

# Removal of Organic Reagent from Synthetic Wastewater Using Ion Flotation

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**ABSTRACT:** Organophosphorus compounds such as diethyl dithiophosphate (DEDTP) are extremely toxic and cause significant environmental and water contaminations in nature. To mitigate its hazardous influence on the wastewater treatment processes, the present study was implemented focusing on the operating variable of the ion flotation technique. The effects of different parameters including initial pH (4-10), impeller speed (700-1000 rpm), and conditioning time (2-4 min) were investigated to maximize DEDTP removal from synthetic wastewater with an initial amount of 58 ppm. The N-Cetyl-N,N,N-trimethyl-ammonium bromide (CTAB) was used as the collector and frother in the ion flotation tests. The experimental results were analyzed based on the foamability, foam stability, and turbidity. The ion flotation experimental results showed that the DEDTP could be removed with the percentage removal of 91 under the optimum operating conditions of pH=10, collector dosage  $1.09 \times 10^{-3}$  M, impeller speed 850 rpm, and conditioning time with the collector for 3 min. It was observed that the percentage removal of DEDTP was dependent on the foam properties and electrostatic interactions between CTAB and DEDTP. The turbidity studies proved that DEDTP formed 1:2 complexes with CTAB at pH 10.

**KEYWORDS:** Ion flotation, Diethyl dithiophosphate (DEDTP); Wastewater treatment; N-Cetyl-N,N,N-trimethyl-ammonium bromide (CTAB).

## INTRODUCTION

Organophosphorus compounds are widely used for mineral processing and agricultural applications. These components can be commonly found on the surface and the groundwaters with concentrations in the levels of ng/L to  $\mu\text{g/L}$  [1, 2]. They are toxic and release substantial pollution into the environment [3-6]. Diethyl dithiophosphate as an organophosphorus compound has been extensively employed as an effective organic collector in the flotation of sulfide minerals [7, 8]. However, the residual DEDTP and its by-products

remaining in the wastewater of tailing dams and recycled water in the processing plants are a worldwide challenge either for the environmental impacts or separation efficiency of sulfide minerals [7, 9]. The typical contaminant of organophosphates is the disruption of nervous function due to the inhibition of the enzyme acetylcholinesterase (AChE) [10,11]. The chemical structure of DEDTP is shown in Fig. 1. Following this, the P=S bond may also be oxidized to paraoxon (P=O), which can more potent AChE inhibitor [11, 12].

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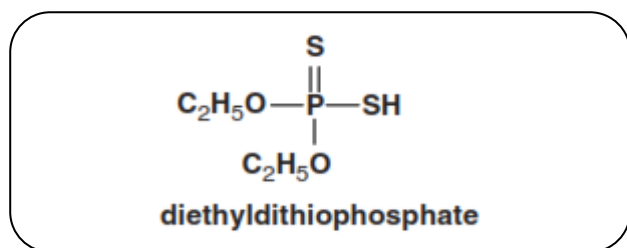


Fig. 1: The chemical structure of DEDTP.

Flotation process in a normal scale consumes ca. 1.9–3.0 m<sup>3</sup> of water per ton of ore processed [13]. However, as widely addressed the availability of water in many areas becomes limited to a specific extent. Therefore, the use of clean recycled water for the mineral processing sector is crucial from several aspects. According to the study results of many researchers, the use of recycled water for flotation processes has major drastic effects on the recovery and grade of valuable minerals [14]. This is because the recycled water includes pollutants such as residual chemical reagents, heavy metals, and solid particles [15, 16]. Therefore, the treatment and removal of organic reagents from wastewater and recycled water is vital not only for environmental protection but also for recovering valuable minerals [17]. Several techniques are available to remove organic flotation-related reagents from wastewater. These approaches can be categorized into physical adsorption, chemical precipitation, flocculation coagulation, biodegradation, and chemical oxidization [7, 18–25]. Detailed technical information regarding each technique can be found elsewhere [26]. Since some of these methods are very limited due to the economic and high energy consumption, it is necessary to develop alternative solutions for treating wastewater of tailings of chemical and mining industries. For this reason, the removal of DEDTP through the ion flotation method is presented in this study. Ion flotation as a separation technology has been known since the early 1960s and was introduced by *Sebba* [27]. During ion-flotation, a solution is initially homogeneous, while after the addition of a surfactant (collector) with the opposite ionic charge of the collagen, the solution becomes heterogeneous, and insoluble complexes (sublate) are formed. The sublate (the colligend– collector product) attaches preferentially to the bubbles passing through the solution leading to the transformation of bubbles to the top of the column [28]. Advantages associated with this technique can be simplification of the operation, low cost, and high separation yields [29–34].

