturator vessel with an 11-L capacity and 20 cm ID by a diaphragm dosing pump. The air-saturated water in the unpacked saturator vessel is then recirculated into the atmospheric column through a needle-flow-control valve. In this system, the sparger is located in the center and is 10 cm higher than the bottom of the atmospheric column. The schematic diagram of the system is presented in Fig. 1. In the experiments with 60 min flotation time, in addition to sampling at the beginning and end of each experimental run, sampling during the runs is also necessary. The bigger diameter of the bottom part of the atmospheric column reduces imbalances between input and output flows to and from the column, especially those caused by the large volume of sample required for analysis (see Section 2.5).

In all experiments, the water level in the column was kept constant at 50 cm above the sparger, which, in this case, the total amount of water in the column is about 4 L. Due to the milky appearance of the water caused by the slowly rising clouds of small air bubbles, the phrase “white water zone” can be used

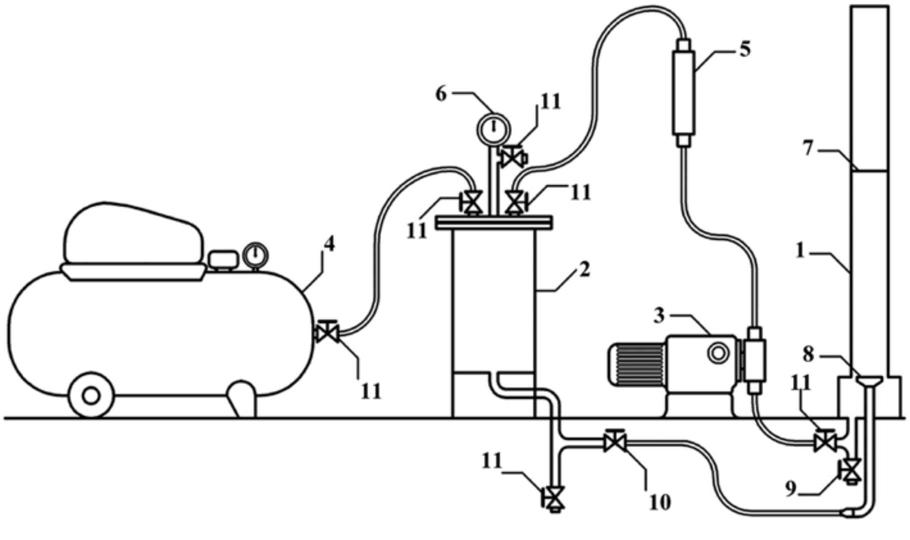

Fig. 1. Schematic diagram of the bench-scale DAF column.
(1) Flotation column; (2) stainless steel unpacked saturator vessel; (3) diaphragm dosing pump; (4) air compressor; (5) rotameter; (6) pressure gauge; (7) water level during the experiments; (8) sparger; (9) sampling port (ball valve); (10) needle flow control valve; (11) ball valves.

Table 2
The main design parameters of the system

Design parameter	Unit	Value
The dosing pump flow rate (at $p = 5$ bar)	L/h	24 ± 1
The mean hydraulic retention time (MHRT)	min	10
MHRT (in the white water zone)	min	6.25

for 0.5 m of the column with 8 cm ID and capacity of 2.5 L, which is, in fact, a useful space for the flotation process in this zone [17]. The main design parameters of the DAF column are presented in Table 2.

2.4. Experimental procedure

After filling the flotation column with the synthetically prepared wastewater, 500 mL of the wastewater was taken from the sampling port, and then its volume was again increased to 6 L. The WS were added to the flotation column as slurry by adding distilled water. A removable mixer with a long shaft equipped with four radial-flow impellers was used to mix the WS inside the column for 10 min at a speed of 33 rpm. Immediately after the mixing, the dosing pump was turned on and 2 L of the wastewater in the atmospheric column was transferred to the saturator vessel, which had already reached the desired pressure. While the pump was still working, by opening the flow-control valve, the water level in the column was kept constant at 50 cm above the sparger. After each sampling, by adjusting the flow-control valve, the water level was slowly returned to the previous position. As shown in Fig. 1, the sampling port is located in the path of continuous flow of the treated water between the atmospheric column and the diaphragm dosing pump; however, a small amount of stagnant water remains in the sampling port. Therefore, before all sampling, about 50 mL of the stagnant water was discarded.

