

Article

Water Decontamination of Sulfide Flotation Effluents: Removal of Sodium Diethyl Dithiophosphate (Sodium Aerofloat) Using Thermochemically Modified Activated Carbon

Daniel Maldonado, Ernesto de la Torre and Carlos F. Aragón-Tobar * 

Department of Extractive Metallurgy, Escuela Politécnica Nacional, Ladrón de Guevara E11-253, P.O. Box 17-01-2759, Quito 170525, Ecuador; danielr.maldonado@gmail.com (D.M.); ernesto.delatorre@epn.edu.ec (E.d.l.T.)

* Correspondence: carlos.aragont@epn.edu.ec; Tel.: +593-(9)8390-2363

Abstract

Mining flotation effluents may contain residual collectors that pose risks to aquatic environments when discharged without adequate treatment. Among these compounds, sodium diethyl dithiophosphate (SDE DTP) is of particular concern due to its persistence and potential ecotoxicological effects. This study evaluated the removal of SDE DTP from aqueous media using commercial activated carbon and thermochemically modified activated carbon prepared through nitric acid oxidation and urea treatment. Batch adsorption experiments were conducted using synthetic SDE DTP solutions and a laboratory-generated flotation effluent obtained from a copper sulfide ore containing approximately 0.5 wt.% Cu. A UV–visible spectrophotometric method was applied for the quantification of SDE DTP in both systems. The effects of adsorbent dosage, solution pH, and surface modification were investigated. Adsorption performance increased with activated carbon dosage and was strongly influenced by pH. Thermochemical modification significantly enhanced adsorption performance, increasing SDE DTP removal from 40% for unmodified carbon to 93% for the modified material. The modified adsorbent also maintained high efficiency in real flotation effluent, achieving 88% removal despite competing dissolved species. These results demonstrate that thermochemically modified activated carbon is a promising functional material for treating flotation effluents contaminated with dithiophosphate collectors.

Keywords: modified activated carbon; effluent treatment; sulfide collector; mineral flotation; adsorption; mining wastewater



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1. Introduction

Flotation is one of the most widely used separation techniques in mineral processing for the selective recovery of valuable minerals from gangue. The process is based on differences in surface wettability, whereby hydrophobic mineral particles attach to air bubbles and are recovered in the concentrate, while hydrophilic gangue particles remain in the pulp [1]. In sulfide flotation systems, this mechanism enables the efficient separation of sulfide minerals from associated silicate and oxide phases. Because water acts as the principal transport medium during grinding, conditioning, and flotation stages, large volumes of process water are required throughout the circuit. Consequently, flotation operations generate significant quantities of effluents containing residual flotation reagents, dissolved metal ions, and suspended fine particles that are not completely recovered in concentrate or tailings streams [2]. Although many mining operations implement

partial water recirculation strategies to reduce freshwater consumption, complete reuse is often limited by the accumulation of dissolved species and residual reagents, which may negatively affect flotation selectivity and metallurgical performance [3].

When flotation effluents are discharged without adequate treatment, they may become an important source of contamination for aquatic environments. These effluents commonly contain residual collectors, frothers, and sulfur-containing reagents such as xanthates and dithiophosphates, in addition to dissolved heavy metals released from sulfide ores [1,4]. Several studies have reported that these compounds can induce acute and chronic toxicity in aquatic organisms, affecting respiratory activity, enzymatic function, growth, and reproduction [2,5,6]. Certain flotation reagents and dissolved metal species may also exhibit persistence and bioaccumulative behavior, increasing their residence time in aquatic ecosystems and their transfer through food chains [2]. Furthermore, inadequate disposal of flotation wastewater can alter water quality parameters such as dissolved oxygen demand, turbidity, and chemical oxygen demand, thereby contributing to ecosystem imbalance and loss of aquatic biodiversity [7].

Human exposure to contaminants derived from flotation effluents may occur indirectly through the use of contaminated surface or groundwater for drinking water production, irrigation, or livestock consumption [8,9]. In this context, residual flotation reagents and associated metal species may enter the human body through water or food intake pathways. Long-term exposure to such contaminants has been associated with neurological, respiratory, immunological, and potentially carcinogenic effects depending on the chemical composition and exposure concentration [5]. These environmental and public health concerns highlight the importance of developing efficient treatment strategies for flotation wastewater before discharge or recirculation within mineral processing operations [10].

Collectors are organic reagents that selectively adsorb onto mineral surfaces and modify their physicochemical properties to increase hydrophobicity [11]. As a result, the treated mineral particles exhibit greater affinity for air bubbles and can be recovered through the froth phase during flotation [1]. A wide variety of collectors are used in flotation processes, including xanthates, thiocarbamates, dithiophosphates, dithiocarbamates, thiols, carboxylic acids, sulfates, and sulfonates, which may be either anionic, cationic, or nonionic depending on their chemical structure [1,4]. The type of collector employed strongly influences flotation selectivity, recovery efficiency, and the chemical composition of the resulting process effluents [12].

Among flotation collectors, phosphorus-containing reagents such as dithiophosphates are widely applied in the beneficiation of sulfide ores because of their high selectivity toward minerals containing copper, lead, zinc, and nickel [13]. These reagents are particularly effective in complex sulfide systems where selective separation is required. Sodium diethyl dithiophosphate (SDE DTP), commercially known as sodium Aerofloat, is one of the most used dithiophosphate collectors in sulfide flotation circuits [7]. Its adsorption onto sulfide mineral surfaces enhances hydrophobicity and improves flotation kinetics and concentrate recovery. The molecular structure of SDE DTP is presented in Figure 1.

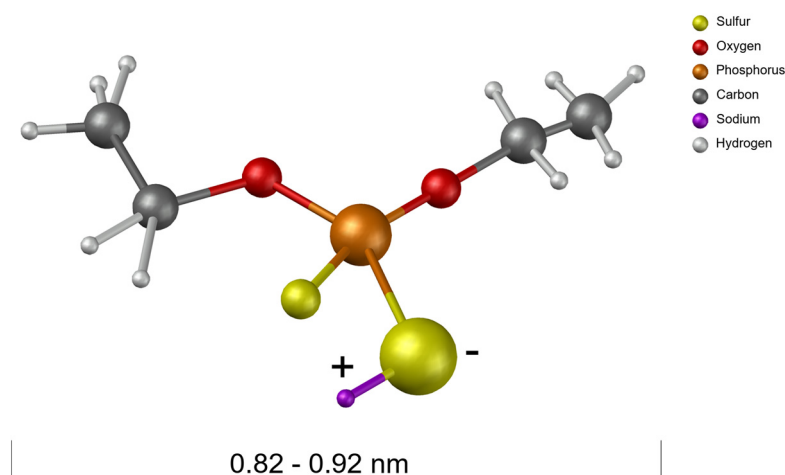


Figure 1. Molecular structure of sodium diethyl dithiophosphate SDE DTP. Redrawn by the authors based on the structural data available in PubChem [14].

Sodium diethyl dithiophosphate (SDE DTP) was selected in this study because of its extensive use in the Ecuadorian mining industry and the difficulties associated with its removal from flotation effluents using conventional water treatment approaches. Residual concentrations of dithiophosphate collectors may remain in process water and tailings effluents after flotation, particularly in operations with limited wastewater treatment or high-water recirculation rates [15]. The environmental concern associated with SDE DTP is related to its persistence, toxicity, and potential effects on aquatic organisms. Previous studies have reported that dithiophosphate-based collectors may affect aquatic species by altering enzymatic activity, respiratory function, and cellular metabolism [2]. In addition, sulfur-containing flotation reagents may undergo degradation reactions that generate secondary compounds with additional environmental risks [16].

Sodium diethyl dithiophosphate (SDE DTP) presents additional environmental concerns due to its chemical stability and strong affinity for mineral and organic surfaces, which may hinder its removal during conventional wastewater treatment processes [17]. Unlike more readily degradable flotation reagents, dithiophosphates can remain dissolved or partially adsorbed in recirculating process water, promoting their accumulation within flotation circuits and tailings effluents [18]. Furthermore, the surface-active nature of SDE DTP can alter interfacial properties in aquatic environments and interfere with biological processes in exposed organisms [2]. Despite the extensive industrial application of sodium diethyl dithiophosphate in sulfide flotation, studies addressing its selective removal from mining effluents remain limited.

