

Communication

Application of a Rapid and Simple UV-Spectrophotometric Method for the Study of Desorption of Esterquat Collectors in Tailings–Seawater Systems

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Abstract: The growing demand for mineral resources followed by the steady increase in mining activity result in the need for the disposal of large amount of tailings. Submarine tailings placements (STPs) is a viable option to land-based waste disposal. However, disposal of tailings with accumulated chemicals continues to contribute to the degradation of the marine environment. Replacement of chemicals towards more environmentally friendly alternatives is a good initiative aimed at preservation and protection of the marine ecosystem. Among the cationic surfactants esterquats-containing reagents have attracted particular attention due to their specific ability to degrade rapidly into non-surface-active and environmentally friendly fragments followed by inorganic end products. The important decomposition reaction is the hydrolysis in the presence of water. In this study the rate of esterquats-containing reagent FLOT 2015 desorption by seawater and the probable mechanism of its chemical degradation in aqueous mediums were investigated with the aid of a simple and adequate UV-spectrophotometric technique. By investigating the desorption characteristics of the adsorbed collector FLOT 2015 on mineral samples, important information regarding its mobility and stability was obtained that would be valuable for environmental impact assessment.

Keywords: submarine tailings placements; esterquats; desorption by seawater; hydrolytic degradation

1. Introduction

The growing demand for mineral resources followed by the steady increase in mining activity result in the need for the disposal of a large amount of tailings. Environmental impacts of mining have been studied and reported by several investigators [1–4]. In particular, the potential harmful impact of waste disposal on the environmental quality of the surrounding ecosystem is attracting an increasing amount of focus, which has led to stricter environmental regulations. Hence, the global mining industry has realized that the initiatives should address the concept of sustainable development.

Submarine tailings placements (STPs) is a viable option to land-based waste disposal and has been utilized at several mineral processing plants around the world [4–6]. The potential environmental impacts of STPs are the results of the oceanographic, biochemical, and ecological conditions of the site, as well as the specific mineral processing solution employed by the plant. The physiochemical properties of the tailings are governed by the preceding comminution and separation processes, but there is considerable potential for improving these characteristics through novel approaches to dewatering and flocculation, as well as the recycling of process water and process chemicals. These are

established unit operations, but they are not necessarily studied and optimized for the reactions that take place in a system where tailings are disposed to the marine environment and fresh process water meets seawater.

Currently, legislation has spurred the industry to continuously replace reagents with more environmentally friendly alternatives. In Norway the esterquats-containing reagent FLOT 2015 is now being used as a more environmentally friendly cationic collector for reverse flotation of silicates in the production of high-purity, micronized calcite slurries. Esterquats constitute a novel class of cationic collectors with the ester bond located between the quaternary ammonium group and the long hydrocarbon chain, and can be decomposed into non-surface-active and more environmentally friendly components [7–9]. When FLOT 2015 molecules bound to a silicate mineral surface via physical adsorption are exposed to seawater with its much higher ionic strength, significant desorption can occur. Furthermore, the fast hydrolysis of the esterquats collector can be initiated in seawater.

A recent review of the literature on this topic [10] found that the primary step in the degradation of esterquats is probably an abiotic degradation via chemical reactions such as oxidation, reduction, and hydrolysis without the participation of biological organisms. The important decomposition reaction is the hydrolysis in the presence of water. Therefore, the degradation starts with the cleavage of the ester bond. Overkempe et al. [9] highlights that the hydrolytic stability of esterquats is influenced by the temperature, pH, formulation pathways, and the chemical structure of the molecule. In general, basic medium hydrolysis gives rise to the formation of fatty acids and small diol/triol quaternary ammonium salts [11]. Although, detailed biochemical studies are not available for all esterquat types, a general explanation of the degradation pathway of esterquats were made based on research with radiolabeled chemicals. Giolando et al. [12] reported that the results from high-performance liquid chromatography (HPLC) with radiometric detection showed the disappearance of dimethyl bis(2-(1-oxooctadecyl)oxyethyl) ammonium chloride (DEEDMAC) in the solution followed by the presence of a fatty acid and a short-chain quaternary ammonium compound. The fatty acids and the short-chain quaternary ammonium compounds are readily biodegradable into inorganic end product such as water, carbon dioxide, and mineral salts [11,13–16]. Furthermore, photochemical reactions have to be taken into account as one of the main pathway of biodegradation of chemicals [17]. While the oxidative photodegradation of organic compounds leads to the formation of carbon dioxide and water, photoactive compounds can be transformed into more persistent compounds under ambient irradiation conditions. Games et al. [18] stated that in their experiments using radiolabelled octadecyltrimethylammonium chloride, no stable intermediates were formed. More recent evidence [10] revealed that the biodegradation of diol/triol quaternary ammonium salts proceeds due to the fission of C–N bonds, resulting in aldehydes and nitrogen derivatives without the formation of resistant intermediates. The aldehydes are oxidized to the respective carboxylic acids to be readily biodegraded via beta-oxidation to water and carbon dioxide [19,20]. Formaldehyde resulting from the cleavage of a methyl group is biodegraded by many metabolizing microorganisms. The tertiary amines formed are also readily biodegradable, as shown by Yoshimura et al. [21]. Moreover, it has been noticed that the results from some screening tests tend to underestimate the biodegradation potential of esterquats in the marine environment. It has been proposed that readily biodegradable quaternary ammonium salts will not accumulate in the most ecosystems. This statement has been confirmed by the half-life period of octadecyltrimethylammonium chloride, which is 2.2 days in river water [22]. The half-life period of the similar alkyltrimethyl quaternary ammonium salt in seawater is 6 days [23].