The current study examines the influences of ion flotation parameters, i.e., collector dosage, initial pH, impeller speed, and conditioning time of collector on the removal of DEDTP from synthetic wastewater. Additionally, foam properties and turbidity were studied to investigate the removal mechanism in depth.

## EXPERIMENTAL SECTION

### Reagents and sample preparation

Sodium diethyl dithiophosphate [(C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>PS<sub>2</sub>Na] was used as the initial component and CTAB [N-Cetyl-N,N,N-trimethyl-ammonium bromide] with 98% purity was applied as both collector and the frother in the flotation experiments. Hydrochloric acid (HCl) and caustic soda (NaOH) were employed to adjust the pH of the synthetic solution. These reagents were all supplied by Merck GmbH (Germany) and prepared using double-distilled water. Flotation tests were performed using a 1 L mechanically agitated flotation machine. The studied variables (collector dosage coded as A, initial pH coded as B, impeller speed coded as C, and conditioning time with collector coded as D) and their levels are presented in Table 1.

The experimental procedure is presented in Fig. 2. The DEDTP concentration of synthetic wastewater was constant at 1.87×10<sup>-3</sup> M (58 ppm) for all tests. Firstly, a solution containing 1.87×10<sup>-3</sup> M DEDTP was added to the flotation cell and then CTAB was added in a given period. Afterwards, a flotation test was carried out by aerating oxygen into the cell and the froth was collected for 5 min. The concentration of DEDTP ion in the cell was determined using an atomic absorption spectrophotometer (standard code number of PO43--P: 4500-P E).

The percentage removal of diethyl dithiophosphate from the synthetic wastewater (*R*, %) was computed according to the following equation [35]:

$$R(\%) = [1 - (C / C_0)] \times 100 \quad (1)$$

where *C* is the residual concentration of the DEDTP ion in the cell (treated synthetic wastewater) and *C*<sub>0</sub> is the concentration of the DEDTP ion in the untreated synthetic wastewater. The process was repeated twice, and the average values were reported.

### Measurements of foamability and foam stability

Before aeration, the synthetic solution containing 1.87×10<sup>-3</sup>M of DEDTP and 0.93×10<sup>-3</sup> M of CTAB were added

Table 1: Levels of parameters studied in the flotation experiments.

Collector dosage (mol)	Initial pH	Impeller speed (RPM)	Conditioning time (min)
A	B	C	D
$0.36 \times 10^{-3}$	4	700	2
$0.69 \times 10^{-3}$	5	850	3
$0.93 \times 10^{-3}$	6	1000	4
$1.09 \times 10^{-3}$	7		
$1.49 \times 10^{-3}$	8		
$1.65 \times 10^{-3}$	10		
$1.87 \times 10^{-3}$			

