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Removal of phenol from aqueous effluents by ionic flocculation treatment

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Abstract

Phenol and its derivatives are toxic pollutants found in industrial wastewater, requiring efficient removal to avoid environmental impacts and health risks, especially in the oil industry. Brazilian legislation sets strict limits for phenols in industrial effluents, emphasizing the need for appropriate treatment solutions. This study investigates ionic flocculation as an effective technique for removing phenol from synthetic aqueous effluents, using anionic surfactants and calcium chloride to promote coagulation and flocculation. Initially, an aqueous solution with phenol was prepared at a concentration of 100 ppm. The experimental methodology was carried out in three stages: kinetic study, evaluation of surfactant concentration and solution pH. The results indicated that ionic flocculation, using surfactants (palmitate, stearate, and sodium laurate) and calcium chloride, can remove more than 57% of the phenol, with efficiency being maximized with higher surfactant concentrations and basic pH. The efficiency of the process increased with contact time and higher surfactant concentrations, but was decreased at acidic pH due to the formation of emulsions and the change in surfactant charge. These findings highlight ionic flocculation as a promising solution for the treatment of phenol-contaminated effluents, contributing to more sustainable treatment practices in the oil industry.

Keywords: surfactant, waste water, toxic pollutants.

1. Introduction

Phenol and its derivatives are common pollutants in wastewater from various industrial sectors and domestic effluents. Their toxicity, even at low concentrations, makes their efficient removal essential before discharge into water bodies [1]. In the oil industry, oil contains, in addition to hydrocarbons, impurities such as phenolic compounds, which pose serious environmental and public health risks. For this reason, the treatment of phenol-contaminated effluents has become a priority [2].

The treatment of oil production water faces challenges due to the complexity of the effluent and the presence of phenolic compounds, which are toxic and difficult to treat. The oil industry are investing in new technologies to improve treatment efficiency, and effective elimination of these compounds is essential to reducing environmental impact. Environmental legislation in Brazil, including CONAMA Resolution No. 357/2005 and CETESB Ordinance No. 8.468/1976, establishes a maximum limit of 0.5 $mg.L^{-1}$ for total phenols in industrial effluents, highlighting the need for efficient treatment solutions [3,4,5].

Ionic flocculation has stood out for its effectiveness in removing phenol from water, surpassing traditional methods in efficiency and adaptability [6]. Using anionic surfactants and cations, such as calcium chloride, this method promotes coagulation and removal of contaminants by sedimentation or filtration [7]. In addition to effectively removing organic compounds, ionic flocculation reduces energy consumption and simplifies the operation of treatment systems, positioning itself as a promising solution for the oil industry.

The aim of this study is to evaluate the effectiveness of a treatment system for removing phenol from synthetic water using ionic flocculation. The research seeks to optimize the conditions of the flocculation process in order to develop a practical and efficient solution for the management of phenol-contaminated effluents. The focus will be on identifying the optimal conditions that maximize the system's efficiency, contributing to more effective and sustainable treatment practices in the management of industrial effluents.

2. Methodology

To carry out the research, the experimental methodology was divided into stages: kinetic study, evaluation of surfactant concentration and solution pH.

2.1 Kinetic Study

The experimental methodology was based on the study by [8]. Initially, an aqueous synthetic effluent containing phenol at a concentration of 100 ppm was prepared. Surfactants synthesized in the laboratory, including sodium palmitate, sodium stearate and sodium laurate, were weighed and divided into 30 mL of distilled water at an initial concentration of 2150 ppm. During the flocculation process, calcium chloride was added to the surfactant at a concentration of 1075 ppm to facilitate the preliminary flocculation of the components. Next, 20 mL of the synthetic effluent with phenol was added to the flocculated surfactant, and the mixture was kept under constant agitation at 150 rpm on an orbital shaker (SL - 180/A). After specific periods of contact between the phases, the solutions were collected and vacuum filtered using qualitative filter paper (15 cm diameter and 80 g/m²). The concentration of unfiltered phenol was measured using a UV-Visible spectrophotometer (ME-UV1100) at a wavelength of 273 nm. The phenol removal efficiency was calculated using Equation (1):

$$\% \, removal = \frac{C_{initial} - C_{diluted}}{C_{initial}} x100 \qquad (1)$$

Where Cinitial is the initial concentration of phenol and Cdiluted is the concentration of phenol in the diluted phase after separation.