The transport and fate of cationic collectors in the environment have been widely analyzed by different methods. Spectroscopic methods have been intensively used for cationic collectors' analysis in an aqueous medium [24–26].

UV-spectrophotometry is a suitable analytical technique of choice in research and industrial laboratories due to its inherent simplicity, portability, and low cost [27]. The principles of UV-spectrophotometry were applied for the determination of cationic surfactants using azo dyes

in acidic or basic mediums [28–32]. In the case of esterquats, the development of a sensitive and simple method for the quantification of the complex systems with several active ingredients still constitutes a major challenge.

The aim of the present study is to investigate the rate of FLOT 2015 desorption via seawater and probable mechanism of its chemical degradation with the aid of a simple and adequate UV-spectrophotometric method. By investigating the desorption characteristics of the adsorbed collector FLOT 2015, important information regarding its mobility and stability could be obtained that would be valuable for environmental impact assessment.

2. Materials and Methods

2.1. Materials

Bromocresol Purple (BCP) and chloroform were purchased from Sigma Aldrich Co., Schnellendorf, Germany. The flotation collector FLOT 2015 was obtained from Omya Hustadmarmor AS, Elnæsivågen, Norway. FLOT 2015 comprises a mixture of reaction products of fatty acids, C16–18, and C18-unsaturated, with triethanolamine and di-methyl sulfate-quaternized (TEA-esterquat) dissolved in 20–30% isopropanol [33]. Table 1 shows the structures and molecular formulas of three main components of FLOT 2015. A tris(2-hydroxyethyl)(methyl)azanium methylsulfate (3HEMA MS) pure sample was obtained from NIVA Tech, Oslo, Norway. Potassium dihydrogen phosphate/disodium hydrogen phosphate buffer solution (0.1 M), pH 7.0 (20 °C), was purchased from Sigma-Aldrich, Darmstadt, Germany, and used to adjust the pH of the reaction solutions for ion-pair complex formation to 7.0. Sodium hydroxide was purchased from VWR Chemicals, Prolabo, Leuven, Belgium. All single chemicals were of analytical-reagent grade and used without further purification. All solutions were made up by doubly deionized water. Artificial seawater was prepared according to the procedure given by Kester et al. [34]. Appendix A contains details of artificial seawater preparation and data supplemental to the main text.

Table 1. Structures and molecular formulas of FLOT 2015 main components (International Union of Pure and Applied Chemistry IUPAC).

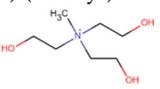
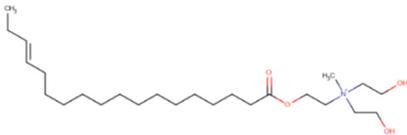
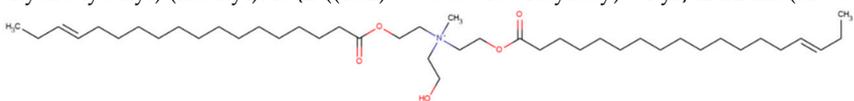
Name and Structure	Molecular Formula
tris (2-hydroxyethyl) (methyl)azanium (3HEMA MS) 	C ₇ H ₁₈ NO ₃
bis(2-hydroxyethyl) (methyl){2-((15E)-octadec-15-enyloxy) ethyl}azanium (monoester) 	C ₂₅ H ₅₀ NO ₄
(2-hydroxyethyl) (methyl)bis {2-((15E)-octadec-15-enyloxy) ethyl}azanium (diester) 	C ₄₃ H ₈₂ NO ₅

Table 2 shows the chemical composition of the ground marble samples (feed for reverse flotation) obtained from Omya Hustadmarmor AS, Elnæsivågen, Norway. The sample consisted of approximately 95% calcite and minor amounts of silicates and graphite.

Table 2. Chemical composition of the ground marble sample (flotation feed), %.

Fe ₂ O ₃	TiO ₂	CaO	K ₂ O	P ₂ O ₅	SiO ₂	Al ₂ O ₃	MgO	Na ₂ O	MnO ₂	LOI *
0.64	0.01	54.76	0.01	0.01	0.44	0.03	1.08	0.02	0.22	42.38

* LOI—loss-on-ignition.

2.2. Methods and Calculations

2.2.1. Instruments and Apparatus

UV-vis spectra were recorded on a DR3900 Laboratory VIS Spectrophotometer (HACH—Lange GmbH, Dusseldorf, Germany), with a wavelength range 320–1100 nm, spectral bandwidth 5.0 nm, and wavelength resolution 1 nm, using 10 mm matched quartz cells, and scanning speed: 8 nm/s (in steps of 1 nm). A Metrohm AG pH-meter instrument (913 pH) (Herisau, Switzerland) equipped with combined pH electrode with integrated temperature sensor (Primatode with a Negative Temperature Coefficient thermistor) was used for measuring the pH values in the solutions and mineral suspensions. The temperature-dependent pH values of the Metrohm pH meter solutions were stored in pH meter instrument for automatic buffer recognition during the pH calibration. By default, the calibration parameters were set for calibration with two Metrohm buffer solutions (pH 4.000 and pH 9.000). A Grant OLS 200 shaking water bath (Cambridge, UK) with a temperature controller (20 °C) and a smooth reciprocal shaking motion (115 oscillations per min) was used for desorption and degradation tests.