Several technologies have been investigated for the treatment of flotation effluents containing collector reagents, including chemical oxidation, advanced oxidation processes (AOPs), biological treatments, membrane bioreactors, and adsorption systems [10]. These methods aim either to degrade flotation reagents into less harmful compounds or to remove them from the aqueous phase prior to discharge or water recirculation. Reported removal efficiencies for sulfur-containing collectors such as aerofloats and related dithiophosphate compounds frequently exceed 80–90% under optimized laboratory conditions [19]. However, treatment performance strongly depends on reagent composition, operating conditions, and the complexity of the effluent matrix.

Chemical oxidation and advanced oxidation processes (AOPs) are among the most studied approaches for flotation reagent degradation. Conventional oxidation methods can rapidly decompose collector molecules through reactions with oxidizing agents, while AOPs generate highly reactive radicals capable of mineralizing organic contaminants [7,20,21]. Removal efficiencies above 84–98% have been reported for

aerofloat-type collectors under controlled conditions [20,21]. Nevertheless, these technologies often require high energy input, strict pH control, and the addition of chemical reagents, which increase operational costs. In addition, incomplete oxidation may generate intermediate byproducts with toxicity comparable to or greater than that of the original contaminant [10].

Biological treatments and membrane bioreactors have also been explored for flotation wastewater remediation [22–25]. Biological processes rely on microbial degradation of dissolved organic compounds and may achieve removal efficiencies close to 88% for certain aerofloat collectors [25]. Membrane bioreactors combine biological degradation with membrane separation, offering advantages such as reduced sludge generation, compact system design, and efficient solid–liquid separation [22,24]. However, the application of these methods to flotation effluents remains challenging because flotation reagents may inhibit microbial activity, particularly at elevated collector concentrations or in the presence of dissolved heavy metals. Furthermore, membrane systems are susceptible to fouling and generally require intensive operational maintenance [23,24].

Among the available treatment alternatives, adsorption has emerged as one of the most promising methods for the removal of flotation collectors from industrial effluents because of its operational simplicity, low energy requirements, and absence of toxic secondary products [26,27]. Activated carbon is particularly attractive due to its high specific surface area, developed pore structure, and tunable surface chemistry, which favor the adsorption of sulfur-containing organic compounds. Previous studies have demonstrated the ability of activated carbon materials to remove dithiophosphate collectors from synthetic aqueous solutions, achieving removals above 80% under controlled experimental conditions involving neutral pH, isolated collector systems, and relatively low concentrations of competing dissolved species [11]. However, in complex flotation effluents, the adsorption performance of conventional activated carbon may decrease due to competition between dissolved species, limited selectivity toward specific collector molecules, and insufficient surface functionality for strong adsorbate–adsorbent interactions [28–30].

To overcome these limitations, several strategies have been proposed to modify the physicochemical properties of activated carbon and improve its adsorption performance. Surface modification may involve thermal, physical, or chemical treatments aimed at altering pore structure, surface charge, and the abundance of functional groups available for adsorption. Thermal activation in the presence of steam, carbon dioxide, or mildly oxidizing atmospheres can enhance pore development and increase the accessibility of adsorption sites [31]. In contrast, chemical modification is primarily used to tailor the surface chemistry of activated carbon by introducing specific functional groups capable of improving selectivity and affinity toward target contaminants. Oxidative treatments using reagents such as nitric acid, phosphoric acid, hydrogen peroxide, potassium permanganate, and sulfuric acid have been widely investigated for incorporating oxygen-containing functional groups, including carboxylic, phenolic, lactonic, and carbonyl groups, onto carbon surfaces [32,33].

Among these approaches, nitric acid oxidation has received considerable attention because it increases surface heterogeneity and promotes the formation of acidic oxygenated groups that can enhance interactions with polar and ionizable organic compounds [34,35]. These surface modifications may improve adsorption through mechanisms such as electrostatic attraction, hydrogen bonding, and surface complexation, particularly in aqueous systems containing sulfur- and phosphorus-bearing flotation reagents. Modified activated carbons have demonstrated improved performance in several environmental applications, including the adsorption of organic pollutants and catalytic gas treatment processes [36]. Nevertheless, the effect of acid-modified activated carbon on the removal of sodium diethyl

dithiophosphate from real sulfide flotation effluents has not been extensively investigated. Given the environmental persistence and potential ecotoxicological effects of dithiophosphate collectors, together with the operational limitations associated with conventional flotation effluent treatment technologies, the development of efficient and sustainable remediation strategies remains a significant challenge for the mining industry.

In this context, adsorption using modified activated carbon represents a promising alternative due to its high removal potential, operational simplicity, and adaptability to complex aqueous matrices. Therefore, this study investigates the removal of sodium diethyl dithiophosphate (SDE DTP) from both synthetic aqueous solutions and real sulfide flotation effluents using untreated and nitric-acid-modified activated carbon.

Special emphasis is placed on evaluating the influence of surface oxidation and solution pH on adsorption performance under conditions representative of flotation wastewater systems. The objective is to determine the effectiveness of surface-modified activated carbon for the decontamination of flotation effluents and to contribute toward the development of sustainable treatment approaches capable of reducing the environmental impact associated with residual flotation collectors in mining waters.

2. Materials and Methods

2.1. Materials

2.1.1. Flotation Reagents

The flotation collectors used in this study were potassium amyl xanthate (PAX, Sigma-Aldrich, St. Louis, MO, USA, technical grade) and sodium diethyl dithiophosphate (SDE DTP, Solvay, Brussels, Belgium, technical grade). Sodium silicate (Na_2SiO_3 , 98–99%, Sigma-Aldrich, St. Louis, MO, USA) and pine oil (technical grade, Sigma-Aldrich, St. Louis, MO, USA) were also used as auxiliary flotation reagents. These chemicals were used for the preparation of synthetic collector solutions and for laboratory-scale flotation tests to generate real flotation effluents.

2.1.2. Activated Carbon

Commercial activated carbon, characterized by a high specific surface area, was used in the collector removal experiments. Prior to use, the material was washed with distilled water to remove potential impurities and contaminants and then dried before adsorption test. The main physical characteristics of the activated carbon are summarized in Table 1. De la Torre [37] characterizes the activated carbon used in this study; some reported values are reflected in Table 1.

Table 1. Physical characteristics of the activated carbon used [37].

Properties	High Specific Surface Area Coal
Raw material	Coconut Shell
Activation method	High-temperature water vapor
Specific surface area $\text{m}^2 \cdot \text{g}^{-1}$	1025
Micropore surface $\text{m}^2 \cdot \text{g}^{-1}$	844
Average pore diameter (nm)	2.9
Average diameter of micropores (nm)	0.65
Maximum micropore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	0.47
Iodine index ($\text{mg I}_2 \cdot \text{g}^{-1}$)	1070
Methylene blue index ($\text{g} \cdot 100 \text{ g}^{-1}$)	0.9
Sugar discoloration index (UBR)	181

2.2. Quantification of Sodium Diethyl Dithiophosphate (SDE DTP) in Aqueous Solutions by UV–Visible Spectrophotometry

The concentration of sodium diethyl dithiophosphate (SDE DTP) in aqueous solutions was determined by UV–visible spectrophotometry using a calibration curve based on absorbance measurements. Analyses were performed with a UV–visible spectrophotometer (Lambda 365, PerkinElmer, Stratford, CT, USA).

An initial spectral scan in the 200–900 nm range indicated that SDE DTP did not exhibit suitable absorbance peaks for direct quantification in the UV–visible region. Therefore, an oxidative digestion and derivatization procedure was employed to convert the phosphorous-containing species into orthophosphate, which subsequently reacted to form the molybdenum blue complex exhibiting maximum absorbance at 890 nm. This indirect quantification approach is based on the presence of phosphorus in the SDE DTP molecule. Under oxidative digestion conditions, the phosphorus-containing moiety is quantitatively converted to orthophosphate, allowing the original SDE DTP concentration to be determined through the measurement of orthophosphate concentration.