2.5. Analysis method

Hydrocarbon concentrations were determined using The TOG/TPH Analyzer InfraCal Wilks Enterprise, Model CVH-50 with a 50 mm cylindrical cell, which is designed for use with EPA Methods 413.2 and 418.1. In order to detect CH bond, the infrared absorption is measured by a dual detector at 3.4 μm with a reference at 2.5 μm. The measurement repeatability of the instrument is ±1 digit. Thus, in order to obtain more accurate measurements, especially in low concentrations, the volume ratio of 16:1 (sample:solvent) was used in the extraction procedure. Consequently, a large sample volume (500 mL) is needed. Prior to the extraction procedure, all sieved PACs (170–325 mesh) must be separated from the samples. For this purpose, before transferring all samples (even influent samples and blanks) into 500 mL volumetric flasks, they were passed through No. 400 mesh (37 μm). The images of microemulsions were captured using the Olympus BH2 microscope (Olympus Optical Company Ltd, Tokyo, Japan) equipped with a digital camera at 1000× magnification.

3. Results and discussion

3.1. Wastewater characteristics

In order to investigate the stability of the synthetically prepared oil–water emulsions by the method mentioned in Section 2.2, O&G concentration at 3–162 h after the preparation and in different intervals was measured. It is seen from Fig. 2 that after about 18 h, O&G concentration has remained relatively stable over long-time intervals (24 h). Although no emulsifier was used for wastewater preparation, heavy oils contain comparatively large amounts of natural emulsifiers such as resins, waxes, and especially, asphaltenes, which can contribute to the formation of stable emulsions [13,18]. As mentioned before, after separation of unstable oils from the contaminated condensate, the O&G concentration decreases to about 15 mg/L. Therefore, after 18 h or maybe less, the prepared wastewater and contaminated condensate would be relatively similar in terms of concentration. After about 42 h (in order to ensure uniform concentration throughout the barrel), the required volume of the prepared wastewater was slowly drained from the bottom of the barrel into another clean container, and then was used in flotation experiments at ambient temperatures (26–30 ℃) and pH 7.3 ± 0.2.

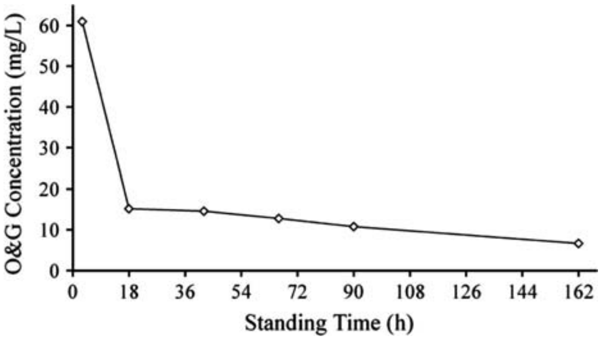

Fig. 2. Effect of standing time on O&G concentration.

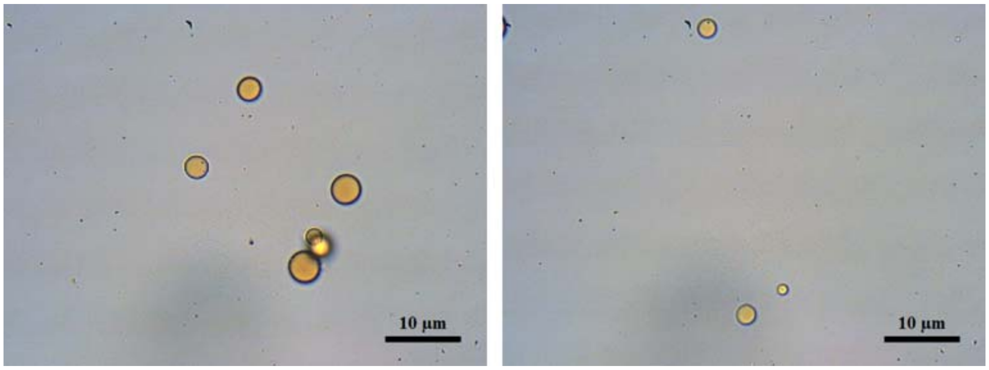

Fig. 3. Selective images of the microemulsions.