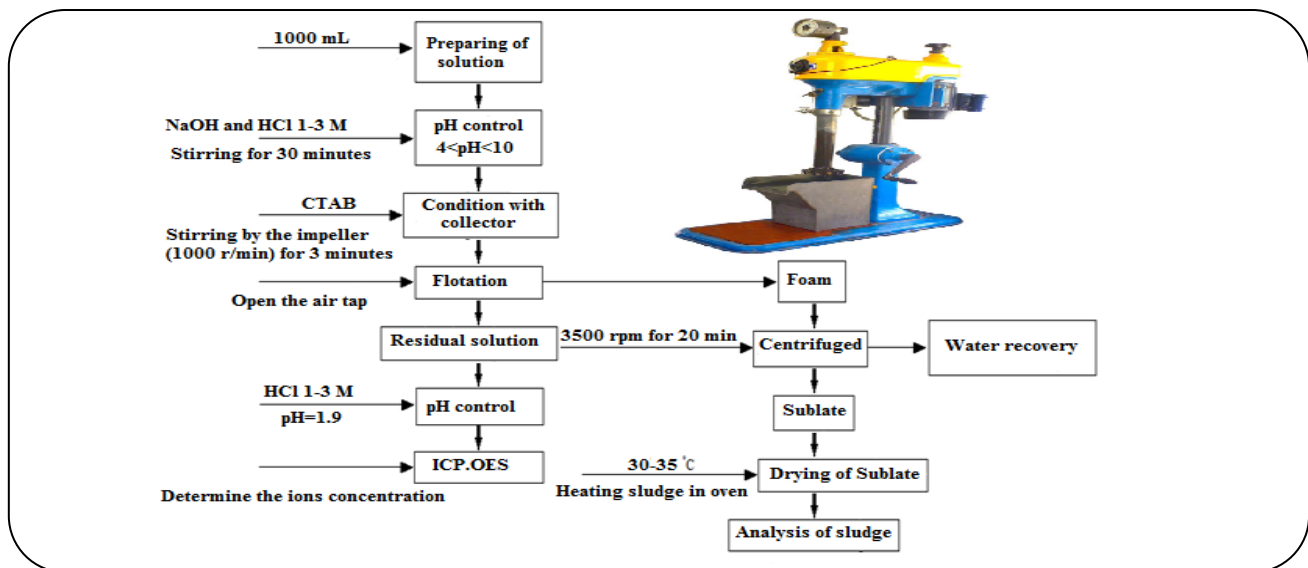


Fig. 2: A schematic view from the procedure of conducting flotation experiments.

into a graduated foam column having 51mm inner diameter and 1.5 m height. Then, air through a gas distributor of 40-60  $\mu\text{m}$  in pore diameter was dispersed into the column at a constant flow of 2.5 L/min for 3 min. At the end of the test, the maximum froth height was recorded for evaluating foamability. When the froth height had dropped to one-half of the initial froth height, the time was recorded for evaluating foam stability [36].

#### Evaluation of foam drainage

Foam drainage properties were investigated using volume ratio ( $V$ ) and concentration ratio ( $C$ ) between formate and residual solution [37]. These terms were calculated based on Eqs (2) and (3).

$$V = \frac{V_f}{V_r} \quad (2)$$

$$C = \frac{C_f}{C_r} \quad (3)$$

Where  $C_r$  and  $C_f$  are the DEDTP concentrations in the residual solution and the formate, respectively (mg/L).  $V_r$  and  $V_f$  denote the volumes of the residual solution and the formate, respectively (L).

#### Turbidity measurements

The interaction of DEDTP with CTAB was studied at pH 10, where the main compound in the synthetic wastewater was  $\text{HPO}_4^{2-}$ . The turbidity of 20 mL synthetic wastewater containing 1 mM DEDTP was measured in the CTAB concentration range of 0- 4 mM at pH 10 using a LAMBDA 45 UltraViolet-Visible (UV/Vis) spectrophotometer. The synthetic solutions were left for 30 min when the CTAB was added and then the turbidity was measured at 240 nm.

### Evaluation of Chemical Oxygen Demand (COD)

COD is generally used as a practical parameter of the pollution level, representing a present organic substance. The COD was determined by the oxidizing agent of potassium permanganate which indicated the standardized analytic procedure. 100 mL of treated and untreated solutions was added into Erlenmeyer flasks, separately. Subsequently, 10 mL of dilute sulfuric acid was added into the flasks and placed in a boiling water bath for 5 min. After that,  $V_1$  mL of 0.02 M potassium permanganate was transferred and heated for 25 min to enhance the rate of oxidation reaction. Then, 0.01 mol/L sodium oxalate solution was added into the flask at 75-80 °C, and titrated with 0.01 mol/L potassium permanganate solution until its color was slightly pink. The end point of titration was determined when it did not fade for 30 s and recorded the dosage  $V_2$  of potassium permanganate solution. The amount of COD was calculated using Equ. (4).

$$\text{COD} = \frac{[(V_1 + V_2 - V_4) \times f - 10] \times 0.01 \times 16 \times 1000}{100} \quad (4)$$

where  $f = (V_3 - V_4) / 10$  each mL of potassium permanganate is equivalent to  $f$  mL of sodium oxalate standard solution  $V_3$  is the dosage of standard solution for titration of sodium oxalate with potassium permanganate solution. Also,  $V_4$  represents the dosage of the blank sample in the potassium permanganate titration.