Standard SDE DTP solutions with concentrations of 5, 10, 20, 50, 80, and 100 mg L^{−1} were prepared using deionized water. For the digestion step, 100 mL of each standard solution was transferred to an autoclave reactor. Potassium persulfate (K₂S₂O₈, ≥99%, Sigma-Aldrich, St. Louis, MO, USA) was added at a dosage of 1 g per reactor, and the solutions were heated at 80 °C for 1 h to oxidize the phosphorus-containing compounds to orthophosphate. After digestion, the solutions were allowed to cool to room temperature.

The molybdenum blue chromophore was then generated by adding 8 mL of an antimony–phosphomolybdate reagent to each digested solution, followed by manual stirring for 1 min. The reagent was prepared according to standard colorimetric procedures [38]. Briefly, 50 mL of 5 N sulfuric acid (H₂SO₄, 95–98%, Sigma-Aldrich, St. Louis, MO, USA), 5 mL of potassium antimony tartrate (K(SbO)C₄H₄O₆·½H₂O, ≥99%, Sigma-Aldrich, St. Louis, MO, USA), 15 mL of ammonium molybdate ((NH₄)₆Mo₇O₂₄·4H₂O, ≥99%, Sigma-Aldrich, St. Louis, MO, USA), and 30 mL of 0.01 M ascorbic acid (C₆H₈O₆, ≥99%, Sigma-Aldrich, St. Louis, MO, USA) were mixed to obtain 100 mL of reagent. All reagents were equilibrated to room temperature prior to preparation.

After 10 min of reaction, the characteristic blue coloration of the molybdenum blue complex developed. Absorbance measurements were recorded at 890 nm, and the calibration curve was constructed from the absorbance values obtained for each standard SDE DTP concentration.

Table 2 presents the absorbance values measured at 890 nm for the standard SDE DTP solutions, while Figure 2 shows the corresponding calibration curve used for quantitative analysis.

Table 2. Absorbance of sodium diethyldithiophosphate as a function of concentration (890 nm).

SDE DTP	
Concentration (mg L ^{−1})	Absorbance
89	0.775
56	0.475
22	0.281
11	0.156
5	0.101

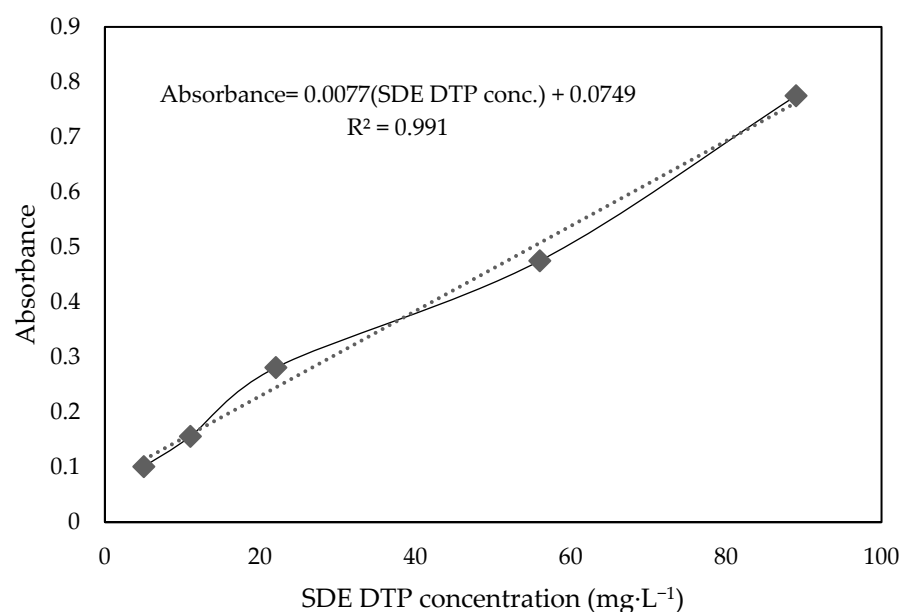


Figure 2. Calibration curve of sodium diethyl dithiophosphate (SDE DTP). The symbols represent experimental data points, and the dotted line represents the linear fitting curve used for calibration.

The limitations of the method are acknowledged due to its simplicity; however, for the present investigation it remains the only viable approach for quantifying the collectors present in this effluent. In future studies, it would be advisable to evaluate additional contaminants using alternative analytical techniques, which would allow diversification of the quantification methods and further strengthen the research conducted with this adsorbent material.

2.3. Preparation of Solutions and Flotation Effluent

2.3.1. Synthetic Collector Solution

A synthetic solution simulating flotation wastewater was prepared using deionized water containing 50 mg·L⁻¹ potassium amyl xanthate (Technical grade, Sigma-Aldrich, St. Louis, MO, USA), 75 mg·L⁻¹ sodium diethyl dithiophosphate (Technical grade, Solvay, Solvay, Brussels, Belgium), 50 mg·L⁻¹ sodium silicate (Na₂SiO₃, 98–99%, Sigma-Aldrich, St. Louis, MO, USA), and 50 mg·L⁻¹ pine oil (Technical grade Sigma-Aldrich, St. Louis, MO, USA) was prepared. These concentrations were selected to represent typical reagent dosages used in sulfide mineral flotation processes.

2.3.2. Laboratory Flotation Effluent

A real flotation effluent was produced using a copper sulfide ore from southern Ecuador containing approximately 0.5 wt% Cu, mainly composed of chalcopyrite, pyrite, and chlorite.

The ore sample (1 kg) was ground with 600 mL of water for 30 min, producing a pulp containing approximately 62.5 wt.% solids. Flotation tests were performed in a 2 L Denver flotation cell (D-12, Denver Equipment Company, Colorado Springs, CO, USA). After grinding, 1400 mL of water was added to the pulp to obtain a flotation feed containing approximately 33 wt.% solids, representative of typical flotation operating conditions.

The pulp was conditioned with 5 mL of 1 wt.% sodium silicate solution for 5 min to disperse fine particles and depress gangue minerals. Subsequently, 10 mL of 1 wt.% potassium amyl xanthate (PAX) solution was added and conditioned for 1 min as the primary collector for sulfide minerals, followed by 10 mL of 1 wt.% sodium diethyl dithiophosphate (SDE DTP) solution for 1 min as supplementary collector to enhance sulfide

mineral flotation. Finally, 5 mL of a 1 wt.% pine oil solution was added and conditioned for 1 min to promote the formation and stability of the flotation froth.

Rougher flotation was then carried out with air injection, and the concentrate was collected for 5 min. Following the first flotation stage, 800 mL of water was added to the remaining pulp, and the conditioning and flotation procedure was repeated under the same operating conditions. The concentrate obtained during this second flotation stage was collected separately.

The tailings slurries and process waters generated during both flotation stages were combined and allowed to settle. After sedimentation, the clarified aqueous phase was collected and used as the real flotation effluent in the adsorption experiments.

2.4. Modification of Activated Carbon

Activated carbon was chemically and thermally modified to introduce oxygen- and nitrogen-containing functional groups. First, 30 g of activated carbon was treated with 300 mL of 3 M nitric acid (HNO_3 , 65%, reagent grade, Sigma-Aldrich, St. Louis, MO, USA) at 60 °C for 6 h under continuous stirring. The carbon was then washed with distilled water until neutral pH was achieved and dried at room temperature overnight.

Separately, 50 g of agricultural-grade urea was dissolved in 500 mL of distilled water and stirred magnetically for approximately 30 min. The washed carbon was then mixed with the urea solution and stirred magnetically for 1 h to allow impregnation.

The treated carbon was separated from the solution and dried at room temperature overnight (~16 h). The dried carbon was then subjected to thermochemical treatment in a Nabertherm tube furnace (RSR 120/500/11, Nabertherm, Berlin, Germany) at 450 °C under a nitrogen atmosphere for 4 h to produce urea-activated carbon. The functional groups introduced by the acid and urea treatments were characterized by Fourier-transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR) using a PerkinElmer Spectrum Two™ spectrometer (Tensor II, Bruker, Karlsruhe, Germany).

