

Article

New Eco-Friendly Xanthate-Based Flotation Agents

Milutin M. Milosavljević ^{1,*}, Aleksandar D. Marinković ², Milica Rančić ³, Goran Milentijević ¹, Aleksandra Bogdanović ², Ilija N. Cvijetić ⁴  and Dejan Gurešić ¹

¹ Faculty of Technical Science, University of Priština, Knjaza Miloša 7, 38220 Kosovska Mitrovica, Serbia; goranmilentijevickm@gmail.com (G.M.); dejan.guresic@pr.ac.rs (D.G.)

² Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P.O. Box 3503, 11120 Belgrade, Serbia; marinko@tmf.bg.ac.rs (A.D.M.); abogdanovic@tmf.bg.ac.rs (A.B.)

³ Faculty of Forestry, University of Belgrade, Kneza Višeslava 1, 11030 Beograd, Serbia; milica.rancic@sfb.bg.ac.rs

⁴ Innovation center of the Faculty of Chemistry, University of Belgrade, Studentski trg 12, 11158 Belgrade, Serbia; ilija@chem.bg.ac.rs

* Correspondence: milutin.milosavljevic@pr.ac.rs

Received: 25 March 2020; Accepted: 10 April 2020; Published: 14 April 2020



Abstract: An optimal laboratory two-step procedure was developed for sodium/potassium *O*-alkyl carbonodithioate (sodium/potassium alkyl xanthates) production in the form of aqueous solutions. Sodium isopropyl xanthate (Na-iPrX), as the most effective salt in a real ore flotation process, was also produced at an industrial level and introduced as a collector for copper ores. In order to reduce toxicity of the flotation process and improve sustainability by minimising environmental impacts, collector efficiency and selectivity in the flotation process were studied in relation to possible synergism of xanthates combined with the derived biomass and biodegradable green reagents levulinic acid, 5-hydroxymethyl-2-furanacrylic acid (HMFA), and condensation product of hydroxymethylfurfural and levulinic acid. Optimal content of 30% of HMFA in the collector pointed to the possibility of substitution of commercial xanthate collector without significantly affecting its efficiency/selectivity. The density functional theory (DFT) calculations provided insights into the interaction mechanism of Na-iPrX and HMFA with copper. The benefits of the presented method highlight production simplicity, mild reaction conditions, high purity and yield of products, no by-products, and technological applicability on an industrial scale.

Keywords: alkyl xanthate; levulinic acid; 5-hydroxymethyl-2-furanacrylic acid; flotation; DFT

1. Introduction

Flotation is the most common process applied in mineral separation to recover valuable minerals. In this process, the surface of a target mineral is rendered hydrophobic by the attachment of a collector by chemical adsorption, van der Waals forces, or electrostatic bonds. Collectors are generally active toward whole mineral classes, e.g., sulfide minerals, rather than toward a specific mineral. The limited resources of today's mining industry increase the need for the development of more efficient collectors, while also reducing environmental risks [1–7]. Since the beginning of the 20th century, xanthates (*O*-alkyl dithiocarbonates) have been widely used as reagents for the flotation concentration of a variety of sulfide and oxide minerals because of their capability to attach to hydrophobic agents [8–10]. Metal-xanthate complexes and their adducts with a variety of Lewis bases have been extensively studied [11] and soluble alkali xanthates widely used in the extraction and purification of Hg, Ag, Cd, etc. [12]. Along with mineral separation to recover valuable minerals, the application of xanthates in flotation processes will enable improved selective adhesion, which can allow economic recycling and contribute to green chemistry in waste water treatment. The difference in the collectors is presented in

their selectivity, which is based on their strength to adjust to hydrophobic agents on one side and bubble of the air on the other. Collector capability can be improved by increasing its activity and adhesive ability. Various studies have emphasized the importance of surface oxidation of sulfide minerals concerning xanthate adsorption and their flotation response [13,14]. According to their chemical compositions and affinities, some flotation collectors tend to be attracted to certain compounds more than others, based on their selectivity. As the process of flotation is based on differences in surface properties of different compounds in an effort to achieve separation, the adjusted selectivity of the collectors presents the aim of the research. The selectivity depends on the structure of the xanthates hydrocarbon (C–H) chain, which affects flotation recovery. The effectiveness and adhesive power of xanthates increase with increasing chain length, depending on the chain structure—branched and straight chains. Although longer chain xanthates are more effective in the flotation of sulfide minerals and thus less collector is needed to achieve the same recovery of sulfides, solubility in water decreases with increasing chains length, reducing their effectiveness. Therefore, there exists an optimum chain length of xanthates for a particular flotation system [15]. The mechanism of mineral-collector bonding depends on the collector type and nature and charge of the mineral surface, and can occur via physisorption or chemical bonding. In the case of physisorption, the collector does not interact with the mineral surface. The bonds are amorphous and the Gibbs free energy of adsorption is relatively low [16].

Xanthates are most commonly obtained by the reaction of alcohol, hydroxide, and carbon disulfide, or by the reaction of alkoxide, which is obtained by the reaction of alcohol and hydroxide, alcohol and alkali metal, ether and hydroxide with carbon disulfide [10]. There are numerous technological procedures for the synthesis of alkaline alkyl xanthates, many of which are applied at the industrial level and protected by patent applications [11–25]. The optimized laboratory two-step procedure presented in this paper relates to the improved process for the production of xanthate collectors at high yield in the form of an aqueous solution or in a solid state (powdery product). Thus, the present research aimed to develop a water-soluble xanthate solution readily applicable at the site of application. However, xanthates have many occupational health and environmental risks due to their toxicity. The mining industry is currently facing significant challenges in identifying and adopting sustainable collector chemistries that can effectively recover valued minerals. On the other hand, the exploitation of biomass-derived molecules is an increasingly developed strategy for cleaner production, improving sustainability by minimising environmental impacts [26]. Among the various strategies for biomass valorization, the production of 5-hydroxymethylfurfural (HMF) from hexoses is a versatile platform for the synthesis of furan-based chemicals. The main aim of this research is to enhance efficiency and selectivity by synergism of xanthate collectors combined with levulinic acid (LA), 5-hydroxymethyl-2-furanacrylic acid (HMFA), and condensation product of HMF and LA (HMF-LA) in the process of separation of different compounds in the flotation process.

Specific objectives of the presented study were directed to: (1) optimization of the process for production of water soluble sodium/potassium alkyl xanthates; (2) xanthate stability testing; (3) industrial production of selected alkyl xanthates; (4) optimization of the content of the product using green flotation additives; (5) and evaluation of the flotation efficiency using real ore samples.

2. Materials and Methods

All reagents and chemicals for the synthesis were purchased from commercial sources (Sigma, St. Louis, MO, USA), while for the biological researches, chemicals were of reagent grade (Merck, Kenilworth, NJ, USA) and used as received. All commercially available chemicals—chloroform, xylene, sodium hydroxide, potassium hydroxide, carbon disulfide, ethanol, zinc chloride, iodide, hydrochloric acid, *D*-fructose, ethyl acetate, sodium sulfate, dichloromethane, pyrrolidine, calcium chloride, malonic acid, piperidine, and hydrogen sulfide—were purchased from Sigma-Aldrich. All solvents were of reagent purity and used without further purification. Flotation experiments were performed with the real ore samples supplied from the region of Elatsite-Bulgaria. Microwave reactions were carried out

in an Anton Paar Monowave 300 microwave (2.45 GHz, Anton Paar GmbH, Graz, Austria). The ^1H and ^{13}C NMR spectral measurements were done on a Varian Gemini 2000 (Varian Inc., Palo Alto, CA, USA). The spectra were recorded at room temperature in deuterated chloroform (CDCl_3) at ambient temperature. The chemical shifts are expressed in ppm values referenced to TMS ($\delta_{\text{H}} = 0$ ppm) in ^1H NMR spectra, and the residual solvent signal ($\delta_{\text{C}} = 39.5$ ppm,) in ^{13}C NMR spectra. The chemical shifts were assigned by the complementary use of DEPT, two-dimensional ^1H - ^{13}C correlation HETCOR, and selective INEPT long-range experiments. Fourier-transform infrared spectra were recorded in transmission mode using a Bomem (Hartmann & Braun, Frankfurt, Germany) spectrometer.

2.1. Optimization of the Sodium/Potassium Alkyl Xanthate Synthesis

Optimization of the sodium/potassium alkyl xanthate synthesis was carried out in relation to: reaction time, temperature, molar ratio of the reactants, and the amount of solvent (the amount of xylene used as solvent determines the obtained percentage of product suspension in the reaction mixture). The synthesis of sodium/potassium alkyl xanthate was carried out according to the reaction scheme presented in Figure 1.

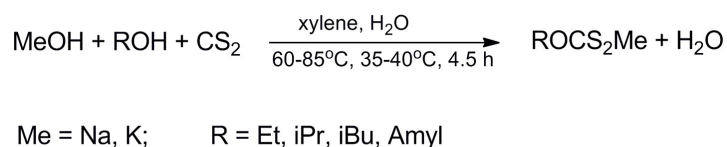


Figure 1. Reaction of alkali alkyl xanthate synthesis.