## RESULTS AND DISCUSSIONS

### Optimization of the flotation parameters

#### Effect of initial pH on the percentage removal

The DEDTP may undergo hydrolysis in the aqueous solution demonstrated in Appendix A (Fig. A1) [38]. The speciation diagrams of hydrolyzed elemental phosphorus as a function of pH are presented in Fig. 3. The diagram was calculated by Visual Minteq ver. 3.0. The speciation diagram for the P(III)-  $\text{H}_2\text{O}$  aqueous solution illustrated that the predominant species in  $1.87 \times 10^{-3}$  M P(III) at  $2 < \text{pH} < 7$  and  $7 < \text{pH} < 12$  only includes  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ , respectively. Therefore, the effect of pH (at values 4, 6, 8, and 10) on the percentage removal of DEDTP was investigated to evaluate the effect of species type on the removal rate of DEDTP. The results are presented in Fig. 4.

According to the given outcomes in Fig. 4, it can be concluded that by raising pH value from 6 to 10, the percentage removal of DEDTP increased to about 87%.

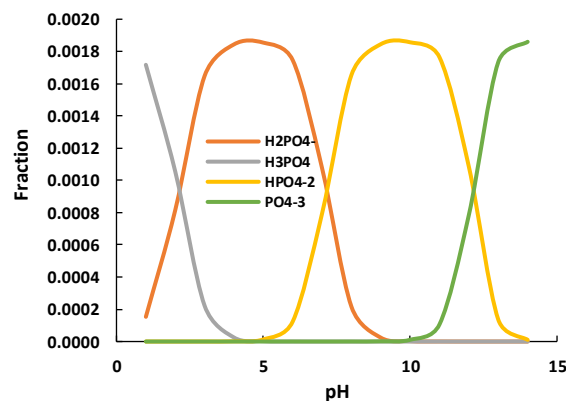


Fig. 3: The speciation diagram of P=O species as a function of pH.

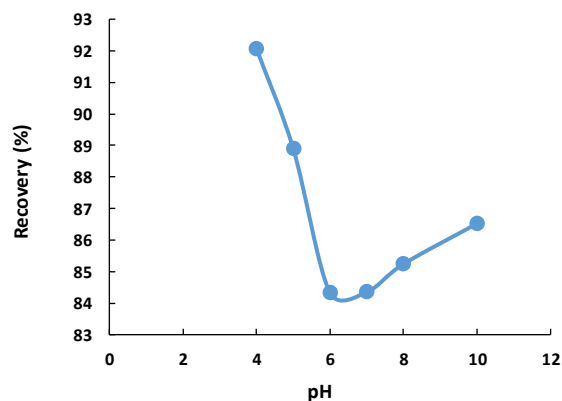


Fig. 4: The effects of pH on the percentage removal of DEDTP (rotation speed=700 rpm, conditioning time= 3 min, collector dosage=  $0.93 \times 10^{-3}$  M).

Such improvement in the DEDTP removal rate was attributed to the higher valence of the surface charge of predominant species and increasing electrostatic interactions between predominant species of  $\text{HPO}_4^{2-}$  and the positive head of CTAB. By reducing pH from 6 to 4, the percentage removal of DEDTP was enhanced to about 92%. This increase in the DEDTP removal rate can be related to the foam drainage properties which is a matter of presentation in the next sections. A study performed by Bahri *et al.* (2016) showed that the pH value had a significant influence on the separation mechanism of the ion flotation. This result is in line with the given information in Fig. 4. Another study also reported that species with the same charges, which had the higher valence, were more predominance for the adsorption to the collector than the other species [27].

### The effects of pH on the foam drainage properties

The impact of pH on the foamability is demonstrated in Fig. 5. The results showed that despite of the lower valence of the surface charge of predominant species ( $\text{H}_2\text{PO}_4^-$ ) at pH 4, the removal of more than 92% of DEDTP was achievable. To investigate the plausible reason for this phenomenon, foam drainage properties were examined based on the concentration and volume ratios. As seen, with the decrease of pH from 6 to 4, the volume ratio increased from 0.33 to 0.74, while it remained almost constant by elevating pH from 6 to 10. The results showed at pH 4, the higher foam drainage occurred. Thus, the higher percentage removal of DEDTP at pH 4 was attributed to the higher concentration ratio.

### Effect of pH on the Foam Properties

The results of the influence of pH on the foam half-life time and foam height of the solution including DEDTP and CTAB are presented in Fig. 6. pH was adjusted from 4 to 10 and all tests were carried out at an ambient temperature. As it can be seen from Fig. 6, increasing the pH level, both the foam half-life period and foam heights were decreased. Values obtained from the foam half-life time and foam height at pH 4 were higher than those given in other pH values. Thus, the increasing level of the percentage removal at pH 4 compared to the rest of pHs was caused by the higher foam stability and foamability. The results showed that when the pH of the solution was higher than 6, insoluble complexes were formed and lower foamability and foam stability were created because of intensifying interactions between DEDTP and CTAB and attenuation of the CTAB dosage.