2.5. Adsorption Experiments

All adsorption experiments were conducted in batch mode using 200 mL of solution in sealed reactors agitated at 60 rpm for 24 h. After equilibration, samples were filtered using each time 1 g of diatomaceous earth (Hyflo Super-Cel, Imerys, Paris, France) to facilitate solid–liquid separation. Residual SDE DTP was quantified using the UV–Visible method described in Section 2.2.

2.5.1. Effect of Activated Carbon Dosage

The effect of adsorbent dosage was evaluated using the synthetic solution at this natural pH (approximately 7). Activated carbon dosages of 1.25, 2.50, 3.75, and 5.00 g·L^{−1} were tested, corresponding to 0.25–1.00 g of activated carbon per 200 mL solution. This parameter was investigated because the amount of adsorbent directly determines the number of available adsorption sites and, consequently, the removal efficiency of the target collector. The dosage providing the highest removal efficiency while maintaining reasonable adsorbent consumption was selected for subsequent experiments. In this study, a maximum activated carbon dosage of 5 g·L^{−1} was selected because concentrations above this level caused persistent turbidity after 24 h of stirring, which interfered with the spectrophotometric quantification of SDE DTP.

2.5.2. Effect of pH

The influence of pH on SDE DTP adsorption was evaluated using the optimal activated carbon dosage determined in the previous stage. Experiments were conducted at pH 3, 7, and 10. Solution pH was adjusted using 1 N H_2SO_4 (H_2SO_4 , 95–98%, Sigma-Aldrich,

St. Louis, MO, USA) to obtain pH 3 and 10 wt.% NaOH (NaOH, 98–99%, Sigma-Aldrich, St. Louis, MO, USA) to obtain pH 10, while the natural pH of the synthetic solution (approximately 7) was used without adjustment. The pH was investigated because it affects both the ionization state of SDE DTP in solution and the surface charge of activated carbon, which can significantly influence adsorbate–adsorbent interactions and adsorption performance. The pH condition yielding the highest removal efficiency was selected for subsequent tests.

2.5.3. Effect of Activated Carbon Modification

After determining the optimal dosage and pH conditions, the influence of activated carbon surface modification was assessed. Adsorption experiments were conducted using thermochemically modified activated carbon under the previously optimized conditions. This stage was designed to evaluate whether the introduction of oxygen-containing surface functional groups through acid treatment could enhance the affinity of the adsorbent for SDE DTP and improve removal efficiency compared with the unmodified material.

2.5.4. Effect of Effluent Type

The effect of solution matrix complexity on SDE DTP adsorption was evaluated by comparing removal efficiencies obtained in the synthetic collector solution and in a laboratory-generated flotation effluent. This comparison was performed because real flotation effluents contain dissolved inorganic species, residual flotation reagents, and suspended matter that may compete for adsorption sites or alter adsorption mechanisms. Therefore, evaluating both matrices provides insight into the applicability of the optimized adsorption process under realistic operating conditions.

3. Results

3.1. Adsorption of Sulfide Collectors onto Activated Carbon in Synthetic Solutions

3.1.1. Effect of Activated Carbon Dosage on the Adsorption of Sulfide Collectors in Synthetic Solution

Figure 3 presents the effect of activated carbon dosage on the removal of SDE DTP from a synthetic effluent at pH 7. The evaluated dosages ranged from 1.25 to 5.00 g·L^{−1} of microporous activated carbon with high specific surface area.

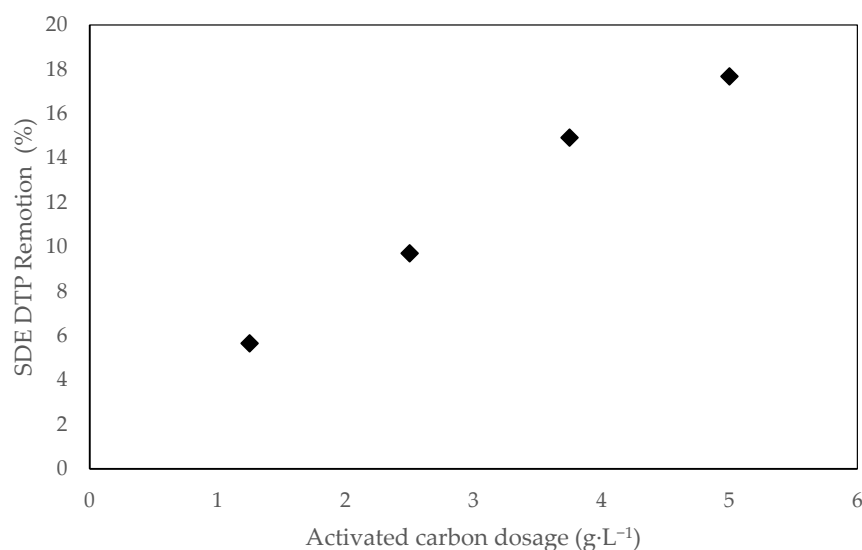


Figure 3. Removal of SDE DTP from a synthetic effluent using microporous activated carbon at pH 7 as a function of adsorbent dosage.

At pH 7, the removal of SDE DTP increases progressively with increasing activated carbon dosage. As shown in Figure 3, a dosage of $5.00 \text{ g}\cdot\text{L}^{-1}$ of microporous activated carbon yields the highest removal efficiency, reaching 17.68%. When the dosage is reduced to $3.75 \text{ g}\cdot\text{L}^{-1}$, the removal decreases to 14.93%, followed by 9.71% at $2.50 \text{ g}\cdot\text{L}^{-1}$, and a minimum value of 5.65% at $1.25 \text{ g}\cdot\text{L}^{-1}$. This trend indicates a direct relationship between adsorbent dosage and removal efficiency, which can be attributed to the increased availability of active adsorption sites as the amount of activated carbon increases. The microporous structure and high specific surface area of the material enhance adsorption performance within the evaluated range. Based on these results, a dosage of $5.00 \text{ g}\cdot\text{L}^{-1}$ of activated carbon was selected for subsequent experiments to evaluate the influence of pH, as it provides the highest removal efficiency and ensures sufficient adsorption capacity under the studied conditions.

3.1.2. Effect of pH on the Adsorption of Sulfide Collectors in Synthetic Solution

Figure 4 shows the effect of solution pH on the removal of SDE DTP from a synthetic effluent. The experiments were conducted at pH values of 3, 7, and 10, using a fixed dosage of microporous activated carbon selected from previous tests ($5.00 \text{ g}\cdot\text{L}^{-1}$).

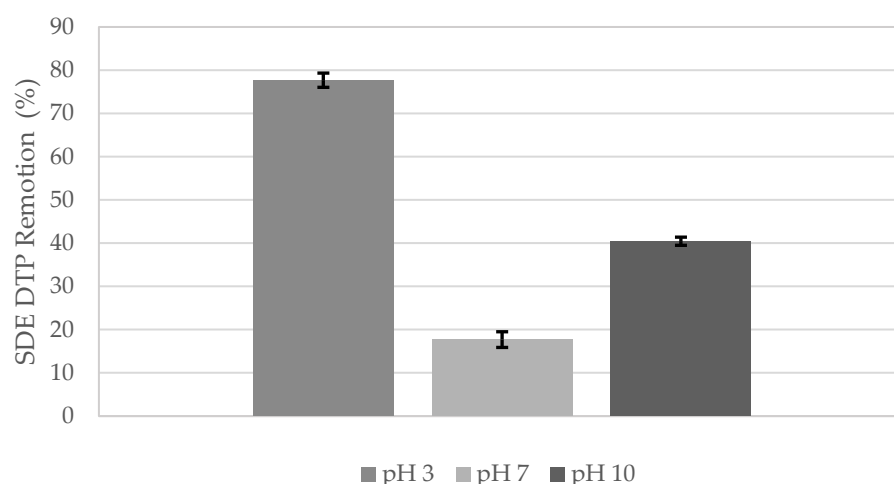


Figure 4. Effect of pH on the removal of SDE DTP from a synthetic effluent using microporous activated carbon ($5.00 \text{ g}\cdot\text{L}^{-1}$).