2.2. Sodium Ethyl Xanthate Synthesis (Na-EtX)

An amount of 96 g (2.30 mol) of 96.7% sodium hydroxide and 25 cm³ of water were added to a 4 dm³ three-necked flask, equipped with a stirrer, dropping funnel, reflux condenser and thermometer, and the mixture was heated until sodium hydroxide was dissolved. Afterwards, a mixture of 110.0 g (2.30 mol) of 96.0% ethanol and 1400 cm³ of xylene was added using a dropping funnel, followed by stirring and heating the reaction mixture at a temperature of 65 °C for 1.5 h. The reaction mixture became silvery-white and quite viscous, so intensive mixing was necessary. After 1.5 h, the reaction mixture was cooled to 35 °C when the addition of 128.0 cm³ (2.1 mol) of 98.0% of carbon disulfide began. Carbon disulfide was added dropwise for 1.5 h while maintaining the reaction mixture temperature in the range of 35–40 °C. Then, 237.5 cm³ of water was added; the reaction mixture was stirred for 5 min and transferred to the separation funnel, extricating the upper layer of xylene from the lower aqueous portion, which is a solution of the synthesized Na-EtX. The upper organic layer of xylene was further used as a reaction medium for the subsequent synthesis of xanthates. The resulting Na-EtX aqueous solution (526.30 g) was analyzed to obtain pure product content (1.82 mol, 50% aqueous solution), obtaining a yield of 87.71%. Synthesis of other sodium/potassium alkyl xanthates was done analogously.

2.3. Analytical Methods of Xanthate Analysis

2.3.1. Laboratory Procedure for Determining the Active Substance Content or Purity of Xanthate in the Synthesized Compounds

The mixture of about 0.5 g xanthate sample accurately weighed on the analytical balance, 50 cm³ of distilled water, and 20 cm³ of 10% BaCl_2 solution was first well stirred, and then left to obtain the precipitate, which was filtered; the filtrate was collected in the Erlenmeyer flask of 300 cm³, then 35 cm³ of 1 M HCl solution was added, and allowed to stand for 40 min. After that, the excess acid was

retitrated with 0.1 M NaOH solution to the endpoint (to a yellow color) with the methyl-rot indicator. The active substance (xanthate) content was calculated using Equation (1):

$$\% \text{MeSCSOR} = \frac{(V_{\text{cm}^3 0.1\text{MHCl}} \cdot F_{0.1\text{MHCl}} - V_{\text{cm}^3 0.1\text{M NaOH}} \cdot F_{0.1\text{MNaOH}}) \cdot E \cdot 100}{m_{\text{sample}}}, \quad (1)$$

where $E = 0.1442$ for Na-EtX; $E = 0.01582$ for Na-iPrX; $E = 0.01722$ for Na-iBuX; $E = 0.01603$ for K-EtX; $E = 0.01883$ for K-iBuX; and $E = 0.02023$ for K-AmX [27].

2.3.2. Laboratory Procedure for Determination of Sulfides in Xanthate

A sample of 2–3 g of xanthate was weighed and quantitatively transferred to a measuring flask of 250 cm³; 50 cm³ of water was added, and then 10 cm³ of 10% BaCl₂ solution was added and filled up to the graduation mark with distilled water. This way, sulfates, sulfites, and carbonates were precipitated. After standing for 30 min, the mixture was filtered, and to 50 cm³ of the filtrate, 50 cm³ of a 1 M solution of HCl was added and left to stand for 1 h. The excess acid was titrated with 0.1 M NaOH solution to the end point with methyl orange (volume A), and then titration continued with phenolphthalein (volume B). The difference B-A refers to the content of sulfide (S²⁻) in xanthate and F to the concentration of HCl; sulfide contents were calculated according to Equations (2) and (3).

$$\% \text{Na}_2\text{S} = \frac{2 \cdot (B - A) \cdot F \cdot 3.9 \cdot 5}{m_{\text{sample}} \cdot 10}, \quad (2)$$

$$\% \text{K}_2\text{S} = \frac{2 \cdot (B - A) \cdot F \cdot 5.5 \cdot 5}{m_{\text{sample}} \cdot 10}, \quad (3)$$

2.3.3. Laboratory Procedure for Determination of Trithiocarbonates in Xanthate

A sample of 2–3 g of xanthate was weighed and dissolved in 20 cm³ of distilled water; 100 cm³ of ethanol and 5 cm³ of 10% zinc chloride solution were then added. After 10 min, the mixture was filtered using the G4 filter, the precipitate was well washed with ethanol, followed by distilled water. The combined filtrate was treated with 15 cm³ of 1 M hydrochloric acid solution and allowed to stand for 30 min. After that, an excess of iodine was added which, after 15 min, was back-titrated with a standard solution of 0.1 M Na₂S₂O₃. Under these conditions, sulfide and thiocarbonate also react, so it is necessary to correct the values by subtraction for a particular sulfide. Equations (4) and (5) were used for the calculation of trithiocarbonates contents.

$$\% \text{Na}_2\text{CS}_3 = \frac{(V_{0.1\text{MJ}_2} \cdot F - V_{0.1\text{MNa}_2\text{S}_2\text{O}_3} \cdot F) \cdot 7.7}{10 \cdot m_{\text{sample}}}, \quad (4)$$

$$\% \text{K}_2\text{CS}_3 = \frac{(V_{m10.1\text{MJ}_2} \cdot F - V_{\text{cm}^3 0.1\text{MNa}_2\text{S}_2\text{O}_3} \cdot F) \cdot 9.3}{10 \cdot m_{\text{sample}}}, \quad (5)$$

2.4. Synthetic Procedures

2.4.1. Synthesis of 5-(Hydroxymethyl)-2-Furfural (HMF)

Process of D-fructose dehydration to HMF was performed as follows: in a G10 vial for a microwave reactor equipped with a magnetic grain and a cover, 10 cm³ of 30% solution of D-fructose in water (D-fructose, C₆H₁₂O₆) and 1.1 cm³ of 0.1 M hydrochloric acid (HCl) solution were added. Closed vials were placed in the reactor bay (Monowave 300, Anton Paar) and the reaction temperature was set to 160 °C and kept constant for 5 min with intensive stirring (800 min⁻¹). After cooling, the product was extracted with ethyl acetate (2 × 10 cm³) and the collected organic extracts were dried with sodium

sulfate. The solvent was removed by distillation, leaving a deep red product. The product was further purified by dissolution in ether and the addition of activated carbon [28].

2.4.2. Synthesis of Levulinic Acid (4-Oxovaleric Acid, LA)

Process of the D-fructose dehydration to levulinic acid (LA) was performed as follows: In a 250 cm³ flask, 50 cm³ of 30% aqueous D-fructose was added. pH was adjusted to 0.46 with 0.1 M hydrochloric acid (HCl) added dropwise to the solution. Afterwards, the solution in the glass was intensively stirred for a few minutes and then transferred to a vial G10 for microwave reactor (Monovave 300, Anton Paar) equipped with a magnetic grain and a cover. The reaction temperature was set to 160 °C and maintained for 5 min with the stirring (1000 min⁻¹). After cooling, active carbon was added and solution was stirred for 30 min and filtrated [29].

2.4.3. Condensation Reaction of HMF and LA (HMF-LA)

In a 5 cm³ round bottom flask, 0.0526 g of 5-(hydroxymethyl)-2-furfural (HMF, 0.4178 mmol) and 0.0485 g of levulinic acid (LA, 0.4178 mmol) were added, followed by addition of 2 cm³ of dichloromethane (DCM) and one drop of pyrrolidine [30]. The reaction mixture was stirred at room temperature for 12 h. The reaction flow was monitored using thin layer chromatography (TLC). After the reaction completion, the reaction mixture was diluted with water and extracted three times with 2 cm³ of ethyl acetate. The organic part was separated and dried by the addition of anhydrous calcium chloride, after which the solvent was evaporated.

2.4.4. Synthesis of 5-Hydroxymethyl-2-Furanacrylic Acid (HMFA)

Synthesis of 5-hydroxymethyl-2-furanacrylic acid was performed from HMF according to the Doebner modification of the Knoevenagel condensation [31]. The HMF (1.2634 g, 10 mmol), malonic acid (2.081 g, 20 mmol), and piperidine (69.1 cm³, 0.7 mmol) were dissolved in pyridine (4.0 cm³, 49.7 mmol) and the reaction mixture was refluxed at 90 °C. The reaction was monitored by TLC until the completion after 5 h. The reaction mixture was quenched by 1 M HCl until pH 1 was achieved. The obtained product was extracted by ether and the solvent was evaporated under reduced pressure to yield 1.612 g of a yellow-orange crystalline powder.

2.4.5. DFT Calculations

The initial 3D structures of HMFA and NaiPrX were generated using CORINA online software (Molecular Networks GmbH, Nürnberg, Germany). The structures were further optimized using the semiempirical quantum chemical PM6 method [32]. The final geometries and electron densities were obtained from DFT calculations using B3LYP functional and 6-311g++(d,p) basis set. Frequency calculations confirmed the absence of imaginary vibrational frequencies, so structures represented the true minima. All geometry optimizations were done using Gaussian 09 [33]. The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), and molecular electrostatic potential (MEP) surfaces were plotted in Gaussview 5.0 [34]. The MEP extrema were calculated using Multiwfn 3.7 [35].

3. Results and Discussion

3.1. Results of the Optimization of Na-EtX Synthesis Parameters

In the experimental part of this paper, optimal parameters of sodium/potassium alkyl xanthate synthesis were determined following the reaction of alcohol, sodium/potassium hydroxide, and carbon disulfide in xylene as the reaction medium. The optimization of the synthesis process was made by determining the yield of the obtained products and the content of the active substance (concentration of the obtained product in the aqueous solution) depending on the reaction parameters: reaction time (Table 1), temperature of the first and second reaction step (Table 2), molar ratio of reactants (Table 3),

concentration of the reaction mixture suspension (Table 4) (solvent used -xylene). The results of the optimization of the Na-EtX synthesis are presented in detail in this paper (Tables 1–4), while that of the other synthesized xanthates are summarised in Table 5.

