Influence of Coagulants in the Chemical Flocculation Process of Pollutants from Petrochemical Wastewater

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ABSTRACT

This study investigated the optimization of chemical methods for the removal of petrochemical pollutants from wastewater. The novelty of this research lies in identifying the optimal concentration of coagulants, particularly the combination of IP1140 polyelectrolyte with Fe^{2+} ions. Five identical reactors were tested using a mixture of $FeSO_4$ (3%), IP1140 polyelectrolyte (0.2 ppm), and $Ca(OH)_2$ (20%) in different molar ratios per 100 mL (v:v:v): 1:1:2, 1:2:2, 2:1:1, 2:1:2, and 2:2:1. Parameters, such as the pH value, COD, BOD, the amount of extractable, and residue, were evaluated. The results demonstrated that after 10 min, the pH increased from 6.5 to 6.8 in reactor A and to 7.2 in reactor E. After 30 min, the pH values ranged from 7.0 to 7.5, reaching a maximum of 8.5 in reactor E after 120 min. The chemical treatment resulted in COD reductions of up to 89% in reactor B and 91.8% in reactor C; BOD reductions of up to 76% in reactor B and 87% in reactor E; extractable substances were reduced by up to 92% in reactor D and 88% in reactor A; while residue decreased by up to 87% in reactor B and 84% in reactor D. The BOD/COD ratio ranged between 0.3 and 0.5, with the best chemical treatment ratio carried out in reactor E with molar ratio/100 mL (v:v:v) 2:2:1.

Keywords-polyelectrolyte; COD; BOD; chemical treatment; coagulation; petrochemical wastewater

I. INTRODUCTION

Many aspects of the technological production process lead to industrial pollution, often resulting in wastewater loaded with various chemical compounds, organic substances, or suspensions being discharged through an outfall pipe [1]. Flotation processes are employed to remove pollutants from effluents derived from various industries, including cellulose industry, textile and dyeing, food, municipal wastewater, wastewater from tanning processes, or wastewater in agriculture, particularly, from modern pest control and animal husbandry operations [2-6].

The removal methods vary depending on the type of pollutants. For instance, petroleum contaminants, consisting mainly of hydrocarbons, waxes, oils, soaps, fatty acids, and tars from oil processing, undergo a primary treatment through a gravitational separation based on density differences [7-9]. This process becomes more efficient when flow rates and contaminant concentrations are equalized. However, the only disadvantage is that emulsified and dissolved petroleum substances are not retained. In such cases, treatment involves coagulation and flocculation of polluting particles [10-14]. Additionally, oil pollution generated by hydrocarbons is difficult to remove entirely using only chemical methods. Oil spills, with diverse composition, are considered a challenging substrate mixture as not all microorganisms can survive to all pollutants. Therefore, chemical treatment is often followed by a biochemical degradation process [15-22]. Methods for complete biodegradation are based on the metabolic reactions of a biocenosis of biological sludge that may contain ciliated microorganisms (Paramecium caudatum), bacteria (Bacillus subtilis, Micrococcus luteus, Pseudomonas aeruginosa), yeast (Saccharomyces sp.), and algae (Chlorella pyrenoidosa). These microorganisms are capable of degrading organic substances to carbon dioxide and water, such as sulphonic acids, asphaltenes, phenol, furfural of diethylene glycol, chlorine, and diesel fuel that were used as carbon sources [23]. The removal of organic substances dissolved in water is made through their adsorption on the surface of the biological cells. The final result of the biological purification process is realized by the total elimination of polluting impurities from the wastewater .

Coagulation is a common chemical process used to remove small, with the same charge chemical pollutants [24]. Coagulants neutralize these electrical charges, leading to the formation of larger particle aggregates, which can cause collisions, and thus sediment [25-54]. The electrostatic structure of a colloidal particle is illustrated in Figure 1. According to Stokes' law, sedimentation time due to gravity is defined by the time required for water to flow vertically over 1 m at 20 °C. Gravitational separation in aqueous solutions is based on the principle that negatively charged colloidal particles absorb the positively ones in the water, forming a rigid layer, where the Zeta potential rapidly decreases [55]. Beyond this layer, a diffuse layer is formed in which the Zeta potential declines very slowly. The destabilization of these colloidal suspensions occurs upon the addition of a chemical reagent, called coagulant. Coagulation begins when Van der Waals attractive forces exceed repulsive forces. This is followed by the flocculation process during which the repulsive forces are eliminated.