As observed in Figure 4, pH has a significant influence on the removal efficiency of SDE DTP. The highest removal is achieved under acidic conditions (pH 3), reaching 77.68%. At alkaline pH (pH 10), the removal decreases to 40.43%, while the lowest performance is observed at neutral conditions (pH 7), with a removal of approximately 20%. This behavior suggests that acidic conditions favor the adsorption process, likely due to changes in the surface charge of the activated carbon and the speciation of the collector. In contrast, at higher pH values, electrostatic interactions and/or solubility effects may reduce adsorption efficiency.

Despite the higher removal observed at pH 3, pH 10 was selected for subsequent experiments. This decision is based on two main considerations: (i) acidic conditions may promote additional degradation mechanisms that interfere with isolating adsorption effects, and (ii) there is limited information regarding the behavior of sulfide collectors under alkaline conditions. Therefore, further experiments were conducted at pH 10 to better understand the system under less-explored and more selective conditions.

3.1.3. Effect of Activated Carbon Modification on SDE DTP Removal

Figure 5 compares the removal of SDE DTP from a synthetic effluent using thermochemically modified activated carbon and non-modified microporous activated carbon with high specific surface area. The experiments were conducted at pH 10 under the previously selected operating conditions.

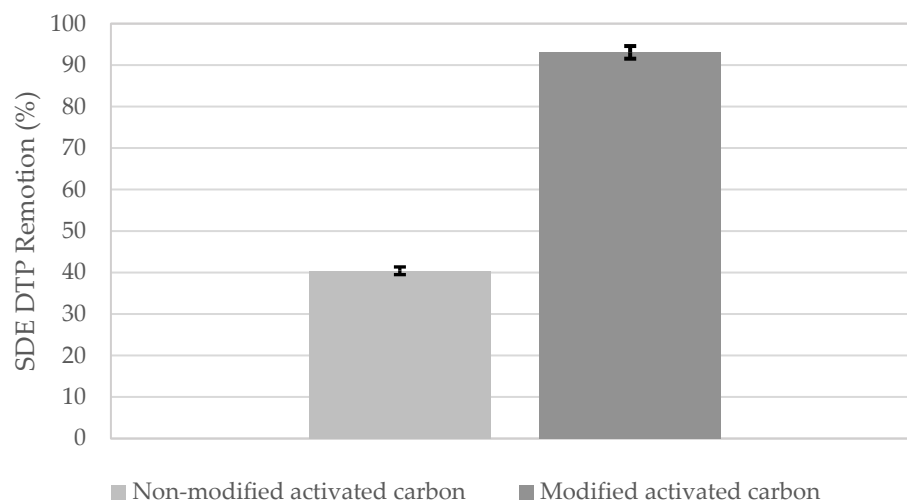


Figure 5. Comparison of SDE DTP removal using thermochemically modified and non-modified activated carbon ($5.00 \text{ g}\cdot\text{L}^{-1}$) at pH 10.

As shown in Figure 5, the thermochemically modified activated carbon exhibits a significantly higher removal efficiency, reaching 93.08% of SDE DTP removal. In contrast, the non-modified microporous activated carbon achieves a removal of 40.43% under the same conditions. This substantial improvement suggests that the thermochemical modification enhances the adsorption performance of the activated carbon, likely by altering its surface chemistry, increasing the number of active sites, or improving the affinity between the adsorbent and the collector molecules. Based on these results, thermochemically modified activated carbon was selected for subsequent experiments, as it provides markedly higher removal efficiency and improves the effectiveness of the adsorption process under alkaline conditions.

3.1.4. Effect of Effluent Type on SDE DTP Removal

Figure 6 presents the removal of SDE DTP using thermochemically modified activated carbon for both a synthetic effluent and a real laboratory effluent under the selected operating conditions.

As shown in Figure 6, high removal efficiencies are achieved in both cases, exceeding 85% of SDE DTP removal. The highest removal is obtained for the synthetic effluent, reaching 93%, whereas the laboratory effluent shows a slightly lower removal of 88%. The difference between both systems can be attributed to the greater complexity of the real laboratory effluent, where the presence of competing species, dissolved organic matter, or inorganic ions may interfere with adsorption and reduce the availability of active sites. Nevertheless, the results demonstrate that the modified activated carbon maintains a high adsorption capacity under more realistic conditions. It is also important to note that activated carbon exhibits a strong affinity for polar compounds, which contributes to the effective removal of SDE DTP from both effluents.

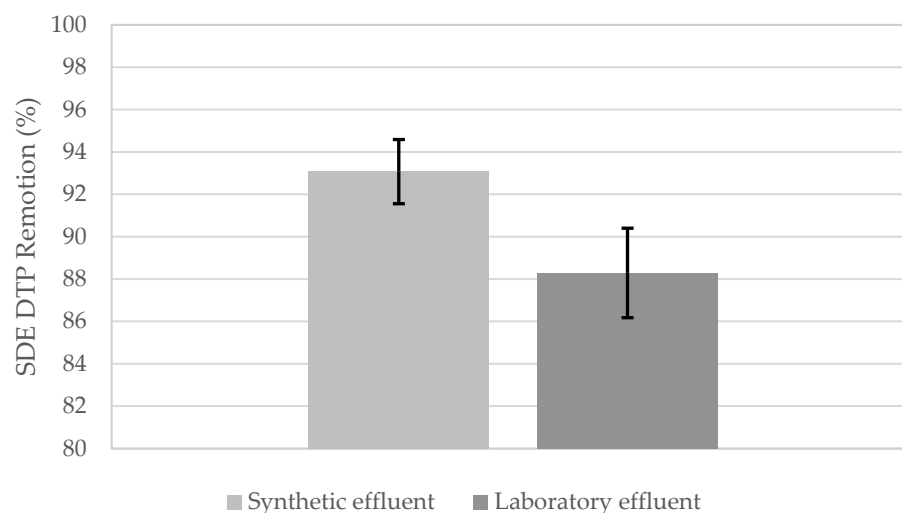


Figure 6. Comparison of SDE DTP removal from synthetic and real laboratory effluents using thermochemically modified activated carbon ($5.00 \text{ g}\cdot\text{L}^{-1}$) at pH 10.

Overall, these results confirm the robustness and applicability of thermochemically modified activated carbon for the treatment of both synthetic and aqueous effluents containing sulfide collectors. The observed trends are consistent with adsorption theory and previous studies, where increasing adsorbent dosage enhances removal efficiency due to the greater availability of active sites, as evidenced by the progressive improvement up to $5.00 \text{ g}\cdot\text{L}^{-1}$. In addition, pH was identified as a key controlling parameter, with maximum removal achieved under acidic conditions (pH 3), likely due to favorable electrostatic interactions and speciation effects. However, alkaline conditions (pH 10) were selected for further investigation to better isolate adsorption phenomena and to evaluate performance under conditions more relevant to industrial flotation effluents. Furthermore, the thermochemical modification of the activated carbon produced a substantial increase in adsorption efficiency, improving SDE DTP removal from approximately 40% to more than 93% under alkaline conditions. This enhancement indicates that surface modification plays a decisive role in improving adsorbent–adsorbate interactions and increasing the accessibility of active adsorption sites. Finally, the high removal efficiencies obtained in both synthetic and real laboratory effluents demonstrate that the modified activated carbon maintains its adsorption capacity even in more complex matrices, highlighting its potential for practical application in wastewater treatment systems associated with mineral processing operations. These findings provide the basis for the following discussion, where the influence of adsorbent dosage, pH, surface modification, and effluent composition on the adsorption mechanism will be analyzed in greater detail.

4. Discussion

4.1. Influence of Molecular Size and Pore Structure on SDE DTP Adsorption

The adsorption behavior of sodium diethyl dithiophosphate (SDE DTP) onto activated carbon is strongly influenced by the relationship between the molecular dimensions of the collector and the pore size distribution of the adsorbent. The projected molecular dimensions of SDE DTP are summarized in Table 3.