2.2.2. Stock and Standard Solution Preparation and Sample Analysis

The BCP stock standard solution 1.25×10^{-4} M was prepared by dissolving accurately weighed amounts of the dye in 10 mL of 0.01 M sodium hydroxide solution and diluting to 100 mL with deionized water. A stock solution of FLOT 2015 was prepared by dissolving 1 g of the reagent in the acidic water solution using HCl (Sigma Aldrich Co., Schnelldorf, Germany) and then made up to 1000 mL to adjust the pH to 5.5. Aliquots of stock solution (1 g/L) were transferred into a set of 25 mL flasks and volumes were completed to the mark with deionized water to produce solutions in the concentration range 1–120 mg/L. The quantitative analysis was conducted according to the following procedure: 25 mL of FLOT 2015 solution, 2.5 mL of buffer solution, 2 mL of BCP solution, and 8 mL of chloroform were inserted into a 70-mL plastic bottle and mixed thoroughly for 2 min. Phases were allowed to separate for 5 min. Using a Pasteur pipette, an aliquot (4 mL) of the chloroform layer was removed and placed in a clean cuvette. The absorption spectra of samples were measured at 380 nm against a blank chloroform sample. After each measurement, a cuvette was rinsed with chloroform to remove any complex adsorbed to the glass walls. The calibration curve was constructed by plotting absorbance of the chloroform layer against the concentration of FLOT 2015 in distilled water. The method was validated for linearity, accuracy, precision, specificity, sensitivity, limit of detection (LOD), and limit of quantification (LOQ) [35–37].

2.2.3. Adsorption Tests

Multiple mineral adsorption tests were conducted in 70 mL plastic bottles, each using 1 g of samples in 30 mL of reagent solutions. The suspension was agitated for 5 to 30 min. The suspension was then centrifuged for 10 min and filtered. A total of 25 mL of the resulting solution was used for FLOT 2015 determination using a UV-method with BCP and chloroform.

2.2.4. Desorption Tests

The mineral sample after adsorption and filtration was mixed with 30 mL of seawater or solutions with different pH values to allow the collector to desorb. The duration of mixing varied from 5 min to

5 days. At the end of the desorption test, the suspension was filtered using the syringe filter, and the solution sample (25 mL) was analyzed in order to quantify the concentration of FLOT 2015.

2.2.5. Degradation Tests

A fresh stock solution of FLOT 2015 was prepared and aliquots of the stock solution (1 g/L) were transferred into a set of 1000 mL volumetric flasks, and volumes were completed to the mark with the water of the different pH to produce solutions of FLOT 2015 with an initial concentration of 4 mg/L. Degradation tests were conducted in 70 mL plastic bottles, each using 25 mL of the reagent solutions in water with different pH (deionized water with pH 6.7, slightly alkaline water with pH 8.0, seawater with pH 8.3, and alkaline water with pH 9.3). The samples were stored at 20 °C in the shaking water bath for 5, 30, 60 min, 2 h, 3 h, 1 day, 5 days, and 15 days, and the solutions were then used for FLOT 2015 determination using the UV-method with BCP and chloroform. No additional organic matter was available in the samples. The conditions for storage could be considered as semi-dark.

2.2.6. Calculations

The concentration of FLOT 2015 at equilibrium (c_{eq}) was measured and the concentration of FLOT 2015 on the mineral surface (c_{ad}) was calculated using the following equation:

$$c_{ad} = c_i - c_{eq} \quad (1)$$

where c_i is the initial concentration of FLOT 2015 in the solution (mg/L).

The adsorption capacity was calculated as:

$$A = (c_i - c_{eq}) \times V/m, \quad (2)$$

where V is the volume of the solution (L) and m represents the mass of the mineral sample (g).

The desorbability of FLOT 2015 was determined as the percentage of desorbed FLOT 2015 with regard to the total initially adsorbed amount:

$$D = (A - A_{after}) \times 100\% / A, \quad (3)$$

where A and A_{after} represent the adsorption capacity (mg/g) before and after desorption, respectively.

3. Results and Discussion

3.1. Validation of the Proposed UV-Spectrophotometric Method

We proposed a simple, rapid, and low cost method for the analysis of esterquats-containing reagents based on the formation of an ion pair between a cationic collector and an anionic dye. When the cationic collector FLOT 2015 is introduced to the anionic dye solution BCP, the solvent rearrangement around free ions leads to ion pair formation [38]. This results in a change in absorbance, observed as a decrease in intensity of the dye color. The ion pair complex is extractible into an organic solvent, while the dye alone is not, so the intensity of the organic phase color is directly proportional to the esterquat concentration [13,39].

The developed method showed that the buffer solution of pH 7.1 gave the maximum color intensity, stability of color, and highest absorbance value using BCP after chloroform extraction with reproducible results at a wavelength of 380 nm. The proposed method showed linearity in the range of 0.5–30 mg/L with a correlation coefficient of 0.9820. The standard deviation and relative standard deviation obtained by intra- and inter-day precision tests of the proposed method were 2.08% and 2.80%, respectively, and were within the permissible bias range (less than 3%), which was considered satisfactory. LOD and LOQ for the BCP-FLOT 2015 system were found to be 1 µg/mL and 2 µg/mL, respectively. Appendix B lists the statistical data on the proposed method.

3.2. Adsorption Kinetics Tests

To verify the relationships between the concentration of FLOT 2015 and the level of its adsorption, a series of tests were set up to determine the adsorption capacity of the reagent on the flotation feed samples. The adsorption capacity was rapidly increased with the increasing concentration of FLOT 2015 and then slowed down when the concentration reached 30 mg/L. This stabilization was caused by the recognition sites on the mineral sample, which were almost completely occupied by FLOT 2015 when exceeding the equilibrium concentration. The adsorbed amount of FLOT 2015 on the mineral also increased with increasing contact time and remained almost constant when the equilibrium condition was established. The optimum agitation time for adsorption experiments was investigated from 1 to 20 min at ambient temperature (20 ± 2 °C). A retention time equal to 10 min was found to be optimal. Figure 1 shows a clear trend in the effect of time on the adsorption capacity of FLOT 2015.