### Effect of collector dosage on the percentage removal

The role of collector dosage in the DEDTP removal from synthetic wastewater at pH 10 is exhibited in Fig. 7. As can be seen, the percentage removal of DEDTP was boosted as the CTAB dosage increased from  $0.36 \times 10^{-3}$  M to  $1.09 \times 10^{-3}$  M. This change occurred because complete complexation was taken place between DEDTP and CTAB and all DEDTP species were absorbed. The low removal rate at a concentration of  $0.36 \times 10^{-3}$  was attributed to an inadequate DEDTP/CTAB ratio. At CTAB dosage higher than  $1.09 \times 10^{-3}$  M, the DEDTP removal was diminished. The reduction of DEDTP removal was ascribed to the re-dissolution of DEDTP-CTAB

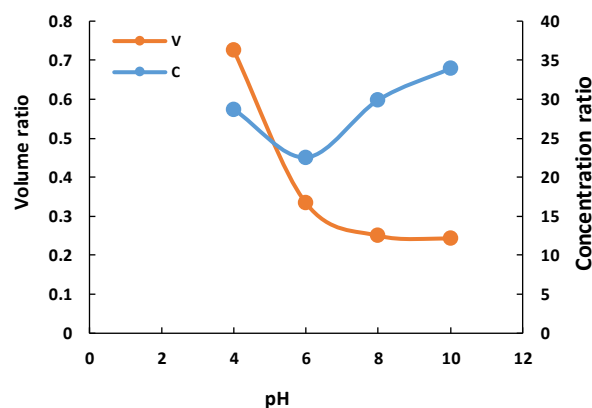


Fig. 5: The effects of pH on the foam drainage properties.

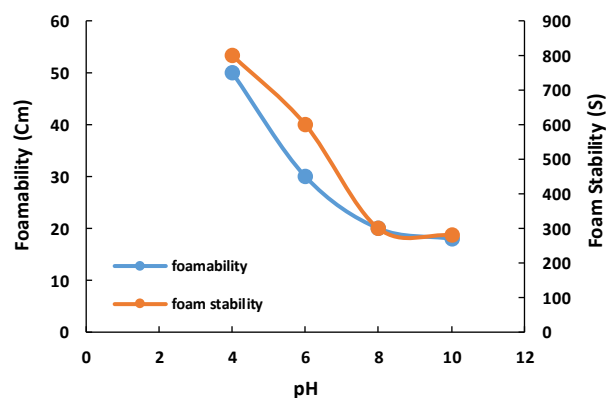


Fig. 6: Effects of pH on the foam properties of the solution containing CTAB and DEDTP.

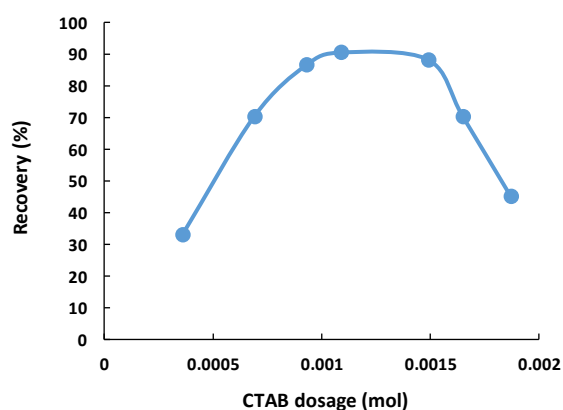


Fig. 7: The effects of collector dosage on the percentage removal of DEDTP at pH= 10, rotation rate of 700 rpm, and conditioning time of 3 min).

complexes using CTAB at this concentration. Regarding this, previous studies showed that in the collector dosage

higher than the CMC (Critical Micelle Concentration), the re-dissolution of insoluble complexes occurred [37]. For this reason, a  $1.09 \times 10^{-3}$  M CTAB was used throughout all tests as an optimum collector dosage.