Table 1. Dependence of Na-EtX yield versus reaction time (reaction conditions: temperature: I reaction step 65 °C, II reaction step 35–40 °C, reagents ratio (mol): EtOH/NaOH/CS₂ = 1.1/1.1/1.1).

Experiment	Time (h)	Na-EtX Yield			Purity ¹ (%)
		(g)	(mol)	(%)	
1	3.00	510.00	1.70	81.60	48.00
2	4.00	511.00	1.71	81.62	48.00
3	4.50	526.30	1.82	87.71	50.00
4	5.00	526.31	1.82	87.70	50.00

¹ Product concentration Na-EtX in water solution.

Table 2. Dependence of Na-EtX yield from temperature (reaction conditions: reaction time 4.5 h; reactants ratio (mol): EtOH/NaOH/CS₂ = 1.1/1.1/1.1).

Experiment	Reaction Temperature ¹ , (°C)		Yield of Na-EtX			Purity ² (%)
	I	II	(g)	(mol)	(%)	
1	65	35	526.30	1.83	87.72	50.00
2	75	35	527.00	1.82	86.71	50.00
3	65	30	512.66	1.78	85.33	48.88
4	60	25	491.25	1.70	80.82	46.93

¹ I-first step and II-second step of the reaction. ² Concentration of the synthesized product Na-EtX in water solution.

Table 3. Dependence of the Na-EtX yield from the reactant ratio (reaction conditions: reaction time 4.5 h; temperature: I reaction step–65 °C, II reaction step–35 °C).

Experiment	EtOH (96.0%)		CS ₂ (98.0%)		NaOH (96.7%)		Yield (%)	Purity ¹ (%)
	(g)	(mol)	(cm ³)	(mol)	(g)	(mol)		
1	100.4	2.10	128.0	2.10	87.6	2.10	83.70	47.81
2	110.0	2.30	128.0	2.10	96.0	2.30	87.70	50.10
3	115.0	2.40	128.0	2.10	100.1	2.40	86.50	49.65

¹ Concentration of the synthesized product Na-EtX in water solution.

Table 4. Dependence of Na-EtX yield from product suspension concentration.

Experiment	Suspension (%)	Reaction Conditions				
		Reaction Time (h)	Temperature (°C) I Step II Step	Reactants Molar Ratio EtOH/NaOH/CS ₂	Yield (%)	
1	10	6.0	60–65 35–40	1.1/1.1/1.0	75.02	
2	15	5.0	60–70 35–45	1.1/1.1/1.0	80.01	
3	20	4.5	60–65 35–40	1.1/1.1/1.0	87.70	
4	25	4.5	65–70 35–40	1.1/1.1/1.0	85.21	

The optimal reaction time of the Na-EtX synthesis was 4.5 h, when a yield of 87.71% was achieved. Extending the reaction time to 5 h does not provide a higher degree of conversion of the reactants into the product.

It is to be noted that the optimal temperature for the first step that represents alcoholate synthesis is 65 °C, while for the second step of xanthate synthesis in xylene in the form of a suspension of 35 °C, the yield is 87.72%. At lower temperatures, the yield decreases, and the resulting product is less pure. This is probably due to the formation of secondary products of tritio carbonate, since the reaction of carbonate sulfide with sodium hydroxide is favored at a lower temperature. It is not recommended to

increase the temperature of the reaction mixture in the second step of the reaction over 40 °C, as it includes easily evaporative and flammable reactants, and consequently, a significant increase in yield is not achieved.

Concerning the results of the dependence test of the yield of Na-EtX synthesis on the molar ratio of reactants (Table 3), the highest conversion (87.70%) was achieved using the molar ratio of the reactants EtOH/NaOH/CS₂ = 1.1/1.1/1.0. Increasing the concentration of reactants does not improve yield due to the formation of the by-product and the residue of unreacted carbon disulfide.

The dependence of the Na-EtX yield on product suspension concentration (Table 4), indicated that the optimal concentration of the suspension is 20%. A yield of 87.70% was achieved when reactants reacted in the present medium xylene in an amount yielding 20% suspension of the final product. Increasing the concentration of reactants in order to increase reactor productivity is not desirable due to the formation of a concentrated product suspension, which causes difficulties in mixing of the reaction mixture and by-product formation. In addition, reducing reactant concentrations does not result in satisfactory yields and product purity due to the lower probability of properly-oriented collisions of the particles that react, even with prolonged reaction times (Experiments 1 and 2).

3.2. Results of Optimization of the Conditions of Sodium/Potassium Alkyl Xanthate Synthesis

In an analogous manner, as per the optimal synthesis of the Na-EtX in laboratory conditions, a series of alkyl xanthates was synthesized: sodium isopropyl xanthate (Na-iPrX), sodium isobutyl xanthate (Na-iBuX), potassium ethyl xanthate (K-EtX), potassium izobutyl xanthate (K-iBX), and potassium amyl xanthate (K-AmX). The obtained results are presented in Table 5.

Table 5. Results of the optimization of sodium/potassium alkyl xanthates synthesis.

Product	Reaction Conditions			Molar Ratio of Reactants ROH ² /MOH ³ /CS ₂	Yield (%)
	Time (h)	Temperature ¹ (°C)	Product Suspension (%)		
Na-EtX	4.5	60–65/35–40	20	1.10/1.10/1.00	87.71
Na-iPrX	4.5	70–75/35–40	20	1.03/1.00/1.04	85.91
Na-iBuX	4.5	75–80/35–45	20	1.03/1.00/1.05	83.30
K-EtX	4.5	55–60/35–40	5	1.10/1.0071.00	87.50
K-iBuX	5.0	80–85/35–45	20	1.05/1.0071.07	83.50
K-AmX	5.0	80–85/35–45	20	1.0571.00/1.06	84.40

¹ Temperature of I reaction step/temperature of II reaction step; ² R-Et, iPr, iBu, Am; ³ M-Na, K.

Based on the experimental results of the optimization of the conditions of the sodium/potassium alkyl xanthates synthesis, the main conclusion is that the reaction time parameter for all the experiments shown is 4.5 to 5.0 h. The reaction time of 5.0 h is optimal in the synthesis of K-iBuX and K-AmX. The molecular ratio of the reactants is intended to be such that alcohols are used from 3% to 10% and carbon disulfide from 4% to 7% in excess. Further reactant addition does not lead to an increase in yield, but widens the possibility of side-effects (the formation of tritocarbonate and sulfide). The optimum temperature for the first reaction step is 60–85 °C, and for the second 35–45 °C, with lower reaction temperatures for the synthesis of Na-EtX, Na-iPrX, and K-EtX. In all the experiments, the concentration of suspension of xanthates products is optimal, except in the synthesis of K-EtX, where the concentration of the suspension was 5%. Increasing the concentration of reactants in order to increase the productivity of the reactor does not result in a quality product due to the inability to efficiently mix the reaction mixture and perform the reaction. The highest yield achieved is in the synthesis of Na-EtX, and the lowest for Na-iBuX, which can be explained by the steric factor of the nucleophile in the reaction of the alkoxide ions to the carbon disulfide. Thus, the nucleophilic attack by the ethoxide ions on carbon disulfide is more efficient than that by isopropoxide and isobutoxide, because of more pronounced steric disturbances.

3.3. The Results of the Flotation Efficiency of the Synthesized Sodium Isopropyl Xanthates and Formulated Products Na-iPrX/HMFA

Flotation efficiency of a synthesized flotoreagent was tested on real samples of copper ores with the aim to determine their efficiency. Results of the investigated flotation efficiency of synthetic alkyl xanthates are presented in Table 6. The process of flotation is based on manipulating the surface properties of minerals such that the mineral of interest acquires a hydrophobic surface. When air bubbles are introduced, the hydrophobic minerals attach themselves to the bubbles and are carried to the surface and skimmed away. The mineral's behavior during froth flotation is controlled by its surface properties, which are a function of its chemistry, structure, and surface species formed by reactions during processing. The nature of the surface products formed as a result of the xanthate chemisorption is still under question.

Table 6. Flotation results obtained using synthesized alkyl xanthate and real ore sample (Elacite–Bulgaria) at the laboratory level (copper content of ore—1.8515%, OKCu—basic flotation (first flotation step), KKCu—extended flotation (second flotation step), UKCu—total floated copper, tailing—residual content of copper).

Xanthate	OKCu	KKCu	UKCu	Tailing
	(%Cu)			
Na-EtX	67.80	23.44	91.24	8.76
Na-iPrX	68.90	23.88	92.78	7.22
Na-iBuX	67.01	24.47	91.48	8.52
K-EtX	66.80	23.64	90.44	9.56
K-iBuX	66.85	24.07	90.92	9.08
K-AmX	66.02	23.96	89.98	10.02

In the flotation pulp, the mineral substrate was preliminarily hydrophobized by the chemically attached xanthate or dixanthogen. Both forms of the physically sorbed collector are found on a hydrophobized substrate (mineral) in the form of separate dispersed particles and cannot increase its hydrophobicity [16]. The highest flotation efficiency showed Na-iPrX (Table 6) due to a balanced contribution of hydrophylic part and coordination power of anionic part.