Fig. 3 shows selective images of the microemulsions with different size and number distribution in one droplet of a sample that was taken from the prepared wastewater (at 42 h). As seen in Fig. 3, all emulsions are less than 10 μm in diameter.

3.2. Effect of pressure

In DAF process with increasing pressure, the dissolved air content increases and microbubbles form in smaller sizes and larger quantities. The rising velocity of the smaller bubbles is less than the larger ones, which leads to a longer residence time in the flotation cell and consequently, more opportunity for collisions with oil droplets. In addition to the air saturator operating pressure, the recycle ratio is also effective on the amount of introduced air to the flotation cell [6,9]. Since in the DAF process a significant part of the energy costs are associated with the air saturation of the water, finding the optimal pressure should be considered. In the absence of surfactants, the minimum required saturation pressure for providing sufficient energy to overcome the air–water surface tension and to form bubbles by the cavity phenomenon, is about 3 atm. But, by reducing the surface tension with surfactants, the DAF process can be possible at a saturation pressure of 2 atm [10,19]. The flotation column used in the present work was designed as a batch process, in which total clarified effluent was being recycled and pressurized. Therefore, the saturator operating pressure was the only parameter to change the amount of air that can be introduced to the flotation column. The effect of different saturator pressures on O&G removal in the absence of WS was investigated and the results are illustrated in Fig. 4.

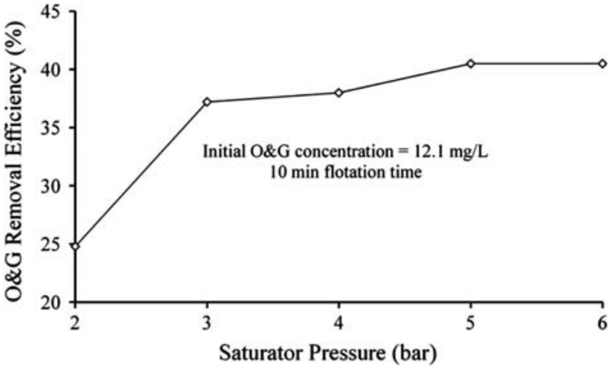

Fig. 4. Effect of different saturator pressures on O&G removal.

As shown in Fig. 4, at 10 min flotation time, with increasing the saturator pressure from 2 to 6 bar, O&G removal efficiency increased from 24.8 to 40.5%. In these experiments, the initial O&G concentrations were identical and equal to 12.1 mg/L. The removal efficiency at a pressure of 2 bar is significantly less than the removal efficiencies at the higher pressures. This can be attributed to insufficient energy to overcome the air–water surface tension in order to release an adequate number of bubbles. According to these results, although increasing the pressure from 3 to 5 bar had very little effect on O&G removal efficiency, 5 bar was chosen as the most effective saturator pressure and was used for all the following experiments.

3.3. Use of WS

3.3.1. Effect of WS doses

In order to determine the effect of different WS concentrations at 10 min flotation time on the DAF performance, after adding certain amounts of WS to the flotation column, doses of 0 (blank), 5, 10, 20 and 40 mg/L WS were studied. As illus-

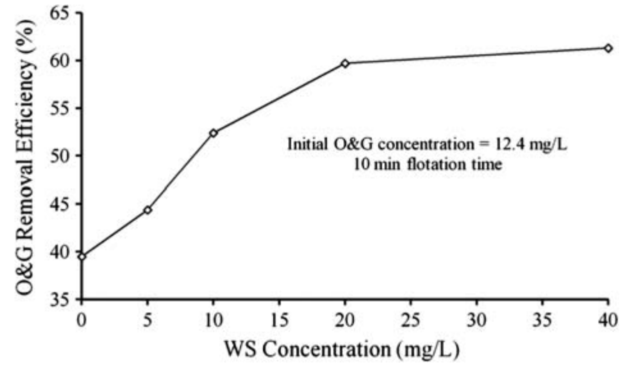

Fig. 5. Effect of different WS doses on O&G removal.

trated in Fig. 5, by increasing the WS concentration from 0 to 20 mg/L, the removal efficiency increased at a relatively constant rate, but the effect of increasing from 20 to 40 mg/L was negligible. Therefore, in order to examine the effect of longer flotation times, a concentration of 20 mg/L WS was used as the optimal dose in subsequent experiments.