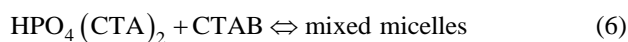
#### Interaction between CTAB and DEDTP at pH 10

The interaction between CTAB and DEDTP was taken into consideration to investigate the DEDTP removal mechanism. The interaction of CTAB with DEDTP was examined in the presence of increasing amount of CTAB at pH 10. Fig. 8 illustrates the turbidity of synthetic wastewater containing 1 mM DEDTP at pH 10 and in the presence of CTAB. The results indicated that for the molar ratios ( $r = [\text{CTAB}] / [\text{DEDTP}]$ ) more than 0.28, an insoluble complex can be observed. Thus, for the formation of insoluble complexes, a minimum concentration ( $r > 0.28$ ) is required. Previous studies showed that the starting point of the insoluble interaction was critical for the aggregation concentration (CAC) [39, 40]. With the increase of the molar ratio ( $0.28 < r < 2.3$ ), the turbidity of synthetic wastewater gradually increased, due to further interaction and precipitation. For the excessive molar ratios of 2.3, the solution turbidity decreases about the formation of CMC and re-dissolution of the precipitate.

Previously, researchers reported that the Maximum Interaction Concentration (MIC) occurred when the turbidity of the solution was maximum and all ions were absorbed [40, 41]. According to this fact, it was found that the molar ratio of 2.3 was mic of the interaction between CTAB and DEDTP. The difference between the mic and cac can be called the association stoichiometry, which is 2.02. Thus, the interaction between CTAB and DEDTP at pH 10 was expressed, according to the following reactions:



and the re-dissolution process of the complexion between CTAB and DEDTP can be defined by reaction 6.



#### The effects of collector dosage on the COD value

Fig 9 presents the influence of collector dosage on the COD value of treated solution. The results suggest that COD concentration from treated solution has decreasing trend in the range of  $0.36 \times 10^{-3}$  to  $1.09 \times 10^{-3}$  M CTAB dosage.

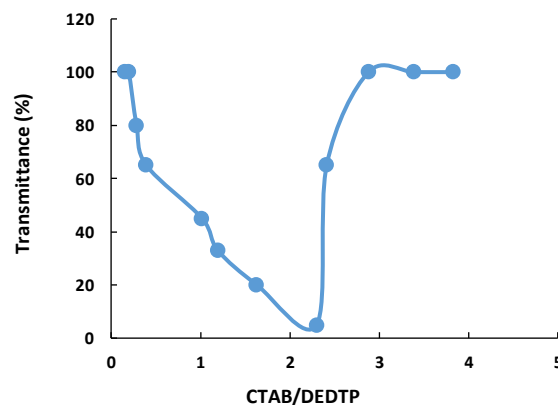


Fig. 8: The turbidity of 1 mM DEDTP solution in the presence of increasing amount of CTAB at pH 10.

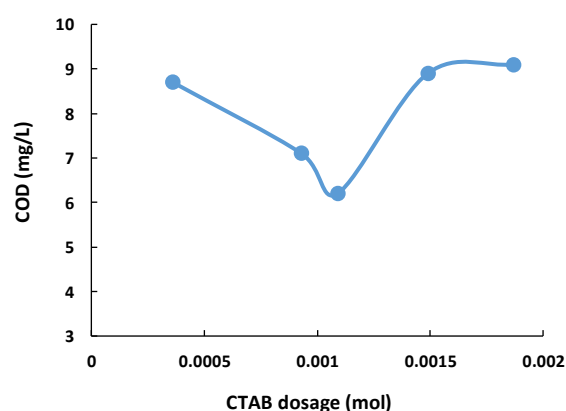


Fig. 9: Effect of CTAB dosage on the COD value.

The reduction of COD was attributed to complete complexation between DEDTP and CTAB, but a rapid increase in COD value was observed when the CTAB concentration was  $\geq 1.49 \times 10^{-3}$  M. This variation was due to the re-dissolution of DEDTP-CTAB complexes using CTAB at these concentrations.

#### Effect of impeller speed on the percentage removal

The impeller speed is an important parameter in the ion flotation that affects on the entrainment and the flotation efficiency [42]. The impeller speed has a significant effect on the bubble size distribution, gas holdup, foam drainage properties and foam properties [43]. The effect of impeller speed on the percentage removal and volume ratio was investigated in the range 700 to 1000 rpm and the results are presented in Fig. 10. As it can be seen, by exceeding impeller speed, the level of the percentage removal gradually increased. The volume ratio (V) was

enhanced with an increase in impeller speed. The results showed that the volume ratio had a direct relationship with the impeller speed. This was due to the fact that increasing impeller speed led to shrinking the mean bubble size and increasing gas holdup. This can consequently result in the creation of a massive surface area of bubbles and an increase in the mass transfer, which ultimately intensifies the DEDTP removal.