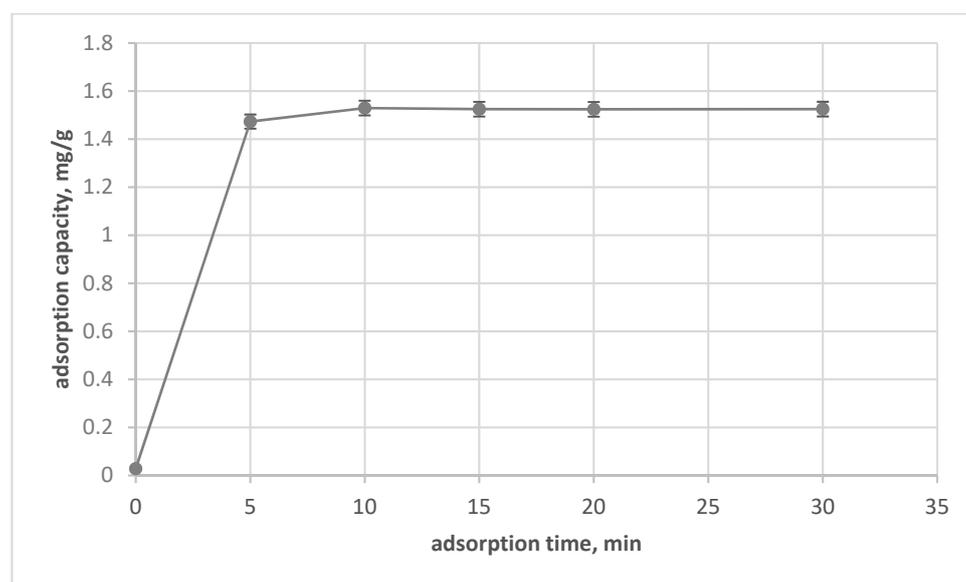


Figure 1. Effect of adsorption time on FLOT 2015 adsorption capacity (initial concentration of FLOT 2015 $C_{\text{FLOT 2015}} = 60$ mg/L).

3.3. Desorption Kinetics Tests

It was noticed that the desorption of FLOT 2015 using seawater was highly dependent on concentration and time. Thus, the adsorption and desorption time values were evaluated in separate kinetic experiments at pH 8.3, obtained after further introducing the mineral sample in seawater. The kinetics tests were carried out at four initial concentrations of FLOT 2015, namely 30, 60, 90, and 120 mg/L, to investigate the desorption of the collector using seawater from flotation feed samples. From a previous study it was proven that multilayer adsorption occurred at 60–120 mg/L, while lower concentrations (less than 30–45 mg/L) showed preferentially monolayer adsorption, which was comparatively stable under the current conditions [40]. The adsorption time was varied from 5 to 30 min, whereas the desorption time was varied from 5 min to 5 days. It was observed that the adsorption capacity was not affected by the adsorption agitation time once the latter had reached 10–15 min. Equilibrium was established at 10 min for all concentrations. Figures 2 and 3 represent the influence of concentration of FLOT 2015 and desorption time on FLOT 2015 desorbability using seawater.

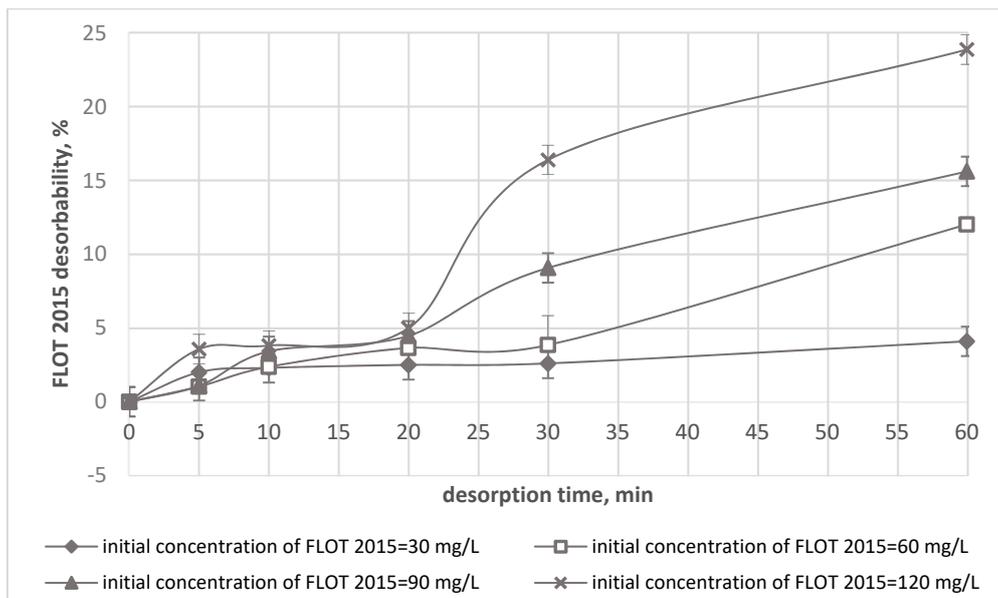


Figure 2. Effect of desorption time on FLOT 2015 desorbability from the flotation feed sample using seawater (adsorption time = 10 min).