2.2 Evaluation of surfactant concentration

The study of surfactant concentration was evaluated for three types (sodium palmitate, sodium stearate and sodium laurate) at different concentrations of 150, 400, 650, 900, 1150, 1400, 1650, 1900, 2150, 2400, 2650, 2900 and 3150 ppm, maintaining a phenol concentration in the synthetic effluent constant at 100 ppm, representative of the range (2.8 to 1220 ppm) observed in water from the petrochemical industry [9]. Samples were prepared in 250 mL Erlenmeyer flasks. The surfactant was weighed and distributed, and calcium chloride was used at half the surfactant concentration for each interval.

2.3 Effect of pH

The effect of solution pH on phenol removal was evaluated at two fixed surfactant concentrations: 1650 ppm for sodium palmitate and sodium stearate, and 2650 ppm for sodium laurate. These concentrations achieved the best removal efficiencies. The phenol concentration was kept constant at 100 ppm throughout the experiment. The process was carried out over a pH range of 3 to 12. After adding the phenol solution to the flakes, the pH was adjusted using a Digimed pH meter, model DM-22. The pH was adjusted after adding the phenol to avoid variations in the pH of the system that could occur if the pH was adjusted beforehand.

3. Results and Discussion

The results will evaluate the effectiveness of the proposed methodology, with emphasis on the kinetic study, variation in surfactant concentration and the effect of pH.

3.1 Kinetic Study

The kinetic study aimed to determine the equilibrium time for phenol removal from a synthetic effluent (100 ppm), using calcium chloride as a flocculant. Calcium chloride promoted coagulation and the formation of larger flocs, facilitating filtration and significantly reducing the concentration of phenol. Phenol removal exceeded 57% for the three types of surfactants studied (sodium palmitate, sodium stearate and sodium laurate) at concentrations of 2150 ppm, with calcium chloride at 1075 ppm, agitation at 150 rpm and a contact time of 180 minutes. Fig. 1 shows the effectiveness of the method according to the specific conditions tested.

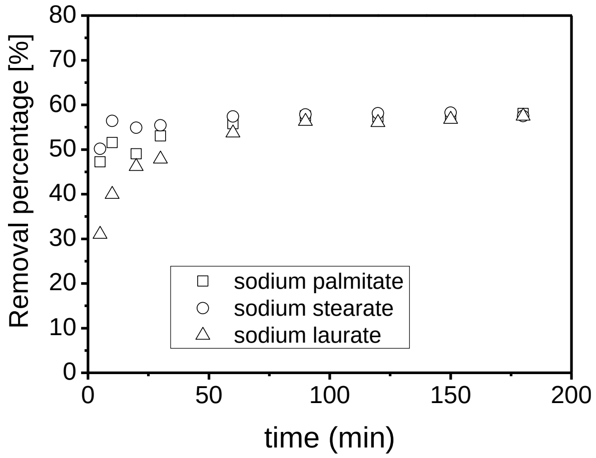

Fig. 1. Percentage of phenol removal as a function of time for different surfactants.

Fig. 1 shows that phenol removal increases with contact time, reaching its maximum efficiency after 90 minutes for the three surfactants analyzed, when the system stabilizes and there is no improvement with longer times. This time is sufficient to achieve optimum efficiency, bringing benefits such as reduced operating costs and process optimization, with less consumption of resources and energy. For example, with sodium laurate, the efficiency was only 31% in 5 minutes, due to its shorter carbon chain, which limits phenol adsorption, highlighting the importance of contact time.