3.3.2. *Effect of flotation time*

As shown in Table 2, the average retention time of the wastewater in the flotation column is equal to 10 min, but all treated effluent after air saturation returns again into the flotation column. In order to find the best flotation time for efficient use of WS capacity, the effect of the adsorption process at longer flotation times can be also investigated. The effects of flotation time on O&G and total petroleum hydrocarbons (TPH) removal in the absence and presence of 20 mg/L WS (the obtained optimal concentration) are presented in Figs. 6 and 7. In these experiments, the initial O&G and TPH concentrations in the absence of WS were 13.9 and 9.3 mg/L and in the presence of WS were 13.7 and 9.1 mg/L, respectively. As illustrated in these figures, a large part of the removal occurs in the first 10 min. It can be seen that without WS, by increasing the flotation time from 10 to 60 min, O&G and TPH removal efficiencies increased from 38.1 and 38.7% to 57.6 and 63.4%, and in the presence of WS at these flotation times, increased from 54.0 and 56.0% to 78.1 and 86.8%, respectively. Therefore, through the removal of soluble oil by using 20 mg/L WS, the O&G removal efficiency increased more than 15 and 20% at 10 and 60 min flotation times, respectively. Achieving concentrations lower than the water solubility of the heavy fuel oil can also be expected through the removal of tiny emulsions by adding coagulant in addition to PAC.

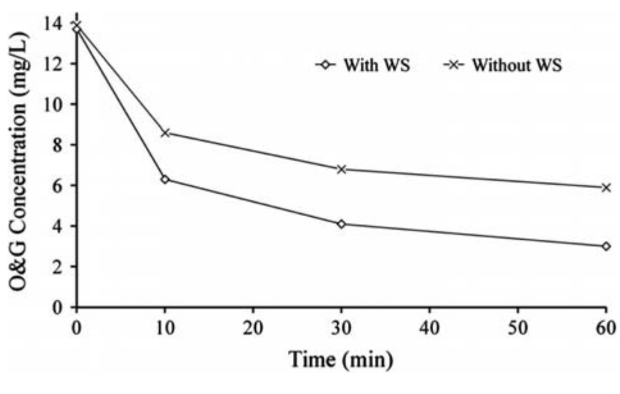

Fig. 6. Effect of flotation time on O&G removal.

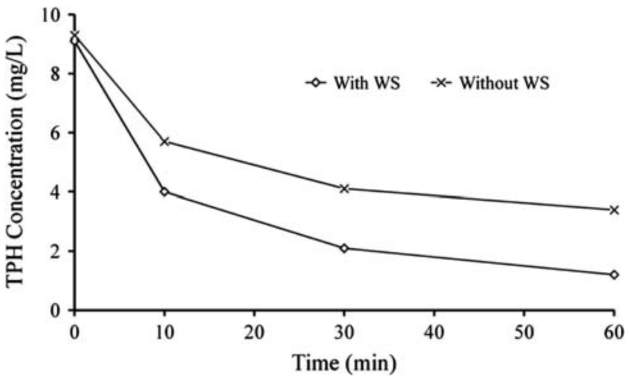

Fig. 7. Effect of flotation time on TPH removal.