The creation of a favourable chemical environment is of major importance for the success of the flotation process. However, due to the complexity of the process and a large number of influential factors and their interactions, it is extremely difficult to ascertain the contribution of each factor to the overall flotation performance. Hence, various reagents can be added to flotation pulps to manipulate the chemical environment in order to create favourable conditions for the separation of the desired mineral from the unwanted gangue. To investigate the flotation capability of synthesized bio-based potential flotation agent, an analysis of the flotation recovery of the formulated product based on xanthates combined with 10, 15, 20, 25, 30, and 35 mass % of LA, HMF-LA, and HMFA. The best flotation performances were obtained with HMFA, and thus, this material was used in a determination of the optimal ratio of Na-iPrX and HMFA (in wt.%). The results of the flotation efficiency of the formulated reagent Na-iPrX/HMFA depending on mass ratio of Na-iPrX and HMFA, are presented in Table 7. Flotation experiments carried out with copper ores in laboratory conditions were performed in “Denver” flotation machines in volume $V = 2.8$ L, on samples weighing 1 kg, under identical test conditions (fineness of grounded material, flotation time, pH value). Although the Na-iPrX/HMFA flotoreagent is a novelty in its application, in addition to the literary known characteristics of Na-iPrX and HMFA, the applied study was estimated to perform a series of three experiments in the same manner; the results were presented as mean value.

Table 7. Flotation results obtained using Na-iPrX/HMFA flotoreagent (copper content of ore—1.8515%, OKCu—basic flotation (first flotation step), KKCu—extended flotation (second flotation step), UKCu—total floated copper, tailing—residual content of copper).

	Na-iPrX/HMFA	OKCu	KKCu	UKCu	Tailing
	(%Cu)				
1	90/10	69.01	23.41	92.42	7.58
2	80/20	68.25	23.76	92.01	7.99
3	75/25	67.41	24.48	91.89	8.11
4	70/30	66.52	25.20	91.72	8.28
5	65/35	60.11	29.07	89.18	10.82

According to the obtained results shown in Table 6, significant flotation recovery of copper was estimated by application of the Na-iPrX flotation reagent synthesized by described laboratory procedure in this research. Namely, the total of floated copper using Na-iPrX represents 92.78%, while by application of Na-iPrX/HMFA, the maximum achieved value is 91.72% (Table 7). This value of total floated copper of 91.72% is achieved by mass ratio Na-iPrX/HMFA = 70/30. Based on the obtained results of the copper flotation test using the Na-iPrX/HMFA reagent, shown in Table 7, significant flotation effect is achieved in the extended flotation process, achieving the same time of flotation, and the highest content of separated copper was obtained by application of the HMFA reagent in concentration of 30 wt.%; while, with further increase of HMFA content, the flotation power significantly decreases, indicating the technological inefficiency and inability of its application in real conditions. The efficiency of the application of the Na-iPrX/HMFA flotation reagent may be affected by pulp distribution from the mill section, by the slide to the open channel, due to inappropriate mass distribution (70:30 wt.%), as well as different pulp characteristics in terms of solid phase fineness and density. These parameters should be considered, as each of these parameters can affect the efficiency of the flotation process.

3.4. DFT Predictions of the Reactivity of Na-iPrX and HMFA

The DFT methodology is a useful tool to predict the strength and mechanism of bonding interactions between flotation reagents and copper [36]. The molecular electrostatic potential (MEP) extrema show the most reactive sites of a molecule, where maxima represent favorable sites for nucleophilic attack and minima represent sites where electrophile will interact with the molecule. The MEP maps of Na-iPrX and HMFA are shown in Figure 2.

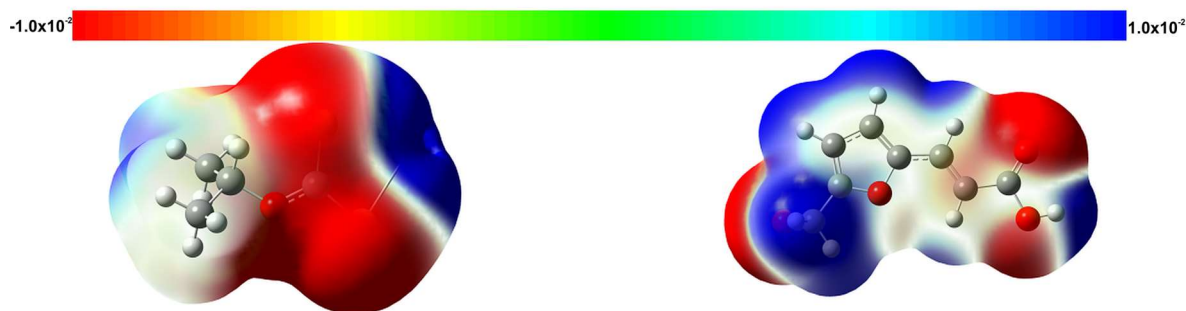


Figure 2. The MEPs of Na-iPrX (left) and HMFA (right) with energy bar in a.u.

The favorable Lewis base sites on Na-iPrX are located at two S atoms, while HMFA is expected to donate electrons to *d*-orbitals on copper surface via carboxylic and hydroxylic O atoms. The electron-accepting sites of Na-iPrX are localized at Na atom, and HMFA might accept electrons around 5-membered HMF ring and at the –COOH and –OH atoms.

The local reactivity of a molecule can also be predicted from HOMO and LUMO distribution. HOMO orbitals are involved in electron-donating reactions, while LUMO are associated with

electron-accepting ability of a molecule. As can be seen from Figure 3, two sulfur atoms of Na-iPrX are electron-donating sites. The flotation agent probably coordinates to Cu ions via donation of S-electrons to the empty *d*-orbitals of metal. Back-bonding between *d*-electrons of a metal surface and LUMO orbital of a flotation agent is less likely, as LUMO density is localized on a sodium atom, which is not a good electron-acceptor.

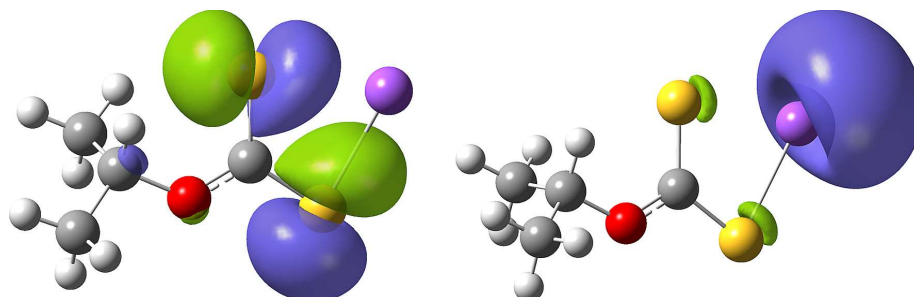


Figure 3. The HOMO (left) and LUMO (right) of Na-iPrX mapped on isovalue of 0.04 a.u.

The HOMO and LUMO of HMFA are more delocalized, compared to Na-iPrX (Figure 4).

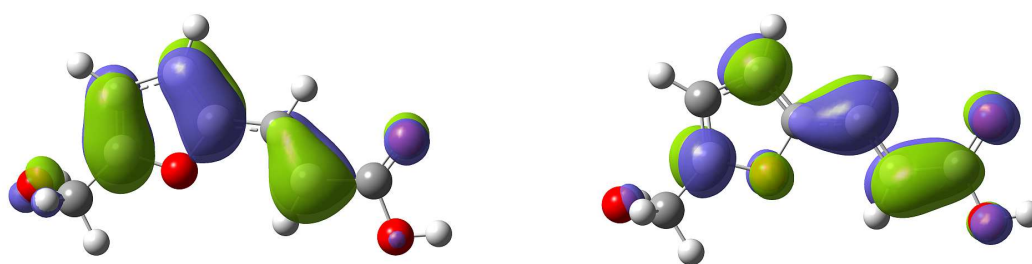


Figure 4. The HOMO (left) and LUMO (right) of HMFA mapped on isovalue of 0.04 a.u.

The HOMO, LUMO energies, dipole moments, and polarizability of Na-iPrX and HMFA are listed in Table 8.

Table 8. Overview of HOMO and LUMO energies, MEP extrema, dipole moments, and polarizabilities for two flotation agents.

Flotation Agent	E_{HOMO} , eV	MEP Max, eV	E_{LUMO} , eV	MEP Min, eV	Dipole Moment, Debye	Polarizability, a.u.
Na-iPrX	−5.586	5.312	−1.548	−1.784	5.004	133.885
HMFA	−6.411	1.970	−2.350	−1.537	1.519	127.244

Higher HOMO energy and more negative MEP minimum indicate higher Lewis basicity of Na-iPrX compared to HMFA and stronger interactions with empty *d*-orbitals of the copper surface. On the other hand, back-bonding with Cu surface is more feasible for HMFA as LUMO energy is lower. Similar study was performed by Ma et. al. [36], showing that the sulfur atoms of S-benzoyl O-isobutyl xanthate (BIBX) are clearly the main electron-donating sites for collector adsorption on the mineral surface. In general, importance of the HOMO orbital from the sulfur atom is of utmost significance to the effective coordination of metal atom, i.e. increased flotation efficiency.