#### *Effect of the conditioning time with the collector on the percentage removal*

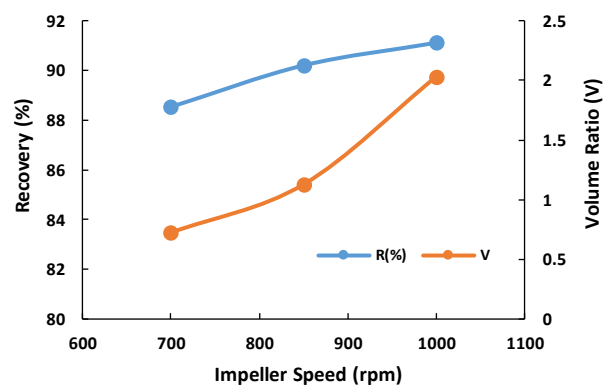
The effect of the conditioning time on the percentage removal of DEDTP was investigated at pH 10. The results are presented in Fig 11. As seen, the percentage removal improves as the conditioning time increases from 2 to 3 min which remains almost constant after this point. The low removal rate at the conditioning time of 2 min was linked to i) a low absorption of DEDTP hydrolysis species existing in the solution with CTAB and ii) incomplete complexation between DEDTP and CTAB.

#### **The effects of conditioning time on the foam drainage properties**

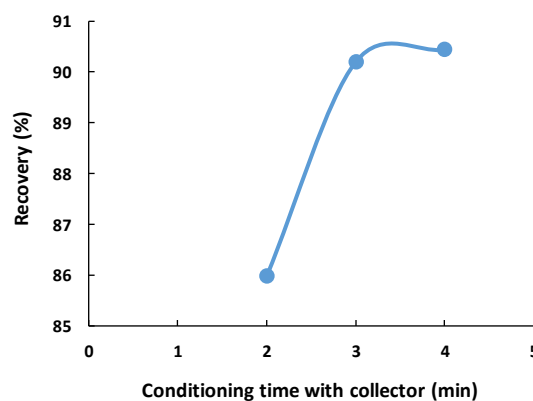
The effects of conditioning time on the foam drainage properties are indicated in Fig. 12. As can be seen, with increasing conditioning time from 2 to 3 min, the volume ratio declines, while the concentration ratio increases. A reduction in concentration ratio and an increase in the volume ratio at a conditioning time of 2 min were assigned to the declination in the interaction between DEDTP and CTAB and an increase in the amount of CTAB present in the solution, respectively. This was the result because CTAB is an effective frother and residual CTAB present in the solution led to higher gas holdup and a bigger surface area of bubbles. The results showed that despite a higher volume ratio and better foam properties at 2 min conditioning time, the concentration ratio and the percentage removal of DEDTP were decreased. Thus, it was acknowledged that the interaction between DEDTP and CTAB was more important than the foam properties of the solution.

#### *Effect of DEDTP concentration on the percentage removal*

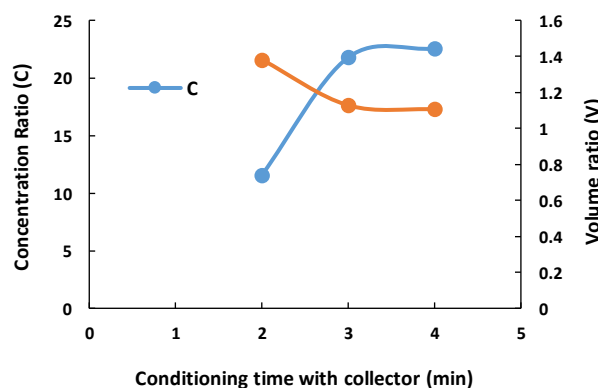
The effect of DEDTP concentration on the percentage removal of DEDTP was studied in the range 20 to 200 ppm under optimal conditions and the results are presented in Fig. 13. As it can be seen, with an increasing DEDTP,



**Fig. 10:** The effects of impeller speed on the percentage removal of DEDTP and the volume ratio (pH= 10,  $1.09 \times 10^{-3}$  M CTAB, and conditioning time= 3 min).



**Fig. 11:** The effects of conditioning time with collector on the percentage removal of DEDTP (pH= 10,  $1.09 \times 10^{-3}$  M CTAB and rotation speed of = 850 rpm).