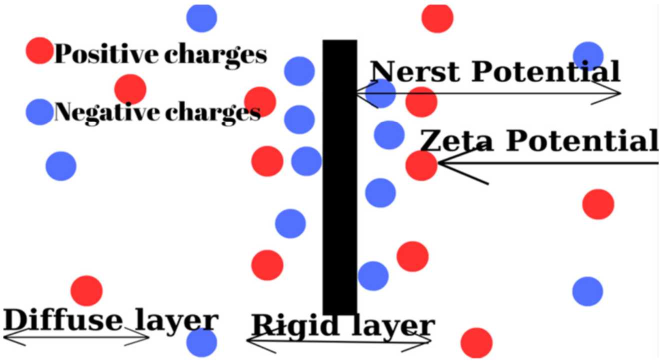

Fig. 1. The electrostatic structure of a colloidal particle.

Flocculation happens due to the use of organic coagulants, such as cationic polyelectrolytes; mineral polymers, such as activated silica; and inorganic compounds, such as ferric sulfate, sodium hydroxide, ferrous sulfate (alone or combined with chlorine and calcium hydroxide), as well as aluminum or iron salts, copper sulfate, and synthetic cationic polyelectrolytes [56-65]. Flocculation can occur in the presence of Al^{3+} ions, with an optimal coagulation pH ranging from 6.0 and 7.4. Otherwise, the process can take place in the presence of Fe^{3+} cations with an optimal pH of less than 5.0, or in the presence of Fe^{2+} ions with an optimal pH coagulation between 8.5 and 8.8. The general mechanism of action for both coagulants and flocculants is presented in Figure 2.

The use of optimum doses of coagulants/flocculants has the advantage of quickly removing a series of pollutants, such as organic and inorganic compounds (sulfates, chlorides, nitrates), which contribute to high turbidity and color changing of wastewater. The chemical composition of wastewater is vital for choosing the best option of doses. Coagulants react with ionized groups on the surface of colloidal particles, with the formation of products with low solubility or insoluble, and the chemical reaction being dependent on the pH of the environment.

Several studies have investigated the removal of pollutants from wastewater using coagulants. Specifically, the removal of petroleum pollutants was investigated through a chemical flocculation method using Fe^{2+} ions and 0.2 ppm of polyelectrolyte per 100 mL sample combined with specific microorganisms: Paramecium caudatum, Aspidisca polistila, Vorticella microstoma, Litonotus setigerum, and Rotifers [65]. The optimal pH for biodegradation was found to be 8.3. Under these conditions, the chemical pollutants were decreased with values up to 86%, extractable substances by 90%, naphthenic acids by 100%, while phenols and COD by 63%. Similarly, in [16], bacteria Bacillus subtilis, Pseudomonas aeruginosa, and Micrococcus luteus have also demonstrated effectiveness in breaking down petroleum contaminants by forming competitive relationships with the target chemical compounds.

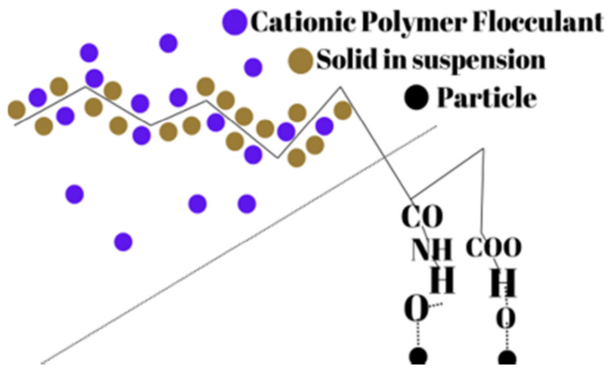

Fig. 2. The general mode of coagulants and flocculants and the structural details of the polymer chain.

Additionally, in [66], the effectiveness of three coagulants including $CuSO_4$, $FeCl_3$, and the combination $CuSO_4$-$FeCl_3$, was assessed for treatment of wastewater from petroleum refinery using coagulation and flocculation processes. The results demonstrated that the mixture of $CuSO_4$-$FeCl_3$ at doses of 0.20 g/L and pH =7.12 provided the best performance with a reduction of COD by 76.77%, turbidity by 89.47%, TDS by 94.16%, and color by 95.29%.