Another study related to the comparative study of thiohexanamide (THA), O-isopropyl-N-ethyl-thionocarbamate (IPETC), and sodium isobutyl xanthate (SIBX) using sulfide ores showed superior selectivity of THA to chalcopyrite [37]. The MEP maps showed the location of most negative regions on C=S and the most positive region on N amide hydrogen atoms. The HOMO density located on sulfur atoms indicated that C=S and −SH groups are the most reactive sites of collectors toward

electrophilic attack. In addition, it was shown that the $-NH_2$ also participates in the creation of the Cu-N bond. The energy gap value ($\Delta E_{HOMO-LUMO}$), as another parameter of chemical reactivity, was the lowest for THA, indicating its highest reactivity.

According to Table 8, similar chemical reactivity of Na-iPrX and HMFA might be expected as $\Delta E_{HOMO-LUMO}$ is quite similar (-4.038 and -4.061 eV, respectively).

Compared to experimental results, it can be concluded that the flotation efficiency does not depend on a single factor such as $\Delta E_{HOMO-LUMO}$, and the effect of crystal structure, morphology, and surface properties of ore and processing conditions should be considered along with collector properties.

In conclusion, the obtained results offer the idea for future design of flotation agents and the selection of most active compounds to increase flotation efficiency.

3.5. Results of the Stability Test of the Synthesized Sodium/Potassium Alkyl Xanthates

In the literature [31], the stability of xanthates in the function of storage time, pH, and temperature was investigated by monitoring the change in the absorption of the solution at a certain wavelength. It was found that with decreasing pH values from 10 to 5, prolongation of storage time and temperature increase resulted in xanthate decomposition. In our work, the stability of synthesized xanthates was studied by analyzing the content of the active substance, sulfide, and trithiocarbonate at certain time intervals at a constant pH of 12 and temperature of 20 °C. Synthesized alkaline alkyl xanthates in the form of aqueous solutions of certain concentrations represent practically final products, which can be used in the flotation process of ore. The obtained results give real conditions of final product storage in warehouses of ready-made goods or in mine warehouses where they are used. In addition to the pure water xanthate flotation reagents, two optimal composition of Na-iPrX/HMFA (70/30 wt.%) and K-iBuX/HMFA (70/30 wt.%) were also subjected to the stability test; the results obtained are given in Table 9.

Table 9. Results of the stability test of the synthesized alkyl xanthates.

Time (Days)	0			30			60			90		
	a.s. ²	Sulf. ³	Trit. ⁴	a.s.	Sulf.	Trit.	a.s.	Sulf.	Trit.	a.s.	Sulf.	Trit.
Xanthate ¹	%											
Na-EtX-1	41.0	1.4	0.30	41.0	1.4	0.30	40.9	1.4	0.30	40.9	1.4	0.30
Na-EtX-2	51.2	1.5	0.31	51.1	1.5	0.30	51.1	1.5	0.31	51.0	1.5	0.31
Na-iPrX-1	55.0	1.8	0.36	55.0	1.7	0.36	55.0	1.8	0.35	54.8	1.7	0.36
Na-iPrX-2	38.0	1.7	0.34	38.0	1.7	0.35	37.9	1.7	0.34	37.9	1.6	0.35
Na-iBuX	41.0	1.7	0.35	41.0	1.7	0.35	40.5	1.7	0.35	38.6	1.6	0.40
K-EtX-1	51.8	1.7	0.40	49.8	1.7	0.42	49.7	1.7	0.40	45.5	1.8	0.43
K-EtX-2	45.1	1.6	0.35	44.8	1.6	0.36	44.0	1.5	0.38	42.9	1.6	0.39
K-iBuX	46.8	1.5	0.32	46.5	1.5	0.31	46.3	1.4	0.32	46.1	1.5	0.32
K-AmX	49.0	1.5	0.34	49.0	1.5	0.33	48.8	1.5	0.34	48.8	1.6	0.35
Na-iPrX/HMFA (70/30 wt.%)	38.1/16.2	1.2	0.24	38.0/15.9	1.2	0.24	37.9/15.9	1.2	0.23	37.8/15.8	1.2	0.23

¹ pH value of the obtained xanthates solution was in the range from 11.7 to 12.2; ² Active substance percentage in the solution; ³ Sulfide percentage; ⁴ Trithiocarbonate percentage.

It can be noted that sodium ethyl xanthate and sodium isopropyl xanthate are stable and that their concentrations remained almost unchanged over a 60-day period. Thus, the investigated sodium ethyl xanthate and sodium isopropyl xanthate were practically not degrading under the test conditions for sixty days or more. This information is important in relation to the storage of products in the form of aqueous solutions at the site of application in mines. The concentration of sodium isobutyl xanthate showed the highest decrease in relation to other sodium xanthates, ranging from 41.0% to 38.6% over a 90-day interval. Results of the xanthate stability test showed that sodium xanthates are more stable than the potassium ones in the same time interval of testing and under the same conditions (temperature of 20 °C and pH in the range of 11.7 to 12.2). The concentration of potassium ethyl xanthate decreased from 5% to 12%, with a greater concentration decrease in more concentrated products. Thus, the concentration of product KEtX-1 decreases from 51.8% to 45.5%, and K-EtX-2 from

45.1% to 42.9%. The decrease in concentration of potassium xanthate K-iBuX and K-AmX amounts to 1.5% and 0.5% over a 90-day period. Thus, the examined potassium xanthates, KiBuX and KAmX, are more stable than KEtX in the same time interval of storage and under the same conditions.

The concentrations of the present sulfides and trithiocarbonates in the final product are in the range of 1.4% to 1.8% for sulfide and from 0.30% to 0.43% for trithiocarbonate. These by-products are formed by reaction of carbon disulfide and alkali present in excess. The developed method, i.e. appropriate control of reaction condition/procedure, minimizes the side-reaction, which generates trithiocarbonate. Namely, if alcohol reacts more readily with alkoxide, then carbon disulfide is mostly consumed in the reaction. Otherwise, if there is a greater amount of free alkalis, the formation of trithiocarbonates will occur, formed by the reaction of the present alkali with carbon disulfide, followed by water release during the xanthate synthesis:



In the initial step of addition of CS₂ to the reaction mixture, xanthate is formed, which is dissolved in the water added at the beginning of the synthesis in the dissolution of sodium hydroxide step and the water formed during the alcohol production step. The obtained alcohol is dissolved in xylene, which is present in the reaction mixture, and the resulting xanthate, insoluble in xylene, is dissolved in water present in the reaction mixture. The resulting alkoxide reacts with carbon disulfide, whereby xanthate is formed, which dissolves in water; thus, further reaction is successively carried out with maximum conversion. In this way, the equilibrium reaction between alcohol and sodium hydroxide is shifted to the formation of alkoxide. As the reaction of CS₂ and the resulting alkoxide in the first stage of synthesis continues, the second step of the xanthate formation virtually moves the balance of the first reaction step to the right. The maximum conversion of the reactants to the xanthate product is achieved and obtained in the form of a suspension in the xylene reaction medium. By adding a certain amount of water to the reaction mixture in order to obtain an aqueous solution, the resulting xanthate is dissolved, and the solvent xylene is separated and used for a new synthesis. Unless xanthates are to be obtained in the form of an aqueous solution of defined concentration, the reaction mixture is cooled down and filtrated after synthesis. The synthesized xanthate is isolated as a filtration cake, and filtrate-xylene is used again for new synthesis reactions.

The products produced in this synthesis are carbonates, trithiocarbonates, and sulfides. Figure 5 shows the reaction of the formation of the by-product in the reaction mixture. If the reaction takes place in excess of the alcohol or the alcohol is a reactant and a reaction medium at the same time, it will react with carbon disulfide to give dialkyl thiocarbonate (I) with the separation of hydrogen sulfide (II). This reaction was favorable to a small extent, confirmed by a special study on the reaction of alkyl xanthic acid with alcohol. The reaction of neutralizing xanthic acid with sodium hydroxide is incomparably faster. Hydrogen sulfide reacted with the present alkali in the reaction mixture with the separation of alkaline sulfide (III). Carbon disulfide reacts simultaneously with the alkali, which is contained in the reaction mixture, resulting in the formation of trithiocarbonate (IV) and carbonate (V).

According to the described optimized laboratory procedure for the synthesis of alkali alkyl xanthates in aqueous solutions, the possibility of producing by-products is minimized. Additionally, the design of the reactor is such that it allows intensive mixing, which is necessary for maximizing the number of collisions of properly oriented reacting molecules. The well-known reactors in which these industrial-scale synthesis reactions take place are called "Malaxers". They comprise of horizontal cylinders with a wrapper that are used for the passage of heating or cooling fluid, with an axially mounted shaft on which the iron rods are located. By rotating the shaft with a gear motor, the rods stir the reaction material and, at the end of the reaction, grind the material during drying. This kind of reactor design is not efficient enough to perform a synthesis reaction due to the formation of dead corners where reaction does not occur, as well as poor mixing. Under these reaction conditions, the obtained product is of lower yield and purity (82–85%). These xanthates are less efficient in the flotation process and they are used in higher quantity because of the impurities present. In contrast,

the procedure described in this work, after filtration of the reaction mixture and drying, produces xanthates in solid state with significantly higher content of active substance and purity of 92–95%, or in the form of water solution of appropriate concentration.