2.2 Evaluation of surfactant concentration

In order to determine the best conditions for phenol removal efficiency, it was essential to analyze the surfactant concentration. The concentration of the surfactant directly influences floc formation and coagulation capacity during the flocculation process. Studying the concentration allowed us to identify the ideal amount of surfactant to maximize phenol removal from the synthetic effluent studied. Figure 2 shows the percentage removed as a function of the surfactant concentrations.

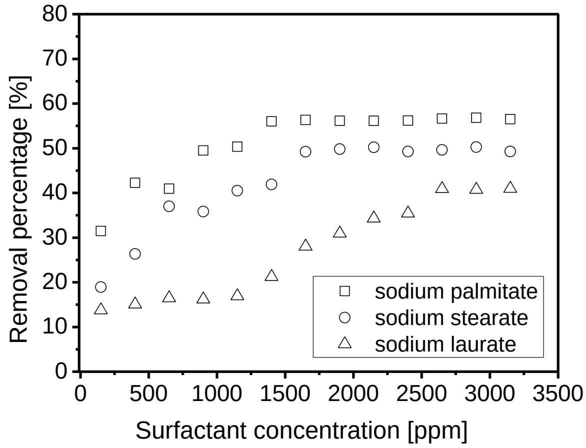

Fig. 2. Phenol removal percentage as a function of surfactant concentration.

Fig. 2 shows that, at low surfactant concentrations, both processes were ineffective at removing phenol, similar to what was observed by [6]. Efficiency increased significantly only at higher concentrations: 56% for sodium palmitate at 1400 ppm, 49% for sodium stearate at 1650 ppm and 40% for sodium laurate at 2650 ppm. Similarly, [6] reported that, below 500 ppm, ionic flocculation was not efficient at removing malachite green, while at higher concentrations, removal stabilized at around 95-96%.

2.3 Effect of pH

Fig. 3 illustrates the percentage removal of phenol for various surfactants as a function of the pH of the aqueous solution.

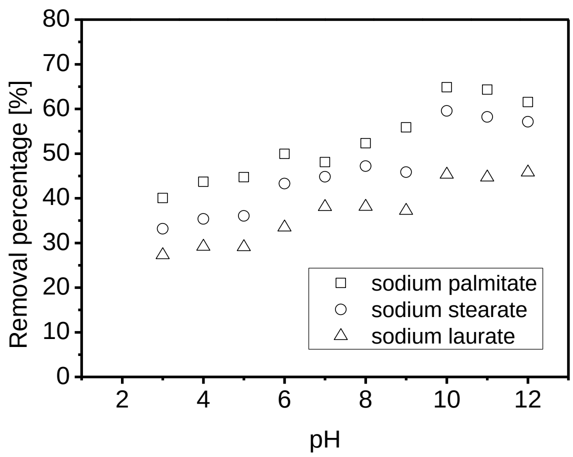

Fig. 3. Phenol removal percentage for different surfactants as a function of pH.

Fig. 3 shows that, at acidic pH (3 to 5), phenol removal efficiency is reduced compared to basic pH (10 to 12). At acidic pH, the formation of an oil-in-water emulsion and the conversion of the surfactant to its acidic form compromise the charge of the carboxylate anions and the formation of stable flocs, reducing the efficiency of phenol removal. [10] found similar results, with lower efficiency at pH below 5 and better performance at pH above 10 for ionic flocculation and oil extraction from produced water. However, oil removal already showed good results at neutral pH (7), showing greater flexibility in pH conditions for oil removal compared to phenol.

4. Conclusions

The experimental methodology demonstrated potential for the removal of phenol from synthetic effluents via ionic flocculation, achieving over 57% efficiency using calcium chloride and different surfactants. The efficiency increased with longer contact time and higher concentrations of surfactants, reaching its maximum under basic pH conditions. Prolonged contact time and proper surfactant concentration were crucial for optimizing removal, while acidic pH reduced efficiency due to emulsion formation and changes in the surfactant charge. These results present a promising alternative for treating effluents containing phenol, aligning with the pursuit of more sustainable methods for the oil industry, although further studies are needed to validate its large-scale application.

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