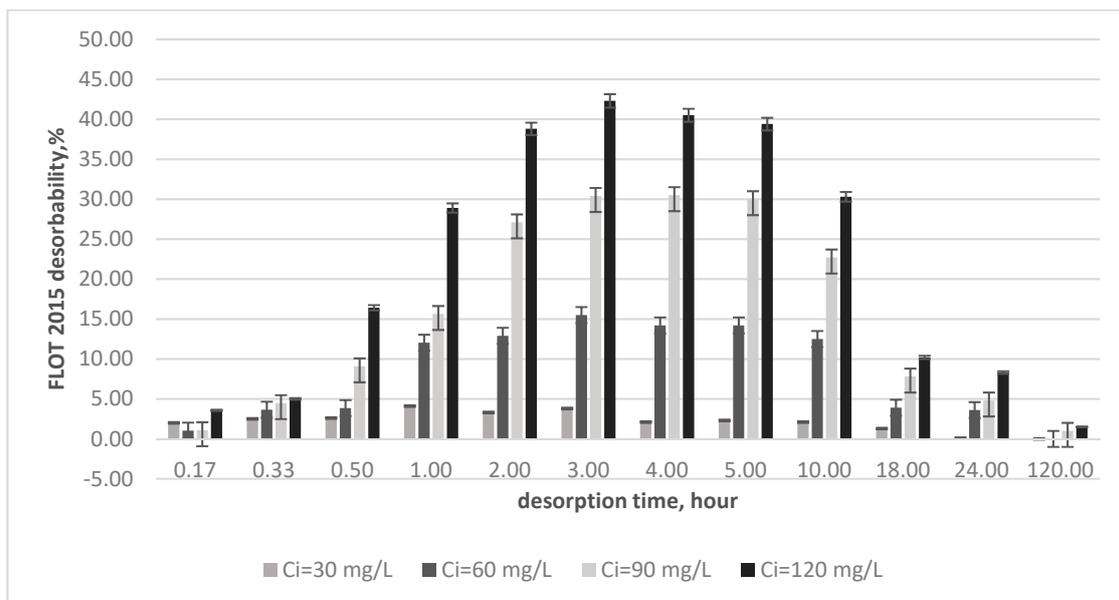


Figure 3. Kinetics of FLOT 2015 desorption from the flotation feed sample using seawater (adsorption time = 10 min).

The experimental results shown in Figure 2 revealed that desorption increased with increasing desorption time for all initial concentrations of FLOT 2015. However, it is apparent that desorption was very limited for desorption times up to 20 min for all concentrations tested. Then, desorbability increased considerably when the retention time was extended up to 60 min and FLOT 2015 desorbed more readily from the mineral sample taken from the system with the highest initial concentration (120 mg/L).

Further increase in desorption time (Figure 3) strongly affected the change in desorption, and the calculated desorbability peaked after 3–5 h. Moreover, it was noticed that desorbability was decreasing and could even be neglected when the time exceeded 18–24 h, especially for smaller concentrations. We suggest two probable explanations for this. First, it was possible that desorbed FLOT 2015 degraded

into compounds that could not be detected using the proposed UV method and the present study elicited the pattern. Second, it is possible that readsorption occurred on the mineral sample. However, only the desorption time changed in the systems studied; therefore, this was not sufficient for this assertion. To investigate the first possibility, a study of the probable middle component after the initial chemical degradation was conducted.

3.4. Study on Tris(2-hydroxyethyl)(methyl)azanium Methylsulfate (3HEMA MS)

As mentioned by Para et al. [11], all esterquats are susceptible to hydrolysis giving intermediate products such as fatty acids and quaternary ammonium compounds (QAC). We supposed that QAC, namely tris(2-hydroxyethyl)(methyl)azanium methylsulfate (3HEMA MS), could be the probable intermediate component after the initial chemical degradation of esterquats-containing reagent FLOT 2015.

The structural formula of tris(2-hydroxyethyl)(methyl)azanium ion with positive charge on nitrogen is presented in Figure 4.

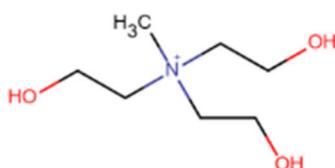


Figure 4. Structural formula of tris(2-hydroxyethyl)(methyl)azanium ion.

3HEMA MS is an ionic liquid and highly polar fluid. The water content of ionic liquids is remarkably important because of its effect on relevant physical properties such as viscosity. The behavior of 3HEMA MS is very different than that of other quaternary ammonium compounds (QAC) related to water affinity [41]. The water–cation interactions could improve with the number of hydroxyethyl chains increased. However, 3HEMA MS possesses a lower water affinity compared to other QAC with a single or double hydroxyethyl chain. Furthermore, Aparicio et al. [42] reported that the ionic liquid in water-rich solutions behaves as isolated non-interacting ions solvated by water molecules, exerting a disrupting effect on the water hydrogen-bonding network. Nevertheless, as ionic liquid concentration increases, interionic association increases, even for diluted water solutions, evolving from the typical behavior of strong electrolytes in solution toward large interacting structures. For ionic liquid-rich mixtures, water exerts a minor disrupting effect on the fluid’s structuring because it occupies regions around each ion (developing water-ion hydrogen bonds) but without significantly weakening anion–cation interactions.

3HEMA MS-BCP Complex Formation

Ion pair complex formation between 3HEMA MS and BCP was studied using the validated UV-method. We used three different solvents for 3HEMA MS dissolution: methanol, ethanol, and acidic water (pH 5.5). The tests were conducted in deionized water and seawater. The procedure was the same as for FLOT 2015 determination. The results are summarized in Table 3.

Table 3. Effect of 3HEMA MS concentrations on ion pair formation with BCP.

Concentration of 3HEMA MS, mg/L	Absorbance	Concentration of 3HEMA MS Found after Addition, mg/L
0	0.00	0.00
20	0.00	0.00
50	0.00	0.00
1000	0.00	0.00

It was found that the type of the solvent did not influence determination. The increase in 3HEMA MS concentrations did not affect the absorbance (no color change in the chloroform layer). It is obvious that 3HEMA MS did not form a color complex with BCP in distilled water and seawater. Furthermore, a small amount of FLOT 2015 (4 mg/L) was added to check the method (Table 4).