**Fig. 12:** Effects of the conditioning time with collector on the foam properties.

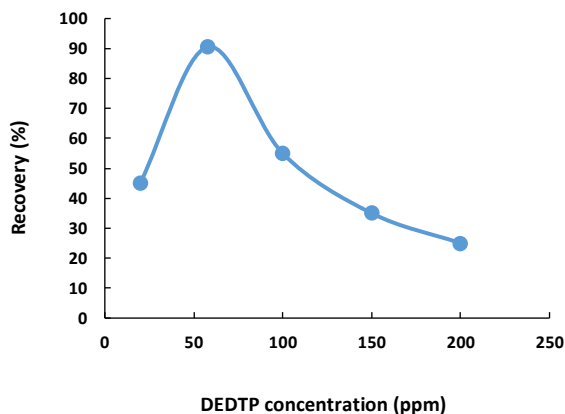


Fig. 13: The effects of DEDTP concentration of synthetic wastewater on the percentage removal of DEDTP (pH= 10,  $1.09 \times 10^{-3}$  M CTAB, rotation speed= 850 rpm, and conditioning time= 3 min).

the level of the percentage removal gradually increased. Low removal at DEDTP concentration of 20 ppm was probably attributed to the formation of cmc and re-dissolution of the precipitate. At DEDTP concentration higher than 58 ppm, the removal of DEDTP was decreased which was an inadequate CTAB concentration and incomplete complexation.

According to the results given in this section, the optimum values obtained for the studied parameters to maximize percentage removal of DEDTP were pH 10,  $1.09 \times 10^{-3}$  collector dosage, 850 rpm impeller speed, and 3 min conditioning time with collector.

## CONCLUSIONS

The present study aimed at optimizing the effect of key operating parameters on removing DEDTP using the ion flotation technique. The impact of pH (4-10), impeller speed (700-1000 rpm), and conditioning time (2-4 min) were examined in detail. The following are the main highlights extracted from the obtained results.

1- The results showed that the separation of DEDTP was possible using ion flotation with a percentage removal of 91% under optimum conditions i.e., pH 10, collector dosage  $1.09 \times 10^{-3}$  M, impeller speed 850 rpm, and conditioning time with collector 3 min.

2- The results proved the high ability of ion flotation in removing DEDTP from a synthesis wastewater.

3- The results disclosed that when the pH of the solution was higher than 6, insoluble complexes

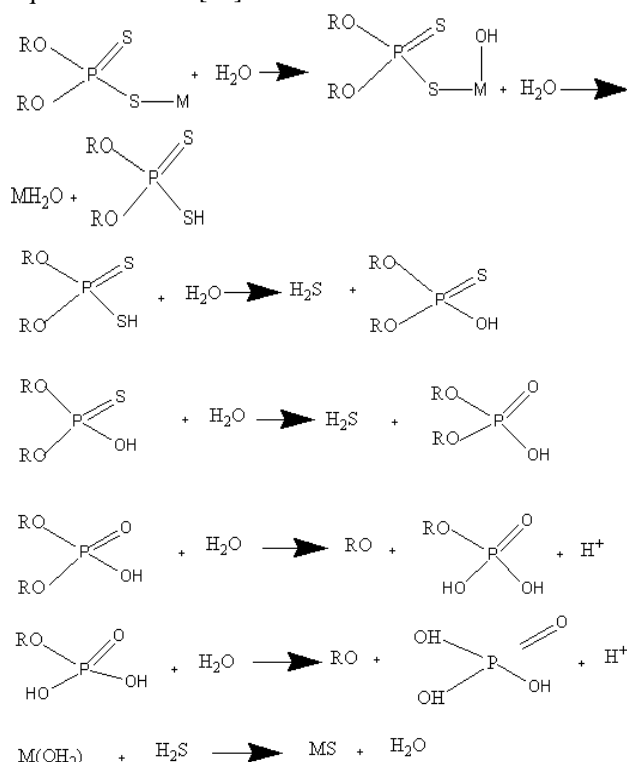
were formed and the lower foamability and foam stability was created because of increasing interactions between DEDTP and CTAB and the reduction of the CTAB dosage.

4- The interaction studies indicated that a minimum concentration was required for forming insoluble complexes. The associated stoichiometry between CTAB and DEDTP at pH 10 was obtained 2.02.

## Appendix A

Fig. A1. exhibits the hydrolysis mechanism of DEDTP in the aqueous solution.

Fig. A1. Hydrolysis mechanism of DEDTP in the aqueous solution [38]



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