In [67], Al and Fe coagulants were examined both individually and in combination with activated carbon, at molar ratios of 1:1, 1:2 and 2:1. The tests were performed at pH = 7 in an electrostatic voltage field. It was found that the combination of activated carbon with Al-Fe in a molar ratio of 2:1 eliminated COD with values ranging from 66% up to 87.14% in 20 min of exposure and the turbidity was reduced with values of up to 99.21%.

The purpose of the experiment was to test different concentrations of flocculants and coagulants to find the best formula that can be successfully applied in the removal of contaminants and the transformation of a sample that cannot be biodegraded in its initial state. Cationic polyelectrolytes IP1140 in combination with $FeSO_4$ and $Ca(OH)_2$ were utilized as coagulants. These substances reacted together by destabilizing and aggregating colloidal contaminants into larger flocs. The parameters involved in the coagulation process are pH, zeta potential, molar ratio of flocculants, pollutant concentration, and agitation time.

II. EXPERIMENTAL METHOD

This study focused on the flocculation of wastewater samples. These samples were sourced from a tank farm storing crude oil residues and from the wastewater treatment plant of a petrochemical refinery.

The experimental setup employed a pH meter, an AREC VELP magnetic stirrer, and chemical reagents, including calcium hydroxide ($Ca(OH)_2$), IP1140 polyelectrolyte, and ferrous sulfate ($FeSO_4$). The reagents were weighed using an OHAUS model AX224M analytical balance (Ohaus Corporation, Parsippany, NJ, USA). pH and oxygen measurements were performed using a WTW inoLab Multi 9630 IDS multi-parameter device (WTW, Weilheim, Germany), which features three galvanically isolated measuring channels. The residence time in a wastewater treatment plant is very important, both for the coagulation and flocculation stages, as it influences the interactions of colloidal particles [68, 69]. A too low dose can produce insufficient flocculation, while a too high dose can lead to additional consumption of reagents without obtaining an efficient result. To monitor the coagulation time in relation to its dose, tests were performed in TURBISCAN Lab (FormulAction, L'Union, France).

Five samples of 0.5 L were collected from different points in the waste storage tank using an immersion probe collector. These were gathered into a vessel and homogenized for 2 hours at 200 rpm using an AREC VELP magnetic stirrer, resulting in a 2500 mL average sample. A volume of 500 mL of the average sample was diluted with 1000 mL of residual water, collected from the Parshall collection area of the petrochemical industry wastewater treatment plant, whose chemical analysis is presented in Table I.

TABLE I. PHYSICOCHEMICAL CHARACTERISTICS OF THE AVERAGE SAMPLE

Analysis performed	**Chemical composition of the average sample**	**Chemical composition of dilution water**	**Standard analysis**
pH	6.5	8.5	-
Dry substance (g/L)	27.8	-	STAS 12586-87
Ash (mg/L)	840	-	
Inorganic substance (%)	28.60	-	
Organic substance (%)	71.40	-	
Extractable in petroleum ether (mg/l)	960	5.8	STAS 12607-88
Residue (mg/l)	1456	188	STAS 6953-81;
CCO-Cr (mg/l) (COD)	880	75	ISO 6060:1996
CBO_5 (mg/l) (BOD)	220	25	ISO 5815-1:2020

The resulting 1500 mL sample, defined as working sample, was again homogenized for 2 hours at 200 rpm and then divided into three identical 500 ml parts for accuracy. Each portion was further subdivided into five 100 mL subsamples, labeled A through E, and placed in 250 mL glass reactors. In each reactor, a stable quantity of flocculants of the following concentrations was added, consisting of $FeSO_4$ at 3%, polyelectrolyte IP1140 at 0.2 ppm, and $Ca(OH)_2$ at 20% , according to the following molar ratio per 100 mL: 1:1:2, 1:2:2, 2:1:1, 2:1:2, and 2:2:1.

The concentrations and doses of the substances introduced into the 5 test vessels are presented in Table II.