Table 4. Effect of 3HEMA MS on FLOT 2015 determination.

Concentration of FLOT 2015, mg/L	Concentration of 3HEMA MS, mg/L	Absorbance	Concentration of FLOT 2015 Found after Addition, mg/L	Total FLOT 2015 Recovered, %	Mean Recovery, %
4.00	0	0.260	4.00	100.00	
4.00	20	0.261	4.00	100.00	100.00
4.00	50	0.260	4.00	100.00	
4.00	1000	0.260	4.00	100.00	

As seen from Table 4, the addition of FLOT 2015 shows the selectivity of the method related to FLOT 2015.

3.5. Degradation Tests

Figure 5 shows the effect of time and pH on FLOT 2015 detection in various mediums.

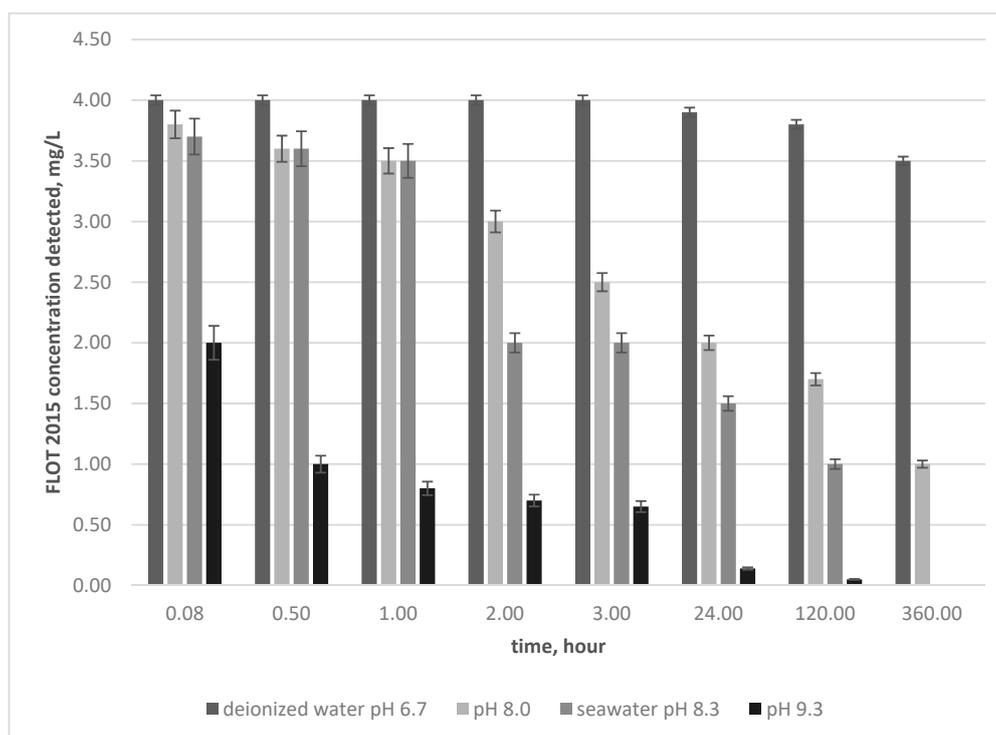


Figure 5. Effect of time and pH on FLOT 2015 determination by the proposed UV-method.

As seen from Figure 5, some differences were observed in the concentrations of FLOT 2015 detected in different samples even after 5 min of storage. In deionized water, the detected concentration of FLOT 2015 did not change from the initial concentration. In the sample with pH 8.0 and the seawater sample, the detected concentrations were slightly less than the initial one. It was probably affected by alkaline pH and ions available in the seawater. However, in the sample with pH 9.3, the level of detection was much lower. These tests revealed that only half of the initial concentration was detected after 5 min of storage. This could be attributed to the fast hydrolysis in the alkaline medium [9]. The storage time less than 24 h did not show a significant change in the FLOT 2015 concentration detected in deionized water, while the concentration in all other samples decreased to 50–70% of

the initial value. Also, it was found that FLOT 2015 was undetectable in samples 3 and 4 (seawater and alkaline water pH 9.3) after storage for 15 days. It seems that after several hours of storage in an alkaline medium, the main components of FLOT 2015 were transformed to the other compounds that could not be detected using the proposed UV method. Our data are consistent with the proposals that seawater or water with an alkaline pH would speed up the chemical degradation of FLOT 2015. Ideally, we would recommend that longer-term storage in alkaline medium should be applicable for the decomposition of FLOT 2015 via chemical degradation (alkaline hydrolysis) and the formation of less toxic compounds for further biodegradation via microorganisms in seawater.

Based on the known mechanism of degradation for several esterquats, tests on 3HEMA MS, and indirect degradation tests, there was evidence to suggest the probable pathways for chemical and biological degradation of FLOT 2015. The degradation of the main component of FLOT 2015 in seawater (pH 8.3) started with the chemical degradation of the reagent via basic hydrolysis and yielded in the fission of C–O bonds. It gave the formation of the fatty acids and the short triol quaternary ammonium salt, namely 3HEMA MS. Brooks et al. [43] have already noted hydrolytic reactions in contact FLOT 2015 with water that result in a mixture of fatty acids and 3HEMA MS. As seen from the study [43], 3HEMA MS is measurable by ultra-high performance chromatography coupled to mass spectrometry and has accumulated in exposed mussels. The fatty acids and 3HEMA MS are readily biodegradable into inorganic end products such as water, carbon dioxide, and mineral salts. The biological degradation of 3HEMA MS proceeds due to a cleavage of the C–N bond, resulting in acetaldehyde and ammonia without the formation of resistant intermediate products. Then acetaldehyde can be oxidized into acetic acid, also giving the same inorganic end products.