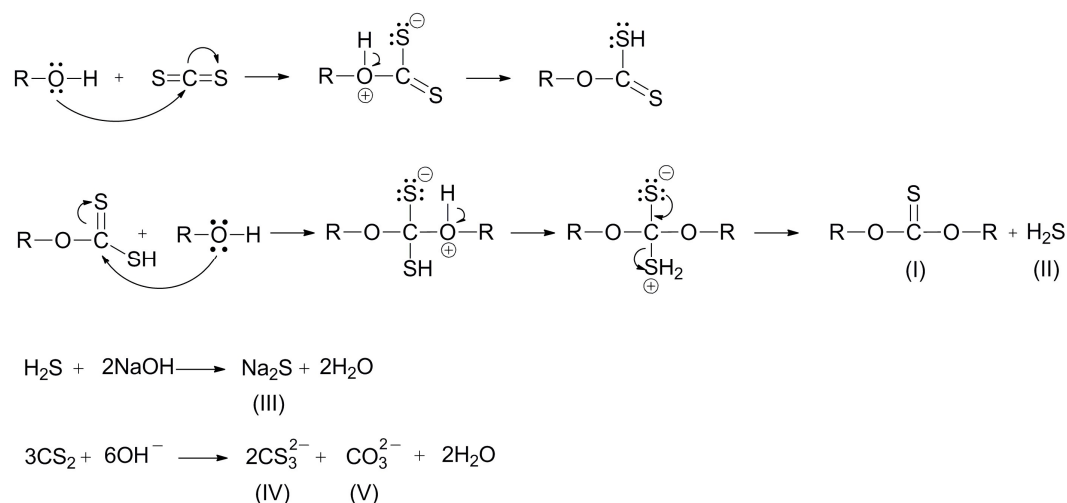


Figure 5. Side reactions in the synthesis of alkyl xanthates.

The reactor used in this synthesis with ideal mixing enables much better phase contact and more efficient mixing, and thus providing better yield and product quality. Furthermore, in this paper, it has been demonstrated that with the extension of reaction time, a larger product yield is provided. Namely, trithiocarbonate (IV), which is produced as a by-product, reacts with the alcohol present in the reaction mixture, separating the xanthate (VI) and releasing sodium hydrosulfide (VII), which reacts with the hydroxide present to produce sulfide (III). The resulting sulfide reacts with the minimum amount of dialkyl thiocarbonate (I) present, which is also formed in the reaction of this synthesis, producing the desired xanthate (VI) and alcoholate (VIII). These reactions are presented in Figure 6.

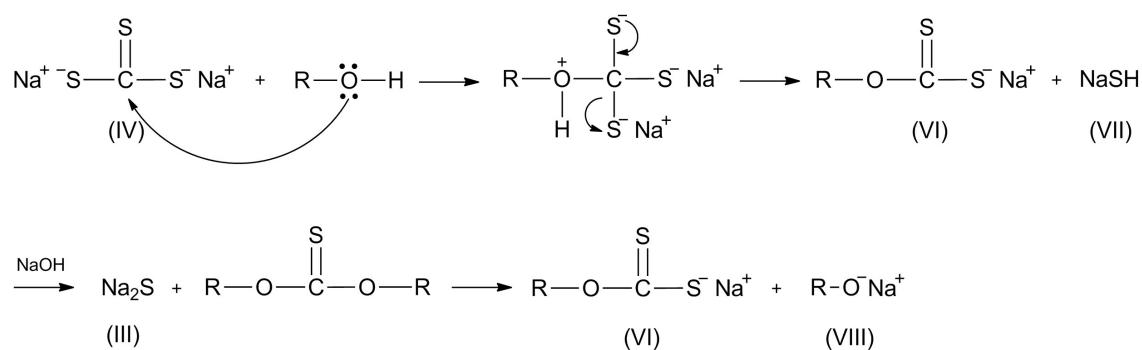


Figure 6. Reaction of degradation of the by-products of trithiocarbonate and disulfide in xanthate synthesis.

The proposed mechanism of alkyl xanthate synthesis helped in the definition of experimental condition (design) to achieve the optimal ratio of reactants and conditions that provide the highest yield and purity of the desired product. Moreover, the results of laboratory analyses of sulfide and trithiocarbonate content in the product show higher quantities of present trithiocarbonate sulfides. The reactions presented in Figures 5 and 6 show that the resulting trithiocarbonates are consumed in the reaction with the excess of alcohol present in the reaction mixture, which is the reason for their presence in the final product to a lesser extent.

Selectivity depends on the structure of the xanthates hydrocarbon chain, which affects flotation recovery. An optimized laboratory procedure for the synthesis of sodium/potassium alkyl xanthates

in the form of aqueous solutions, the reaction of alkoxide obtained in the reaction of alcohol, and sodium/potassium hydroxide (step I reaction) and carbon disulfide, was performed to obtain the corresponding sodium/potassium alkyl xanthate (II reaction step). Xylene is used as a solvent since it dissolves alkoxide, while the xanthate product builds a suspension. By adding water to the reaction mixture at the end of the reaction, the resulting xanthates is dissolved and the layers are separated. Xanthate dissolves in water; therefore, the suspension disappears, and xylene can be separated from xanthate water dispersion as an upper organic layer and returned to the synthesis process.

3.6. Synthesis of Alkyl Xanthates at the Industrial Level

Based on the defined parameters of the process on optimization of the laboratory procedure for the synthesis of alkali alkyl xanthates in the form of aqueous solutions of certain concentrations, a trial production was conducted in industrial conditions. The technological scheme of the trial industrial production is presented in Figure 7.

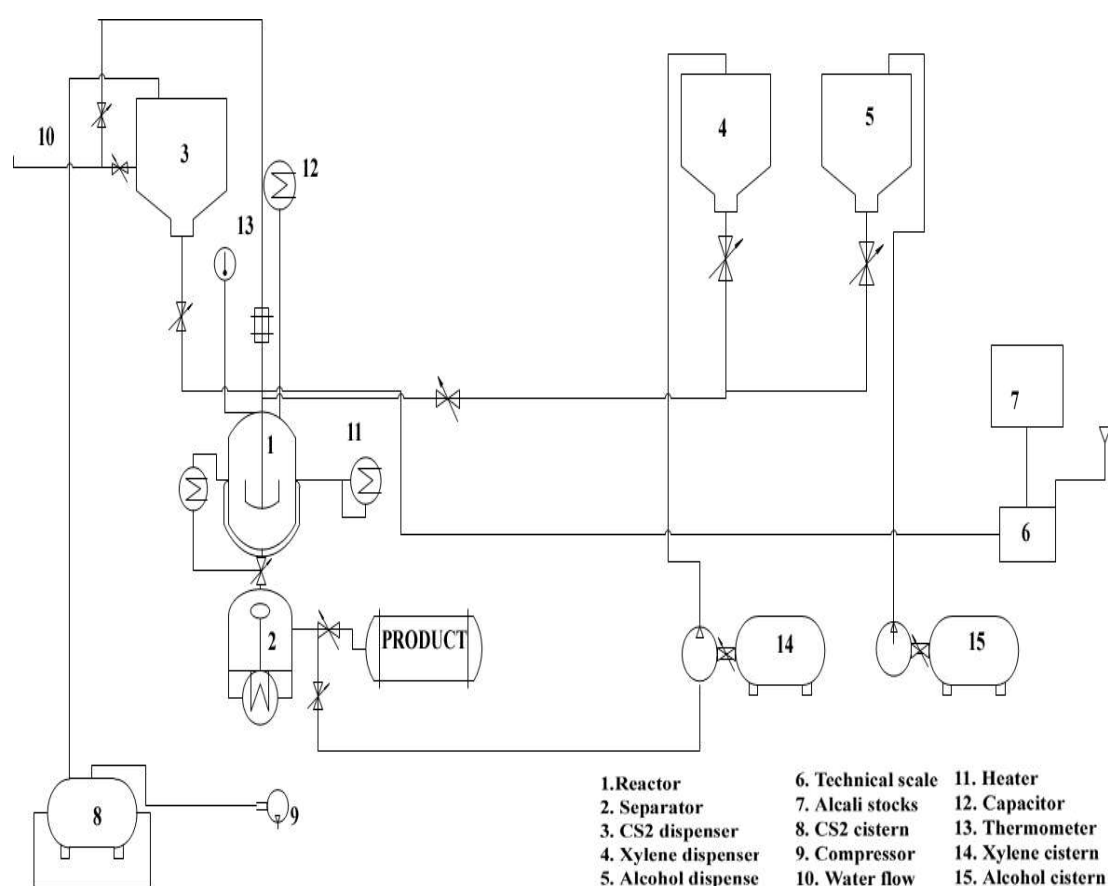


Figure 7. Schematic overview of the technological process for the production of liquid alkyl xanthate.

In the 5 m³ reactor (1), 60.0 kg (1.1 kmol) of 98% potassium hydroxide and 130 L of water were placed; the heating was switched on in a manner that the temperature of the reactor mass was kept at 65 °C. Then, 60.8 L (1.1 kmol) of ethanol from dose (5) was added and mixing was initiated; 3.25 m³ xylene was added from dosage unit (4). The reaction mixture was stirred at a temperature of 60 °C for 1.5 h. Thereafter, the reaction mixture was cooled to about 35 °C, and 61.5 L (1.0 kmol) of carbon disulfide were added from dosage unit (3). The addition of carbon disulfide was carried out for 2.5 h, providing a constant temperature of 35 °C. Then, 134 L of water was added and the reaction mixture was stirred for 5 min. Afterwards, the reaction mixture was transferred to the separator (2), where the upper layer of xylene were separated from the lower aqueous portion, which is an aqueous solution of synthesized potassium ethyl xanthate. The resulting product was analyzed for content of the active

substance, i.e. concentration of aqueous xanthate solution (50.1%), trithiocarbonate content (1.3%), and sulfide (0.3%).