TABLE II. DOSES AND CONCENTRATIONS OF SUBSTANCES USED IN TESTING

Sample	**$FeSO_4$ (3%)**	**IP114 (0.2 ppm)**	**$Ca(OH)_2$ (20%)**
A	5 mL	5 mL	10 mL
B	5 mL	10 mL	10 mL
C	10 mL	5 mL	5 mL
D	10 mL	5 mL	10 mL
E	10 mL	10 mL	5 mL

The flocculation process, as illustrated in Figure 3, utilized a combination of polyelectrolyte and $FeSO_4$ solution. By stirring, the flocculation phenomenon incorporated the particles into the water. An artificial particle-air bubble conglomerate with an apparent specific gravity lower than that of the liquid, constituted the main phase. The pH was adjusted with a 25% hydrated lime solution ranging from 8.5 to 8.8.

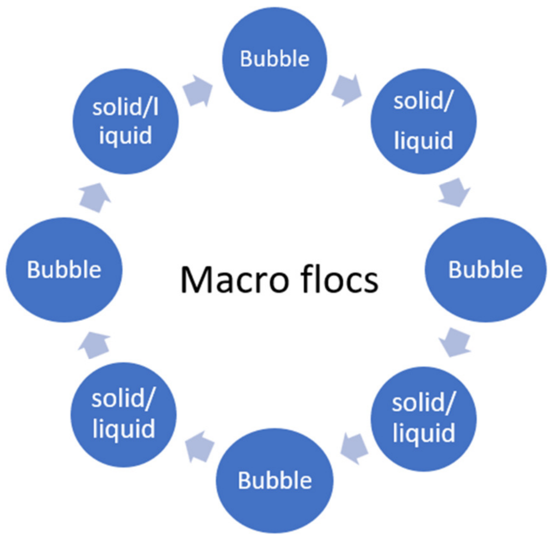

Fig. 3. The flocculation process.

III. RESULTS AND DISCUSSION

The colloidal stability of the flocs in relation to the variation in particle size due to flocculation was detected and quantified based on the backscatter (*BS*) and transmission (*T*) signal intensities, as displayed in Figure 4. The highest sediment layer was obtained in the presence of flocculants at a molar ratio per 100 mL 2:2:1. The combination of flocculants in that ratio was more efficient, easily forming flocs that enclosed polluting particles in the analyzed water.

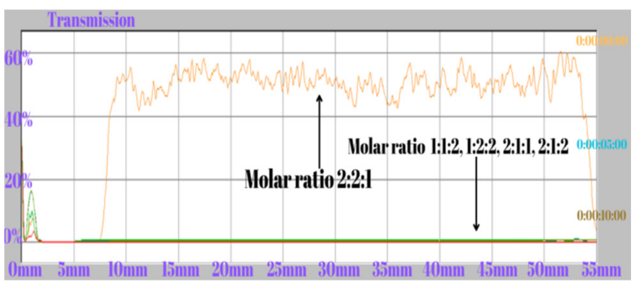

Fig. 4. Turbiscan transmission, *T* (%) on various dosage of floculants versus sample height (mm) durring 5 min of exposure.

After the stirring step, aliquot volumes of water were collected from the supernatant of each sample by aspiration at time intervals of 10, 20, 30, 60, and 120 min of rest, and chemical analyses were performed measuring the pH value, COD, BOD, as well as the amount of extractable and residue.

The pH evolution over time is depicted in Figure 5, while the final experimental results are illustrated in Figure 6.

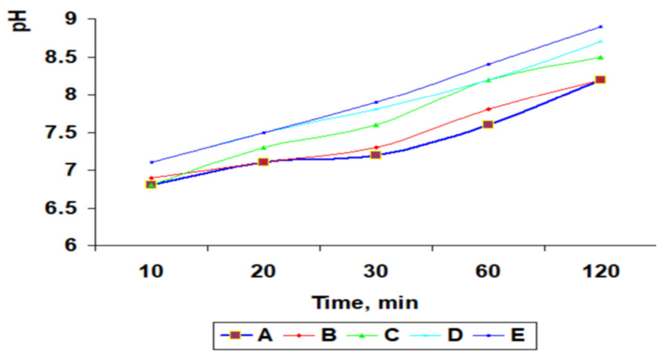

Fig. 5. pH results obtained during the experiment.