Table 3. Molecular dimensions of sodium diethyl dithiophosphate (SDE DTP).

Parameter [39]	Size (nm)
Minimum projection diameter	0.82
Maximum projection diameter	0.92

The dimensional variation presented in Table 3 is associated with the stereochemical configuration and conformational flexibility of the SDE DTP molecule [39]. The activated carbon used in this study is predominantly microporous, with an average micropore diameter of approximately 0.65 nm (see Table 1). Since the minimum molecular diameter of SDE DTP exceeds the average micropore width, the accessibility of the collector to the internal microporous structure is expected to be restricted. Consequently, adsorption is likely to occur preferentially within wider pores and mesoporous regions of the carbon structure. This limitation may partially explain the moderate adsorption performance observed for the non-modified activated carbon under alkaline conditions.

In adsorption processes involving activated carbon, the relationship between pore size distribution and adsorbate dimensions is a critical factor governing adsorption capacity and adsorption energy [40]. Adsorption is generally favored when the pore width is comparable to the molecular dimensions of the adsorbate, since this configuration maximizes adsorbent–adsorbate contact and enhances intermolecular interactions within the pore structure [41]. Conversely, when the pores are significantly larger than the adsorbate molecules, the adsorption potential decreases due to the reduced overlap of interaction forces.

According to micropore filling theory, adsorption potentials from opposite pore walls overlap when the pore width becomes smaller than approximately twice the molecular diameter of the adsorbate [41]. Under these conditions, the adsorbate experiences stronger attractive forces that promote confinement within the pore structure. However, steric hindrance and size exclusion effects may occur when the pore diameter is lower than approximately 1.7 times the second-largest molecular dimension of the adsorbate, thereby limiting diffusion into narrow micropores [41]. In the present study, the dimensions of SDE DTP suggest that a significant fraction of the microporous network may be inaccessible to the molecule, reducing the contribution of micropore filling to the overall adsorption process.

Furthermore, adsorption within mesoporous regions is generally associated with weaker adsorption forces due to the lower degree of contact between the adsorbate and the adsorbent surface [42]. Therefore, the enhanced performance observed after thermochemical modification with HNO_3 is likely associated not only with changes in surface chemistry, but also with improved accessibility to adsorption sites and the incorporation of oxygen-containing functional groups that increase the affinity of the carbon surface toward polar sulfur-containing collector molecules [34,35]. This interpretation is consistent with the substantially higher removal efficiencies obtained with the modified activated carbon, particularly under alkaline conditions.

4.2. Influence of Adsorption Conditions on SDE DTP Removal onto Activated Carbon

The adsorption performance of activated carbon toward sodium diethyl dithiophosphate (SDE DTP) was strongly influenced by the operational conditions evaluated in this study, particularly solution pH and adsorbent dosage. Both parameters directly affect the physicochemical interactions between the collector molecules and the activated carbon surface, thereby controlling adsorption capacity and removal efficiency.

Solution pH is one of the most critical parameters governing adsorption processes because it influences both the speciation of the adsorbate and the surface charge of the adsorbent [43]. Changes in pH modify the degree of protonation and dissociation of functional groups present in SDE DTP, altering its ionic state, polarity, and reactivity in aqueous solution. As a consequence, the affinity between the collector molecules and the activated carbon surface may vary significantly depending on the chemical environment.

In contaminant removal, the charges on the surface of activated carbon are of paramount importance. Studying these surface charges would allow us to determine why certain contaminants adsorb more readily at pH 10 and pH 3. Methods such as spectroscopy and thermal analysis exist to quantify the functional groups present in activated carbon, but they have a drawback: the analysis must be performed with extreme care because the correction of values and baselines can lead to data loss and, consequently, misinterpretation of the results. One method for determining which charges dominate the adsorption chemistry at different pH values is the Boehm titration. This method allows for high precision in the quantification of functional groups on activated carbon [44]. It also enables the detailed characterization and behavior of the functional groups that produce acidic and basic pH results when reacting with the titrant [45].

The experimental results demonstrated that acidic conditions favored SDE DTP removal, reaching the highest adsorption efficiency at pH 3. This behavior may be associated with changes in electrostatic interactions between the collector molecules and the activated carbon surface, as well as modifications in the speciation of the sulfur-containing collector under different pH conditions [46]. Under acidic conditions, protonation phenomena may reduce electrostatic repulsion and enhance the interaction between SDE DTP molecules and the adsorbent surface, thereby favoring adsorption [47]. In contrast, under alkaline conditions, increased ionization of the collector molecules may reduce adsorption affinity due to stronger solvation effects and electrostatic repulsion [48].

Similar pH-dependent adsorption behavior has been reported for flotation reagents and sulfur-containing organic compounds adsorbed onto activated carbon and other porous adsorbents [49]. In flotation systems, pH not only controls the surface chemistry of minerals but also significantly affects the stability and reactivity of flotation collectors in aqueous media [50].

Although the highest removal efficiency was achieved at pH 3, alkaline conditions were selected for subsequent experiments in order to minimize possible degradation reactions of the collector and better isolate adsorption phenomena. Furthermore, alkaline conditions are more representative of industrial sulfide flotation effluents, where flotation circuits commonly operate at elevated pH values due to lime addition for pyrite depression and process selectivity [51].

Adsorbent dosage also exhibited a significant influence on SDE DTP removal. Increasing the activated carbon dosage from 1.25 to 5.00 g·L⁻¹ progressively improved removal efficiency, indicating a direct relationship between adsorbent mass and adsorption capacity. This trend is commonly associated with the increase in available surface area and the greater number of active adsorption sites accessible for contaminant uptake [52]. At higher dosages, the probability of interaction between SDE DTP molecules and adsorption sites increases, promoting greater collector removal from solution.

The progressive increase in removal efficiency observed with increasing activated carbon dosage is consistent with adsorption behavior reported in the literature for flotation reagents and sulfur-containing organic pollutants treated with activated carbon systems [49]. However, the increase in adsorption efficiency was not proportional to the increase in adsorbent dosage, suggesting that part of the adsorption capacity may remain unused at higher dosages due to limitations in adsorbate concentration or mass transfer effects [53].

Overall, the results demonstrate that adsorption conditions play a decisive role in controlling SDE DTP removal efficiency. The combined influence of pH, adsorbent dosage, molecular speciation, and adsorbent surface interactions determines the adsorption performance of activated carbon toward sulfide flotation collectors. These findings highlight

the importance of optimizing operational parameters to maximize contaminant removal in mining wastewater treatment applications.

4.3. Effect of Thermochemical Modification on the Adsorption Performance of Activated Carbon

The thermochemical modification of activated carbon produced a substantial improvement in the removal of sodium diethyl dithiophosphate (SDE DTP), increasing adsorption efficiency from approximately 40% for the untreated material to more than 90% for the modified carbon. This enhancement indicates that surface modification significantly altered the physicochemical properties of the adsorbent, improving the interaction between the activated carbon surface and the collector molecules. Similar improvements in adsorption performance after chemical or thermochemical treatment of activated carbon have been reported for flotation reagents and sulfur-containing organic contaminants [36,54].

Figure 7 presents the FTIR spectra of the untreated microporous activated carbon and the thermochemically modified carbon, while the functional groups associated with the principal absorption bands are summarized in Table 4. The spectra reveal important differences between both materials, confirming that the acid–urea treatment modified the surface chemistry of the activated carbon and introduced additional functionalities capable of influencing adsorption behavior.