At the facility in Chemical Industry “Župa” Kruševac, a trial production of three batches of aqueous xanthate solution was done according to the procedure described above. The obtained products were analyzed for content of the active substance, i.e., the concentration of aqueous xanthate solution, the content of trithiocarbonate, and sulfide. The results of the analysis of the synthesized alkali alkyl xanthates under industrial conditions are given in Table 10.

Table 10. Results of synthesis of alkali alkyl xanthates at industrial-level production.

Batch	Alcohol ¹ (kg/L)	NaOH/KOH ² (kg)	CS ₂ ³ (kg/L)	H ₂ O (L)	Xylene ⁴ (kg/m ³)	Time (h)	Temperature (°C)	Xanthate (kg/% a.m.)	Yield (%)
KEtX	48.0/60.8	60.0	77.55/61.5	134.0	2800/3.25	4.0	55–60/35–40	268.2/50.1	88.0
NaiPrX	250.0/318.1	156.0	300.0/238.0	450.0	2400/2.8	4.5	70–75/35–40	519.3/55.0	86.0
NaEtX	220.0/278.8	192.0	322.0/255.4	720.0	2800/3.25	4.50	60–65/35–40	1310.0/45.0	87.0

¹ Density: d (ethanol, 96%) = 0.789 g/cm³; d (isopropanol, 95%) = 0.786 g/cm³; ² 98% sodium/potassium hydroxide was used in the production process; ³ Density: d (carbon disulfide, 98%) = 1.261 g/cm³; ⁴ Density: d (xylene) = 0.86 g/cm³.

Based on the obtained results from trial alkali xanthates production in the industrial conditions presented in Table 10, it can be seen that satisfactory yields have been achieved, and the obtained products in the form of aqueous solutions show a high degree of purity.

3.7. Application of Innovated Product of Mine Sample Flotation at Laboratory and Industrial Levels

Comparative flotation analysis of the powdery Na-iPrX produced at the Chemical Industry “Župa” Kruševac by conventional industrial process and those obtained by the described innovative process using liquid Na-iPrX are presented in Tables 11 and 12. Flotation behavior of sulfide ores was investigated by bench-scale tests, which are described in detail in the Supplementary Materials Section.

Table 11. Copper flotation efficiency obtained by using Na-iPrX powder (produced by a conventional process).

	T ¹ [g]	t ² [%]	Cu [%]	Cu [g]	ICu ³ [%]
Entrance	994.9	100	1.1767	11.7070	100
OKCu	98.8	9.9306	7.49	7.4001	63.21
KKCu	106.2	10.674	2.94	3.1223	26.67
UKCu	205.0	20.605	5.1329	10.522	89.88
Tailing	789.9	79.395	0.15	1.1849	10.12

¹ T-ore weight mass; ² t-ore sample mass %; ³ ICu-copper content.

Table 12. Floating power by applying liquid Na-iPrX (produced by an innovative process).

	T ¹ [g]	t ² [%]	Cu [%]	Cu [g]	ICu ³ [%]
Entrance	993.5	100	1.1767	17.5551	100
OKCu	105.8	10.65	11.45	12.1147	69.10
KKCu	126.9	12.68	3.40	4.3150	24.58
UKCu	232.7	23.42	7.06	16.4298	93.59
Tailing	760.8	76.57	0.14	1.1252	6.41

¹ T-ore weight mass; ² t-ore sample mass %; ³ ICu-copper content.

Results from Tables 10 and 11 imply that better effects of copper concentration in ore flotation are obtained using Na-iPrX in the form of a water solution produced by the innovative industrial process (93.59%, Table 12), compared to Na-iPrX from a conventional industrial process (89.88%, Table 11) applied under the same technological parameters. The optimized technological procedure for the synthesis of xanthates, presented in this paper, is economically justified, in comparison to the classical

methods due to lower energy costs (no drying phase), higher conversion rate, cleaner product being obtained, and lower consumption of the obtained products in the flotation process.

The results demonstrated that compared to other known collectors, Na-iPr exhibited high recovery efficiency towards copper. According to previous literature data, the recoveries of chalcopyrite were 90.84%, 85.83%, 84.65%, 83.39%, and 82.49%, for S-benzoyl O-isobutyl xanthate (BIBX), sodium isopropyl xanthate (Na-iPrX), thiohexanamide (THA), sodium isobutyl xanthate (SIBH), and O-isopropyl-N-ethylthionocarbamate (IPETC), respectively [36,37], while for Na-iPrX in the form of a water solution produced by the innovative industrial process, recovery was 93.59%, and 89.88% for Na-iPrX with the conventional industrial process. Additionally, selectivity determined by Hassanzadeh et al. [38] is similar to that obtained in this work, i.e., K_{MCu} and K_{MFe} values are 42.2 and 6.23, respectively. This result indicates good separation feasibility of the Na-iPr collector.

4. Conclusions

In this paper, a laboratory procedure for the synthesis of sodium/potassium alkyl xanthate in the form of aqueous solutions was optimized in terms of synthesis parameters (reaction time, temperature, molar ratio of the reactants, and amount of solvent), and a trial industrial production was performed. The defined procedure in this paper reduces the production of side products to a minimum. The benefits of the presented methods are based on production simplicity, mild reaction conditions, high purity and yield of products, decreased by-products, and technological applicability at an industrial scale. The results demonstrated that Na-iPrX exhibited better flotation affinity in the form of a water solution produced by the innovative industrial process (93.59%), compared to Na-iPrX from the conventional industrial process (89.88%) applied under the same technological parameters.

Additionally, biomass derived furan-based compounds were tested as potential selective green frothers in the bulk flotation of ore using sodium isopropyl xanthate as a collector. Optimal 30% HMFA content in the flotoreagent formulation shows that it has a promising future as a biodegradable alternative for commercial xanthate without significantly affecting its efficiency and selectivity. The DFT calculations provided insights into the interaction mechanism of Na-iPrX and HMFA with copper.

Since the mining industry is currently facing significant challenges in identifying and adopting collector chemistries that can effectively recover valued minerals while minimising environmental impacts, future studies should be directed to the synthesis of new greener and biodegradable biomass-derived compounds that are appropriate for replacing toxic xanthate flotation collectors without affecting efficiency and selectivity.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/10/4/350/s1>, Figure S1. Dependence of Na-EtX yield on product suspension concentration and reaction conditions, Figure S2. View Optimal Reaction Conditions for Maximum Yield of Na-EtX (overlay plot), Figure S3. Flow diagram and conditions of bench-scale flotation test, Table S1. Box-Behnken design for the experiment for dependence of Na-EtX yield from product suspension concentration, Table S2. Variance Analysis (ANOVA) for the surface quadratic model of the response to of Na-EtX yield, Table 3. Model assessment, Table S4. The XRF test results of the samples for bench-scale flotation [39–45].

Author Contributions: Conceptualization, A.D.M.; Data curation, A.B.; I.N.C.; Investigation, A.D.M., M.R., D.G., and G.M.; Methodology, M.M.M. and A.D.M.; Writing—original draft, M.R. and A.B.; Writing—review & editing, M.M.M. and A.D.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Education, Science and Technological Development of Serbia, grants numbers: 43007, 451-03-68/2020-14/200169 and 451-03-68/2020-14/200135.

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

References

1. Kemppinen, J.; Aaltonen, A.; Sihvonen, T.; Leppinen, J.; Sirén, H. Xanthate degradation occurring in flotation process waters of a gold concentrator plant. *Miner. Eng.* **2015**, *80*, 1–7. [CrossRef]
2. Ozun, S.; Ergen, G. Determination of optimum parameters for flotation of galena: Effect of chain length and chain structure of xanthates on flotation recovery. *ACS Omega* **2019**, *4*, 1516–1524. [CrossRef] [PubMed]