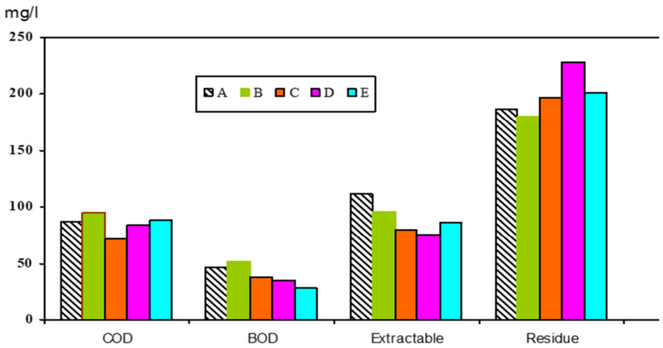

Fig. 6. Experimental results obtained at the end of the experiment

The pH increased gradually during the experiment, with values rising from an initial 6.5 to 6.8 in system A and 7.2 in system E after 10 min. After 30 min, the values raised to 7-7.5, peaking at 8.5 in system E after 120 min.

As for the determination of the samples' quality, the analysis was carried out at the end of the experiment in accordance with the analysis standards for COD and BOD, with biological sludge collected from the biological stage of a wastewater treatment plant in the petroleum industry, according to ISO 5667-15:2010 standards. BOD measures the amount of dissolved oxygen required by microorganisms to biologically decompose organic matter, while COD represents the oxygen needed for chemical oxidation.

The percentage of reduction ($IR(\%)$) for each analyzed parameter was calculated by:

$$IR = C_i - \frac{C_f}{C_i} * 100\% \quad (1)$$

where C_i (mg/L) is the initial concentration for an analyzed parameter, and C_f (mg/L) is the final concentration for an analyzed parameter.

The treatment results demonstrated notable reductions across all measured parameters. COD was reduced by 89% in B system and 91.8% in C system. BOD decreased by 76% in B system and 87% in sample E. Similarly, the amount of extractable was removed by 92% in D system, while in sample A, it was reduced by 88%. The residue content decreased by 87% in B system and 84% in D system.

The removal efficiency of organic substances from the analyzed water sample after treating is assessed by the BOD/COD ratio, as portrayed in Figure 7. This ratio represents the oxygen consumption necessary for the metabolic reactions required by the microorganisms in the BOD test on the substrate, reported to the chemical oxygen consumption by the oxidative method of the substrate with $KMnO_4$.

The effectiveness of organic pollutant removal was also assessed using the BOD/COD ratio. The obtained results are graphically presented in Figure 7. This ratio ranged from 0.3 to 0.5, with the lowest value being detected in system E.

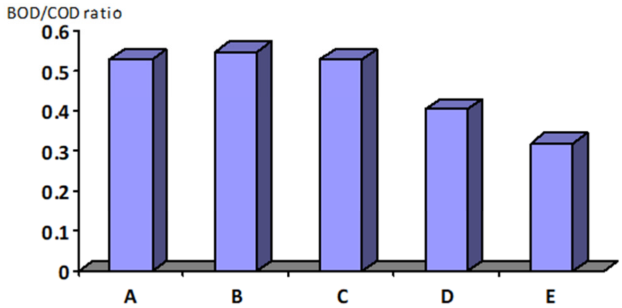

Fig. 7. BOD/COD ratio in the 5 test systems

IV. CONCLUSIONS

This study investigated the optimal chemical method for removing petrochemical pollutants. The treatment was conducted using a combination of $FeSO_4$ (3%), polyelectrolyte IP1140 (0.2 ppm), and $Ca(OH)_2$ (20%), tested in five different molar ratios per 100 mL: 1:1:2, 1:2:2, 2:1:1, 2:1:2, and 2:2:1. Throughout the experiment, key parameters such as pH, COD, BOD, extractable content, and residue were monitored across all tested systems.

The results indicated that the most efficient treatment was achieved in reactor E, corresponding to the 2:2:1 ratio. This formulation demonstrated the highest pollutant removal efficiency, including a significant reduction in COD, BOD, extractables, and total residue, alongside a favorable BOD/COD ratio, which supports its suitability for integration with biological treatment systems.

The novelty of this study lies in the identification of the optimal concentration of coagulants, specifically, the incorporation of IP1140 polyelectrolyte with Fe^{2+} cation for the treatment of pollutants from the oil industry. Future research should focus on the use of different coagulants, including Al^{3+} and Fe^{2+} cations, combined with polyelectrolyte IP 1140 in environments enriched with specific microorganisms.

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