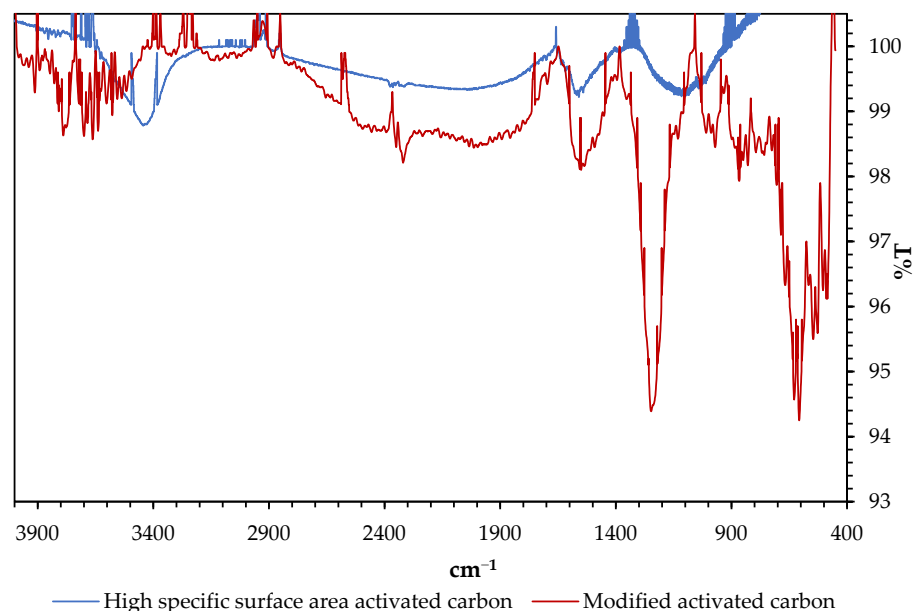


Figure 7. FTIR spectra of the untreated microporous activated carbon and the carbon modified with acid and urea.

Table 4. Spectra functional groups from microporous activated carbon sample.

Type of Coal	Functional Group [55]	Range (cm ^{−1})
Microporous activated carbon with a high specific surface area	O-H t	~3400
	C-O t	1260–1000
	N-H d	1640–1550
Modified microporous activated carbon	C,N t (triple bond)	~2250
	N-H d	1640–1550
	C-N t (alkyl)	1200–1025
	C-H d	~970
	N-H d	~800
	C-Br t	650–510
	C-Cl t	785–540

The FTIR spectrum of the untreated activated carbon exhibits characteristic bands commonly associated with oxygen-containing surface groups present in activated carbon materials [34,35]. A broad absorption band centered near 3400 cm^{-1} corresponds to O–H stretching vibrations associated with hydroxyl groups and adsorbed moisture. Signals within the $1260\text{--}1000\text{ cm}^{-1}$ region are attributed to C–O stretching vibrations of alcohols, phenols, or carboxylic functionalities, whereas the band between $1640\text{--}1550\text{ cm}^{-1}$ is associated with N–H bending vibrations and/or aromatic C=C stretching [55]. These surface functionalities are characteristic of heterogeneous carbonaceous surfaces and contribute to the adsorption properties of activated carbons.

In contrast, the modified activated carbon presents additional absorption bands and changes in band intensity, indicating successful surface functionalization after acid and urea treatment. The appearance of a distinct band near 2250 cm^{-1} is attributed to $\text{C}\equiv\text{N}$ stretching vibrations, typically associated with nitrile-type functionalities, suggesting the incorporation of nitrogen-containing groups during thermochemical treatment. Furthermore, intensified bands in the $1200\text{--}1025\text{ cm}^{-1}$ region correspond to C–N stretching vibrations characteristic of alkyl amines, while additional signals near 970 cm^{-1} and 800 cm^{-1} are associated with C–H and N–H bending modes, respectively [54,56]. These observations support the incorporation of nitrogen-based functional groups onto the carbon surface [56].

The incorporation of nitrogen functionalities is particularly relevant because nitrogen-containing groups can modify the electronic properties, polarity, and acid–base behavior of activated carbon surfaces [57]. Previous studies have reported that nitrogen doping may increase adsorption affinity toward sulfur-containing organic compounds through hydrogen bonding, donor–acceptor interactions, and enhanced surface basicity [58,59]. In addition, nitric acid treatment can alter the pore structure and surface oxygen chemistry of activated carbon, promoting the development of new adsorption sites and improving pore accessibility [34,35,60].

The modified carbon also exhibited bands associated with C–Cl and C–Br stretching vibrations within the $785\text{--}510\text{ cm}^{-1}$ region. Similar halogen-related signals have been reported in activated carbons subjected to strong acid treatments and in carbon materials applied for the adsorption of cyanide and gold-processing residues [55]. However, the exact contribution of these species to flotation collector adsorption remains insufficiently understood and should be further investigated through comparison with similar adsorption systems reported in the literature [61,62].

The improved adsorption performance observed after thermochemical modification can therefore be attributed to the combined effects of surface functionalization, modification of acid–base properties, and possible changes in pore accessibility. These modifications likely enhanced the interaction between the activated carbon surface and SDE DTP molecules, facilitating collector uptake under alkaline conditions. Moreover, despite the slight reduction in removal efficiency observed for the real flotation effluent (88%) compared with the synthetic solution (93%), the modified activated carbon maintained high adsorption performance, demonstrating its resistance to interference from competing species and the complexity of real aqueous matrices [63,64].

Overall, the FTIR analysis confirms that thermochemical treatment generated a chemically distinct activated carbon surface with enhanced adsorption properties. The incorporation of nitrogen-containing functionalities and the modification of surface chemistry appear to play a decisive role in improving the removal of sulfide flotation collectors from aqueous systems.

4.4. Adsorption Performance in Real Flotation Effluents and Study Limitations

The adsorption experiments conducted using real laboratory flotation effluents demonstrated that the thermochemically modified activated carbon maintained a high removal efficiency toward sodium diethyl dithiophosphate (SDE DTP), achieving approximately 88% removal under alkaline conditions. Although this value was slightly lower than the removal obtained for synthetic solutions (93%), the results confirm that the modified activated carbon preserves a high adsorption capacity even in complex aqueous matrices.

The decrease in adsorption efficiency observed in the real effluent can likely be attributed to matrix effects associated with the presence of competing dissolved species, suspended solids, residual flotation reagents, and inorganic ions commonly found in flotation process waters [63,65,66]. These components may compete with SDE DTP molecules for active adsorption sites or interfere with mass transfer processes, thereby reducing the effective adsorption capacity of the activated carbon. Similar reductions in adsorption performance have been reported in studies involving activated carbon treatment of industrial and mining effluents, where contaminant competition and solution complexity strongly influence adsorption behavior [49]. Despite these interferences, the modified activated carbon exhibited considerable adsorption stability and maintained high collector removal efficiency, suggesting that the thermochemical treatment improved not only the affinity of the adsorbent surface toward sulfur-containing collector molecules, but also its resistance to competitive adsorption phenomena [63,64]. These findings highlight the potential applicability of modified activated carbon for the treatment of flotation wastewaters under conditions more representative of industrial systems.

Nevertheless, several limitations should be considered when interpreting the present results. The adsorption experiments were conducted under batch conditions and at laboratory scale, which may not fully represent the hydraulic and chemical complexity of industrial flotation circuits. In addition, the interaction mechanism between SDE DTP molecules and the modified activated carbon surface has not yet been completely elucidated. Parameters such as surface charge distribution, point of zero charge (pHpzc), pore accessibility, and the contribution of specific functional groups require further investigation to better understand the governing adsorption mechanisms [67,68].

Future research should therefore focus on detailed adsorption equilibrium and kinetic studies, including the application of adsorption isotherm models and kinetic models to determine adsorption capacities and rate-controlling mechanisms [43,69,70]. Additional spectroscopic characterization techniques such as X-ray photoelectron spectroscopy (XPS), zeta potential analysis, and surface charge measurements could provide deeper insight into the interaction mechanisms between activated carbon and sulfur-containing flotation collectors [71–73].

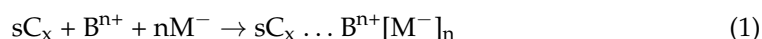
Furthermore, evaluating adsorbent regeneration, long-term adsorption performance, and continuous-flow operation will be essential for assessing the technical and economic feasibility of scaling up this process for industrial wastewater treatment applications associated with sulfide flotation operations [74].