4. Conclusions

A method for rapid assessment of the concentration of chemicals and their probable degradation in aqueous systems prior to tailings deposition would constitute a useful tool in environmental impact analysis. A robust, simple, and low-cost UV-spectrophotometric method was validated and proposed for quantification of an esterquats-containing reagent FLOT 2015 in marine ecosystems. Our research found that the rate of FLOT 2015 desorption using seawater increased in time and the calculated desorbability peaked after 3–5 h. Moreover, it was noticed that desorbability was decreasing and could even be neglected when the time exceeded 18–24 h, especially for smaller concentrations. Our data are consistent with the proposals that seawater or water with alkaline pH would speed up the chemical degradation of FLOT 2015 and longer-term storage in alkaline medium should be applicable for the cleavage of FLOT 2015 via chemical degradation and formation of less toxic compounds for further biodegradation via microorganisms in seawater. Based on known mechanism of degradation for several esterquats, tests on 3HEMA MS, and indirect degradation tests, the probable pathways for chemical and biological degradation of FLOT 2015 were suggested. Combined with techniques for the direct characterization of surface-adsorbed species, this selective and specific method can be applied efficiently in aqueous mineral processing systems and offers new insight into the fate of flotation chemicals when the tailings are exposed to seawater.

Author Contributions: O.I. and R.A.K. designed the conceptualization; O.I. designed methodology and validation of the method; O.I. contributed to investigation and analyses of the results; O.I. and R.A.K. wrote the article; R.A.K. contributed to funding acquisition and supervision.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Artificial seawater was prepared according to the procedure given by Kester et al. [34]. Composition of artificial seawater is presented in Table A1.

Table A1. Composition of artificial seawater.

Contributions of Ions	Concentration, %
Cl ⁻	19.353
Na ⁺	10.764
SO ₄ ²⁻	2.700
Mg ²⁺	1.297
Ca ²⁺	0.408
K ⁺	0.387
HCO ₃ ⁻	0.142
Br ⁻	0.066
Sr ²⁺	0.014
H ₃ BO ₃	0.026
F ⁻	0.001
Total	35.158

To avoid precipitation of insoluble compounds two separated containers were used for artificial seawater preparation. Tables A2 and A3 show the compositions and concentrations of salts in containers 1 and 2, respectively.

Table A2. Composition and concentration of salts in container 1.

Salts	Concentration, g/kg of the Solution
NaCl	23.926
Na ₂ SO ₄	4.008
KCl	0.877
NaHCO ₃	0.196
KBr	0.098
H ₃ BO ₃	0.026

Table A3. Composition and concentration of salts in container 2.

Salts	Concentration, mol/kg of the Solution
MgCl ₂ ·6H ₂ O	0.05330
CaCl ₂ ·2H ₂ O	0.01030
SrCl ₂ ·2H ₂ O	0.00009

In container 2, the concentration of the chlorides ions was determined using the Mohr method [44]. Artificial seawater was obtained by combining the solutions from two containers and was aerated by drawing laboratory air through the final solution until the pH value did not change (pH 8.2). This procedure tended to stabilize artificial seawater using atmospheric gases and carbon dioxide. The chlorinity of artificial seawater was also determined using the Mohr method.

In order to determine the chlorinity of artificial water prepared using the Mohr method, AgNO₃ (0.1 M) (VWR Chemicals, Prolabo, Leuven, Belgium) and K₂CrO₄ (indicator) (HACH LANGE, Duesseldorf, Germany) were used. A total of 20 mL of the seawater sample was taken in 100 mL flask and deionized water was added up to the mark. A total of 10 mL of the new solution was taken, and 50 mL of water and one pellet of K₂CrO₄ were added to the new solution. The final solution was titrated with 0.1 M AgNO₃. The tests were repeated three times to get the representative result and the average volume of AgNO₃ was calculated. The moles of AgNO₃ and the moles of chloride ions reacting were determined using the equation: Ag⁺(aq) + Cl⁻(aq) → AgCl(s). Then the

concentration of chloride ions in the diluted seawater and the original undiluted seawater were calculated. The concentration of sodium chloride in the seawater was determined in %.

The chlorinity of artificial seawater was equal to 19.397 with a salinity of 35.222.

Appendix B

Figure A1 represents the corresponding UV spectrum of BCP in deionized water recorded at 574 nm. Chloroform extracts of the systems FLOT 2015-BCP were measured at 380 nm against chloroform as a blank and a corresponding UV spectrum of the FLOT 2015-BCP complex is shown in Figure A2. A calibration curve, which showed a linear response, was constructed by plotting the absorbance of the FLOT 2015-BCP complex or extract in chloroform versus the concentration of FLOT 2015 in the initial water solution (Figure A3). The linear regression analysis of the calibration data gave the regression results shown in Table A4 with correlation coefficients close to unity.

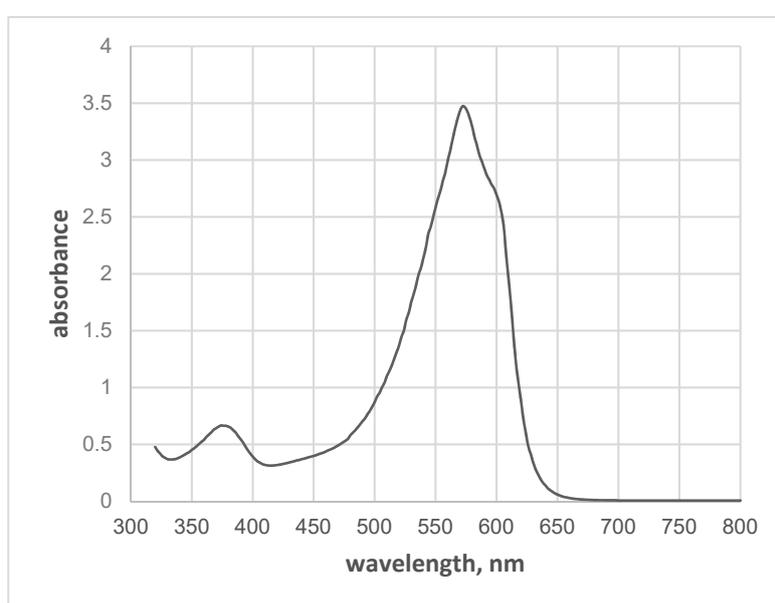


Figure A1. UV spectrum of BCP in deionized water.