In order to survey the effect of adsorption independently from the effect of bubble flotation, the differences in residual O&G and TPH concentrations caused by using the flotation process in the presence vs. in the absence of WS can be used. These differences are summarized in Fig. 8. The difference in initial concentration (0.2 mg/L) was considered in obtaining these results. According to these results,

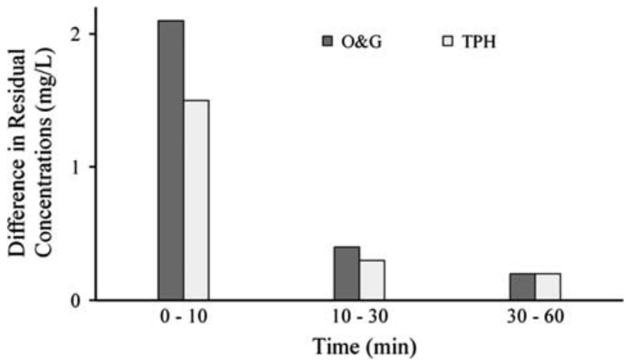

Fig. 8. The differences in residual concentrations caused by using the flotation in the presence vs. in the absence of WS.

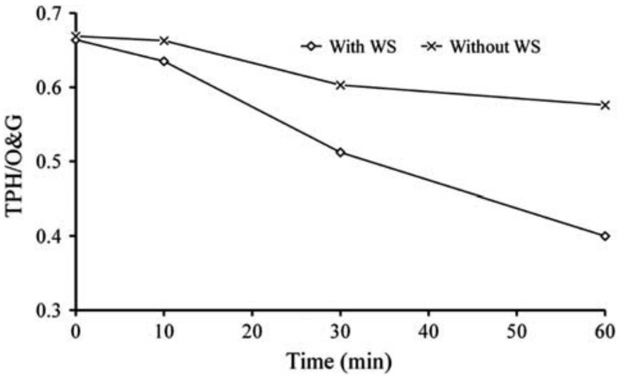

Fig. 9. Effect of flotation time on the TPH/O&G ratio.

about 78% of the adsorbed O&G and 75% of the adsorbed TPH on WS during the 60 min flotation time have been removed after 10 min flotation time or 20 min by considering the mixing time before starting the flotation process, which is approximately equal to the used retention times in a conventional DAF system. Therefore, a majority of its capacity can be used during the flotation process, especially when it is added into the flash- mixing tank prior to the flocculation basins due to the increase in contact time between PAC and adsorbable hydrocarbons.

As Fig. 9 shows, the ratio of TPH to O&G was decreasing with increasing the flotation time. After 60 min flotation time, the TPH/O&G ratio decreased from 0.67 to 0.4 and 0.58 in the presence and absence of WS, respectively. Despite the higher O&G and TPH removal efficiencies in the first 10 min of the flotation process, this decreasing trend was slower relative to the longer flotation times, which can be attributed to the lower content of the soluble hydrocarbons compared to the total oil content (emulsified and soluble hydrocarbons) in the first minutes as a result of the change in the ratio of the nonpolar to the polar hydrocarbons, which can only occur in water soluble fractions of oil. In general, molecules with low polarity, and consequently, low water solubility have a greater tendency to adsorb onto the activated carbon [13]. Therefore, as demonstrated in Fig. 9, the decreasing trend of the TPH/O&G ratio was more evident in the presence of WS.

4. Conclusions

According to the obtained results, by using only 20 mg/L WS, which was obtained as the optimal concentration, the O&G removal efficiency increased more than 15 and 20% at 10 and 60 min flotation times, respectively. It was found that a large part of the adsorbed O&G and TPH on WS during the flotation time has been removed in the early minutes of the flotation. Since a majority of the WS capacity can be used in the first minutes, using it in the conventional DAF systems would be cost effective. The ratio of TPH to O&G was decreasing with increasing flotation time. This decreasing trend was more severe at longer flotation times. Due to the low water solubility of heavy fuel oils, achieving oil contents below the feed water limits for industrial water tube boilers can be expected through the use of modified DAF unit by adding both coagulant and PAC as a pretreatment for ultrafiltration or even microfiltration. It should be mentioned that when the influent oil concentration is high and the modified flotation column by adding PAC is not able to reduce the oil concentration below the allowed limits, the role of PAC on the total removal efficiency will be insignificant and consequently, the use of PAC would not be cost effective.

Acknowledgments

This work was partially supported by the Energy & Environment Research Center, Niroo Research Institute (NRI), Tehran, Iran. The authors would also like to thank Mr. Mohammad Zabihi and his colleagues, for giving us permission to use their already prepared activated carbon in this study.

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