4.5. Proposed Adsorption Mechanism of SDE DTP onto Activated Carbon

To better understand the adsorption behavior of sodium diethyl dithiophosphate (SDE DTP) onto activated carbon, a hypothetical adsorption mechanism based on electrostatic interactions and ion association is proposed. The model considered in this study was originally developed to describe the adsorption of polar and ionic species onto activated carbon surfaces, particularly in systems involving cyanide complexes and dissolved ionic compounds [37].

This adsorption model assumes that certain dissolved species are preferentially adsorbed onto activated carbon after associating with cations present in solution, forming electrically neutral or weakly charged complexes that exhibit greater affinity for the carbon surface. According to this approach, adsorption is governed not only by pore accessibility and surface area, but also by electrostatic interactions between the adsorbate species, dissolved ions, and the activated carbon surface [37].

The adsorption equilibrium can be represented by Equation (1):



where

sC_x : Activated carbon surface

B^{n+} : Alkaline cation, alkaline terrain or hydronium (H^+ , Na^+ , K^+ , Li^+ , Ca^{2+} o Mg^{2+})

$sC_x \dots B^{n+}[M^-]_n$: Species adsorbed in activated carbon

According to this mechanism, adsorption may occur through the association of negatively charged species with dissolved cations prior to adsorption onto the activated carbon surface. In the case of SDE DTP, the collector molecule exhibits polar and anionic characteristics in aqueous solution, particularly under alkaline conditions, suggesting that similar ion-association phenomena may contribute to its adsorption behavior [75].

However, the applicability of this adsorption model to SDE DTP systems remains hypothetical and requires additional experimental validation. Future studies should therefore include zeta potential measurements, pHpzc determination, adsorption thermodynamics, and advanced spectroscopic analyses such as FTIR after adsorption, XPS, or Raman spectroscopy to confirm the nature of the adsorbate–adsorbent interactions and identify the dominant adsorption mechanisms [76,77].

Therefore, experimental validation of the mechanism requires a multidimensional approach: zeta potential and pHpzc measurements to define the surface charge of the coal; adsorption thermodynamics studies (ΔG° , ΔH° , ΔS°) to distinguish between processes dominated by physical interactions, ion-association or complexation, confirming the formation of surface complexes or the participation of specific bonds [78].

Finally, integrating this model with kinetic data and pseudo-second-order isotherms, Langmuir, Freundlich, or more advanced models would allow us to evaluate whether the adsorption of SDE DTP follows a predominantly monomolecular mechanism at energetically homogeneous sites, or whether there is a significant contribution from surface heterogeneity and multilayers associated with the formation of ionic aggregates at the interface. A deeper understanding of these aspects would not only strengthen the validity of the hypothetical mechanism but also facilitate the optimization of activated carbon treatment strategies for the removal of flotation collectors from mining effluents, allowing for adjustments to operating conditions and material design based on collector speciation and medium chemistry [79].

The adsorption reaction described by Equation (1) is reversible and may be influenced by variations in collector concentration, ionic strength, and temperature [37]. Consequently, understanding these interactions in greater detail may contribute to the optimization of activated carbon treatment strategies for the removal of flotation collectors from mining wastewaters.

4.6. Future Perspectives on the Removal of Flotation Reagents Using Modified Activated Carbon

Within the framework of this research, several elements have been identified that, while contributing conceptual value, exceed the experimental scope of this study. Therefore, it is considered pertinent to point out that certain aspects should be addressed in future work in order to expand and consolidate the available knowledge on this adsorbent.

This research would benefit in the future from studies that include adsorption kinetics, adsorption isotherms, and the ability to determine under which isotherms the removal of these types of contaminants occurs. Similarly, a more in-depth characterization would allow for a full understanding of the range of applications in different industrial sectors. However, for now, this research aimed to elucidate the efficiency of this new type of activated carbon in removing sulfide collectors. A future proposal could delve even deeper to further enrich the research on this material.

In line with this need for further investigation, it is essential to consider that the characterization of activated carbon is a key component for understanding its adsorptive performance. A more complete characterization would not only allow for the validation of the proposed mechanisms but also for the establishment of stronger relationships between the material's structure and its efficiency in contaminant removal.

Characterizing activated carbon is essential because structural modifications—such as changes in functional groups, specific surface area, and pore distribution—directly influence its adsorption performance. To obtain a comprehensive understanding of the material, additional analyses are recommended, including CHNS elemental analysis, BET surface area measurements, Boehm titration for quantifying acidic and basic surface groups, as well as adsorption isotherm modeling and kinetic evaluations. Together, these techniques provide deeper insight into the physicochemical properties of the adsorbent and its interaction mechanisms with target contaminants [80].

Furthermore, from an applied perspective, it is essential to consider the adsorbent's stability under real-world operating conditions. The durability and regeneration capacity of activated carbon determine its industrial viability; therefore, studies aimed at evaluating its behavior under repeated adsorption–desorption cycles are indispensable for its large-scale implementation.

At the industrial level, the focus is generally on adsorbent materials that maintain long-term stability and can be regenerated as many times as possible to reduce costs, a critical factor for industrial viability. It has already been observed that thermochemically treated activated carbons with nitrogen functional groups on their surface become more resistant to oxidation, reducing oxidation by up to 40% over 100 load-discharge cycles of the adsorbate. Furthermore, to complement this study, the scope could be extended to investigate the long-term degradation effect of this thermochemically treated activated carbon [81].

Finally, the advancement of emerging technologies offers new opportunities to optimize both the characterization and adsorptive performance of activated carbon. The integration of machine learning tools and electroadsorption techniques allows for modeling, predicting, and improving the material's efficiency under dynamic conditions, significantly expanding the scope of future research.

The incorporation of new machine learning technologies has significantly boosted the simulation and prediction of the adsorptive performance of activated carbons used to remove methylene blue from wastewater. Recent studies demonstrate that machine learning models, especially algorithms like random forest, can accurately predict adsorption capacity from key variables such as specific surface area, pore volume, and initial dye concentration [82]. This predictive capability reduces the need for extensive experimentation and allows for the optimization of adsorbent design and operating conditions. In parallel, emerging technologies such as electroadsorption, combined with intelligent control systems, have demonstrated improved process efficiency under dynamic conditions, reinforcing the role of AI as a tool for optimizing real-time operations. Overall, the recent literature agrees that the next critical step is to further characterize the adsorption equilibrium, integrating advanced predictive models that allow for a more accurate description of

isotherms and molecular capture mechanisms, in order to develop more robust, efficient, and sustainable decontamination systems [83]. Future work should study these systems in depth in combination with new technologies, thus providing a full range of applications for this adsorbent material.

5. Conclusions

This study demonstrated the effectiveness of activated carbon for removing sodium diethyl dithiophosphate (SDE DTP) from both synthetic solutions and real flotation effluents associated with sulfide mineral processing. Adsorption performance was strongly governed by operational conditions, surface chemistry of the adsorbent, and the physicochemical characteristics of the collector.

Activated carbon dosage and solution pH were key parameters influencing SDE DTP removal. Increasing the dosage from 1.25 to 5.00 g·L⁻¹ progressively enhanced adsorption due to the greater availability of active sites. Solution pH played a decisive role: the highest removal efficiencies were observed under acidic conditions (pH 3), highlighting the importance of electrostatic interactions and collector speciation. Nevertheless, alkaline conditions (pH 10) were selected for further evaluation because they better represent industrial flotation effluents and minimize potential collector degradation.

Thermochemical modification of activated carbon through nitric acid oxidation and urea treatment substantially improved adsorption performance. Under alkaline conditions, the modified carbon increased SDE DTP removal from approximately 40% (unmodified carbon) to over 90%, demonstrating that surface functionalization markedly enhances adsorbent–adsorbate interactions.

The modified activated carbon also maintained high efficiency in real flotation effluent, achieving removal above 85% despite the presence of competing dissolved species. These results confirm the practical applicability of the modified material for treating mining wastewater under realistic operating conditions.

Overall, the results suggest that thermochemically modified activated carbon represents a promising and practical option for improving wastewater management in mineral processing operations. Its high efficiency, stability under operational conditions, and compatibility with conventional adsorption systems position it as a feasible technology for reducing collector contamination and supporting compliance with environmental discharge standards.

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