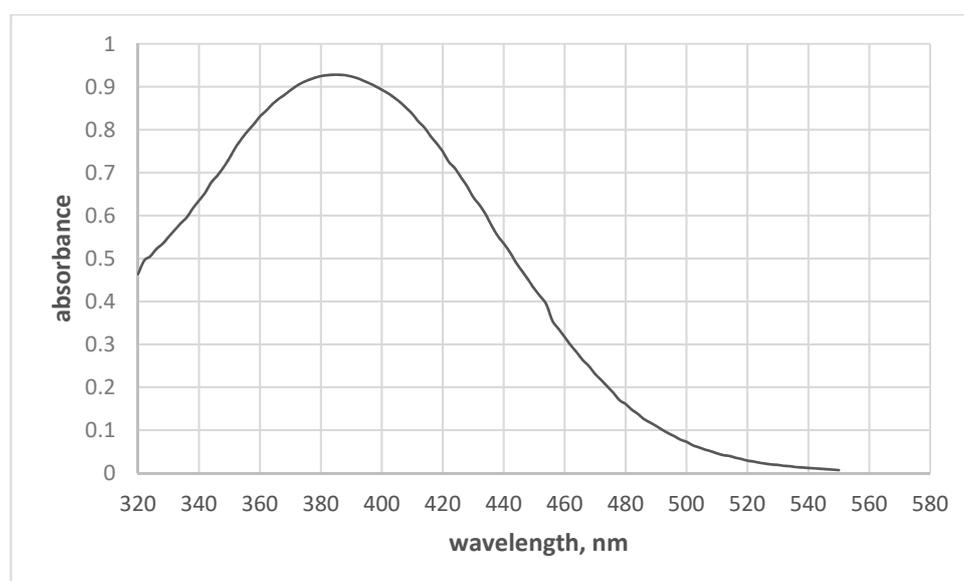


Figure A2. Absorption spectrum of the FLOT 2015-BCP ion pair complex in chloroform.

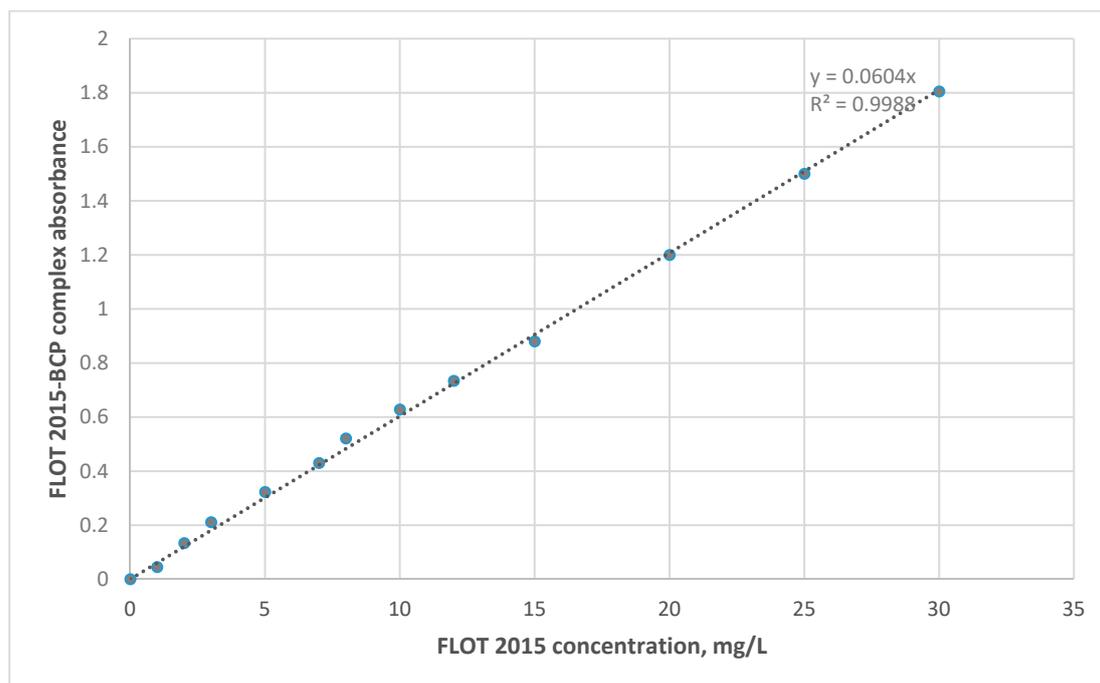


Figure A3. Linearity of the FLOT 2015-BCP complex absorbance corresponding to the concentration of FLOT 2015 in the water solution.

Table A4. Validation parameters.

Parameter	Result
Absorption maximum (nm)	380
Linearity range (mg/L)	0.5–30
Standard regression equation	$y = 0.0604x$
Correlation coefficient R^2	0.9988
Standard deviation (SD)	0.00515
Relative standard deviation (RSD)	0.5789
Intraday precision (RSD%)	2.08
Interday precision (RSD%)	2.8
LOD (mg/L)	1
LOQ (mg/L)	2

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