3. Bai, L.; Liu, J.; Han, Y.; Jiang, K.; Zhao, W. Effects of xanthate on flotation kinetics of chalcopyrite and talc. *Minerals* **2018**, *8*, 369. [[CrossRef](#)]
4. Abramov, A.A. Physico-chemical modeling of flotation systems. *Min. Proc. Ext. Met. Rev.* **1998**, *19*, 409–459. [[CrossRef](#)]
5. Abramov, A.A.; Forsberg, K.S.E. Chemistry and optimal conditions for copper minerals flotation: Theory and practice. *Min. Proc. Ext. Met. Rev.* **2005**, *26*, 77–143. [[CrossRef](#)]
6. Li, Z.; Rao, F.; Song, S.; Uribe-Salas, A.; López-Valdivieso, A. Reexamining the Adsorption of Octyl Hydroxamate on Malachite Surface: Forms of Molecules and Anions. *Min. Proc. Ext. Met. Rev.* **2020**, *41*, 178–186. [[CrossRef](#)]
7. Bakalarz, A.; Gloy, G.; Luszczkiewicz, A. Flotation of sulfide components of copper ore in the presence of n-dodecane. *Min. Proc. Ext. Met. Rev.* **2015**, *36*, 103–111. [[CrossRef](#)]
8. Rao, S.R.; Finch, J.A. Base metal oxide flotation using long chain xanthates. *Int. J. Miner. Process.* **2003**, *69*, 251–258. [[CrossRef](#)]
9. Lin, S.; Liu, R.; Bu, Y.; Wang, C.; Wang, L.; Sun, W.; Hu, Y. Oxidative depression of arsenopyrite by using calcium hypochlorite and sodium humate. *Minerals* **2018**, *8*, 463. [[CrossRef](#)]
10. Zhang, Y.; Shao, Y.; Zhang, R.; Li, D.; Liu, Z.; Chen, H. Dating ore deposit using garnet U–Pb geochronology: Example from the xinqiao Cu–S–Fe–Au deposit, eastern china. *Minerals* **2018**, *8*, 31. [[CrossRef](#)]
11. Xiong, R.G.; Yu, Z.; Liu, C.M.; You, X.Z. Crystal structure and magnetic properties of a novel cis-4,4'-bipyridine polymeric complex of Ni(II). *Polyhedron* **1997**, *16*, 2667–2670. [[CrossRef](#)]
12. Reddy, P.C.; Rangamannar, B. Comparative substoichiometric extraction and quantification of mercury in geological water samples with potassium salts of ethyl, propyl, butyl, pentyl and benzyl xanthates. *J. Radioanal. Nucl. Chem.* **1996**, *213*, 9–19. [[CrossRef](#)]
13. Niu, X.; Chen, J.; Li, Y.; Xia, L.; Li, L.; Sun, H.; Ruan, R. Correlation of surface oxidation with xanthate adsorption and pyrite flotation. *Appl. Surf. Sci.* **2019**, *495*, 142439–143411. [[CrossRef](#)]
14. Nava-Alonso, F.; Pecina-Treviño, T.; Perez-Garibay, R.; Uribe-Salas, A. Pulp potential control in flotation: The effect of hydrogen peroxide addition on the extent of xanthate oxidation. *Can. Metall. Quart.* **2002**, *41*, 391–397. [[CrossRef](#)]
15. Kim, D.S.; Kuh, S.E.; Moon, K.S. Characteristics of xanthates related to hydrocarbon chain length. *Geosyst. Eng.* **2000**, *3*, 30–34. [[CrossRef](#)]
16. Chanturiya, V.A.; Kondratiev, S.A. Contemporary Understanding and Developments in the Flotation Theory of Non-Ferrous Ores. *Min. Proc. Ext. Met. Rev.* **2019**, *40*, 390–401. [[CrossRef](#)]
17. Kyzas, G.Z.; Matis, K.A. The flotation process can go green. *Processes* **2019**, *7*, 138. [[CrossRef](#)]
18. Milosavljević, M.M.; Mijin, D.Ž.; Milisavljević, S.S.; Elezović, N.M.; Milanović, J.K. New facile one-pot synthesis of S-alkyl thiolcarbamates from xanthate in water. *Monatsh. Chem.* **2013**, *144*, 1833–1837. [[CrossRef](#)]
19. Mohamed, A.A.; Kani, I.; Ramirez, A.O.; Fackler, J.P. Synthesis, characterization, and luminescent properties of dinuclear gold(I) xanthate complexes: X-ray structure of $[Au_2(nBu-xanthate)_2]$. *Inorg. Chem.* **2004**, *43*, 3833–3839. [[CrossRef](#)]
20. Milosavljevic, M.M.; Sovrljic, M.; Marinkovic, D.A.; Milenkovic, D.D. A synthesis of N-alkyl and N,N-dialkyl O-ethyl thiolcarbamates from diethyl dioxanthogenate using different oxidants. *Monatsh. Chem.* **2010**, *141*, 749–755. [[CrossRef](#)]
21. Milosavljević, M.M.; Vuković, G.D.; Marinković, A.D.; Aleksić, R.R.; Uskoković, P.S. Synthesis of N-(3-and 4-substituted phenyl)-O-isobutyl thionocarbamates from O-isobutyl xanthate and amines using a nano-platinum multi-walled carbon nanotube catalyst. *Monatsh. Chem.* **2011**, *142*, 1045–1053. [[CrossRef](#)]
22. Milosavljević, M.M.; Mijin, D.Ž.; Konstantinović, S.S.; Elezović, N.M.; Takić, L.M.; Dražević, L.M. A new procedure for the treatment of an industrial waste containing flotation reagents. *Hem. Ind.* **2014**, *68*, 331–339. [[CrossRef](#)]
23. Shen, Y.; Nagaraj, D.R.; Farinato, R.; Somasundaran, P. Study of xanthate decomposition in aqueous solutions. *Miner. Eng.* **2016**, *93*, 10–15. [[CrossRef](#)]
24. Vorobyev, S.A.; Saikova, S.V.; Novikova, S.A.; Fetisova, O.Y.; Zharkov, S.M.; Krylov, A.S.; Likhatski, M.N.; Mikhlin, Y.L. Colloidal and Immobilized Nanoparticles of Lead Xanthates. *ACS Omega* **2019**, *4*, 11472–11480. [[CrossRef](#)]

25. Crozier, R.D.; Daisy, L.; Ridgefield, C. Process for Producing Alkyl Xanthogen Alkylformates. U.S. Patent US4354980A, 19 October 1982.
26. Weien, P.; Tao, S.; Weiping, L. Preparation Method of Xanthate. CN 104774166 (A), 28 April 2015.
27. National Standard of Chinese Standard YS/T271.1-1994. Methods for Chemical Analysis of Xanthates. The Lead-acetate Titration Method for Determination of Xanthate Content, 27 January 1987. China Non-ferrous Metal Corporation: Beijing, China; pp. 1–7. Available online: <https://www.chinesestandard.net/PDF/English.aspx/YST271.1-1994> (accessed on 14 April 2020).
28. Hansen, T.S.; Woodley, J.M.; Riisager, A. Efficient microwave-assisted synthesis of 5-hydroxymethylfurfural from concentrated aqueous fructose. *Carbohydr. Res.* **2009**, *344*, 2568–2572. [[CrossRef](#)]
29. Morone, A.; Apte, M.; Pandey, R.A. Levulinic acid production from renewable waste resources: Bottlenecks, potential remedies, advancements and applications. *Ren. Sust. Energ. Rev.* **2015**, *51*, 548–565. [[CrossRef](#)]
30. Skowronski, R.; Grabowski, G.; Lewkowski, J.; Descotes, G.; Cottier, L.; Neyret, C. New chemical conversions of 5-hydroxymethylfurfural and the electrochemical oxidation of its derivatives. *Org. Prep. Proced. Int.* **1993**, *25*, 353–355. [[CrossRef](#)]
31. Mustafa, S.; Hamid, A.; Naeem, A.; Sultana, Q. Effect of pH, Temperature and time on the stability of potassium ethyl xanthate. *J. Chem. Soc. Pak.* **2004**, *26*, 363–366.
32. Stewart, J.J.P. Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and application to 70 elements. *J. Mol. Model.* **2007**, *13*, 1173–1213. [[CrossRef](#)]
33. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. *Gaussian 09, Revision C.01*, Gaussian Inc.: Wallingford, CT, USA, 2009.
34. Dennington, R.D.; Keith, T.A.; Millam, J.M. *GaussView 5.0*; Gaussian Inc.: Wallingford, CT, USA, 2008.
35. Lu, T.; Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580–592. [[CrossRef](#)]
36. Ma, X.; Xia, L.; Wang, S.; Zhong, H.; Jia, H. Structural modification of xanthate collectors to enhance the flotation selectivity of chalcopyrite. *Ind. Eng. Chem. Res.* **2017**, *56*, 6307–6316. [[CrossRef](#)]
37. Jia, Y.; Huang, K.; Wang, S.; Cao, Z.; Zhong, H. The selective flotation behavior and adsorption mechanism of thiohexanamide to chalcopyrite. *Min. Eng.* **2019**, *13*, 187–199. [[CrossRef](#)]
38. Hassanzadeh, A.; Hasanzadeh, M. A study on selective flotation in low and high pyritic copper sulphide ores. *Sep. Sci. Technol.* **2016**, *51*, 2214–2224. [[CrossRef](#)]
39. Iqbal, M.; Iqbal, N.; Bhatti, A.I.; Ahmad, N.; Zahid, M. Response surface methodology application in optimization of cadmium adsorption by shoe waste: A good option of waste mitigation by waste. *Ecol. Eng.* **2016**, *88*, 265–275. [[CrossRef](#)]
40. Karanac, M.; Dolić, M.; Veličković, Z.; Kapidžić, A.; Ivanovski, V.; Mitrić, M.; Marinković, A. Efficient multistep arsenate removal onto magnetite modified fly ash. *J. Environ. Manage.* **2018**, *224*, 263–276. [[CrossRef](#)] [[PubMed](#)]
41. Xiyili, H.; Cetintas, S.; Bingol, D. Removal of Some Heavy Metals onto Mechanically Activated Fly Ash: Modeling Approach for Optimization, Isotherms, Kinetics and Thermodynamics. *Process Saf. Environ.* **2017**, *109*, 288–300. [[CrossRef](#)]
42. Georgiev, G. A genetic model of the Elatsite porphyry copper deposit. *Geochem. Mineral. Petrol.* **2008**, *46*, 143–160.
43. Quadt, A.; Peytcheva, I.; Kamenov, B.; Fanger, L.; Heinrich, C.A.; Frank, M. The Elatsite porphyry copper deposit in the anagyurishte ore district Srednogorie zone Bulgaria U-Pb zircon geochronology and isotope-geochemical investigations of magmatism and ore genesis. *Geol. Soc. Lond. Spec. Publ.* **2002**, *204*, 119–135. [[CrossRef](#)]
44. Wills, B.A. *Mineral Processing Technology*; Butterworth Heinemann: Oxford, UK, 2006.
45. Xu, M. Modified flotation rate constant and selectivity index. *Miner. Eng.* **1998**, *11*, 271–278. [[CrossRef](#)]

