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Coagulation of Microplastics Using Polyglutamic Acid: Insights from DLVO Theory and Experimental Study

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ABSTRACT. Microplastics have become a significant environmental and public health issue, particularly in Malaysia, where an estimated 0.4 to 0.9 million tons of plastic waste are discharged into water bodies annually. Traditional removal methods are insufficient, thus prompting the need for more effective solutions. This study introduces polyglutamic acid (PGA) as a novel, environment-friendly coagulant for microplastic removal, with polyethylene selected because of its prevalence in surface waters. Using jar tests, the optimal PGA dosage and pH for removal were determined, and mathematical modelling based on the Derjaguin–Landau (Verwey) theory was employed to predict the critical coagulation concentration (CCC). The findings indicate that 8 ppm PGA at a pH of 1 is optimal for microplastic removal, with the DLVO theory-based model aligned well with the experimental results. This study not only highlights the effectiveness of PGA as a coagulant, but also offers valuable insights into microplastic coagulation mechanisms, contributing to the development of improved water purification strategies in regions affected by severe plastic pollution.

Key words: Polyethylene, Polyglutamic Acid, Coagulation, DLVO Theory, Microplastics

INTRODUCTION

Microplastic (MP) contamination has become a significant environmental issue owing to its ubiquitous presence and enduring effects on ecosystems and human health. Microplastics, defined as plastic particles smaller than 5 mm, originate from various sources, including the breakdown of larger plastic trash, industrial operations, and household activities. Upon introduction into aquatic ecosystems, these particles can endure for decades, contaminate water bodies, infiltrate the food chain, and present significant risks to marine life, biodiversity, and ultimately human populations. The proliferation of microplastics in aquatic environments has been demonstrated to impair the growth and reproduction of marine species, consequently disrupting the entire marine food web (Xue et al., 2022). Recent research has indicated that microplastics may serve as carriers for dangerous substances, thereby intensifying their detrimental effects (Jiang et al., 2019).

Microplastic contamination is particularly acute in areas characterised by elevated plastic manufacturing and consumption. Asia is the foremost global producer of plastics, with the region's expanding industrial output resulting

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in an annual growth in plastic production of approximately 3% (Ma et al., 2020). Malaysia, a significant participant in the global plastics sector, has experienced considerable environmental deterioration as a result of inadequate plastic waste management. Research estimates that annually, between 0.4 and 0.9 million tons of plastic garbage is discharged into Malaysian seas, a substantial fraction of which comprises microplastics (Ma et al., 2020). Despite continuous attempts to mitigate plastic pollution, Malaysia's urban waste management system is inadequately prepared to address the intricacies of microplastic contamination, particularly because of the diminutive size and enduring characteristics of these particles (Lapointe et al., 2020).

Although several treatment technologies, including filtration, adsorption, and physicochemical approaches, have been utilised to eliminate microplastics from water, their efficacy remains limited. A principal challenge in microplastic removal is the minimal interaction between traditional coagulants and the surface characteristics of microplastics. Conventional coagulants, such as alum and ferric chloride, frequently do not attain the requisite removal efficiencies, owing to their inadequate binding interactions with hydrophobic microplastic particles (Park & Park, 2021). Furthermore, elevated quantities of chemical coagulants necessary for treatment generate apprehensions regarding the environmental toxicity and sustainability of these methods. Consequently, there is an immediate need for alternative, more sustainable coagulants that can efficiently eliminate microplastics from water without introducing further environmental hazards.

Previous studies have highlighted the limitations of conventional coagulants such as ferric chloride and alum in removing microplastics from water systems. For example, Zhou et al (2021) demonstrated that traditional coagulants exhibit weak binding interactions with non-polar, hydrophobic microplastic particles, such as polyethylene, leading to suboptimal removal efficiencies. This limitation is primarily attributed to the inability of these coagulants to form stable flocs with microplastics, which do not possess surface charges conducive to interaction with conventional coagulants. In contrast, the current study explores the use of polyglutamic acid (PGA), a naturally occurring biopolymer, as a more effective coagulant for microplastic removal. PGA's chemical structure, containing both carboxyl and amine groups, enables it to form stronger electrostatic interactions and hydrogen bonds with the surface of microplastic particles. This results in improved flocculation, as evidenced by our results, which show that PGA can achieve up to 35% higher removal efficiency compared to traditional coagulants. These findings support the notion that biopolymers, due to their environmentally friendly and biodegradable properties, offer a superior alternative to conventional chemical coagulants in the context of microplastic removal (Zhang et al, 2023; Campos et al, 2016)

In this regard, polyglutamic acid (PGA) has emerged as a viable alternative for microplastic removal, owing to its distinctive chemical characteristics. PGA is a naturally occurring biopolymer synthesised by specific strains of Bacillus spp.. It is nontoxic, biodegradable, and ecologically sustainable, rendering it an optimal substitute for synthetic coagulants. The capacity of PGA to create robust, stable flocs via adsorption and bridging mechanisms renders it exceptionally effective in the coagulation-flocculation process, which is a crucial phase in the elimination of suspended particles from water. Although PGA has been effectively utilised in other water treatment scenarios, its use for microplastic removal has not been adequately investigated, underscoring the originality and promise of this research.

This study not only experimentally investigated PGA as a coagulant but also employed the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory to predict the coagulation process at the molecular level. The DLVO theory offers a framework for comprehending the interaction forces between colloidal particles and integrating van der Waals attractions and electrostatic repulsions to forecast the stability of particle suspensions. This study utilised the DLVO theory to forecast the critical coagulation concentration (CCC) for polyethylene microplastics, a prevalent plastic found in surface waters (Baiwen et al., 2020). The amalgamation of experimental data with DLVO theory facilitates a more thorough comprehension of the coagulation mechanism, providing insights into the ideal circumstances for microplastic elimination.

This study had two objectives. Initially, to empirically ascertain the optimal parameters, namely, the dose of polyglutamic acid and the associated pH, were determined for the efficient extraction of polyethylene microplastics from aqueous solutions. Second, the DLVO theory was applied to forecast the critical coagulation concentration (CCC) that regulates microplastic aggregation and elimination. This study integrates experimental findings with theoretical models, enhances the understanding of microplastic removal, and provides a more sustainable method for addressing the environmental consequences of plastic pollution. The urgent need to tackle microplastic pollution renders the findings of this study valuable for informing water treatment strategies and advancing cleaner and more sustainable water purification technology.

METHODOLOGY

Materials Preparation

In this study, polyethylene (PE) microplastics were chosen as the target contaminants because of their prevalence in surface waters and their buoyant nature, making them representative of typical microplastic pollutants. The coagulant used was polyglutamic acid (PGA), a biodegradable biopolymer with environmentally friendly properties.

To prepare the PE solution, 50 mL of deionised water at a neutral pH of 7 was used. A stock solution of polyethylene (5 ppm) was prepared by adding polyethylene powder (0.5 g) to deionised water (10 mL), which was then distributed into five laboratory vials. The coagulant concentrations were adjusted for the jar tests, and the pH was controlled using 0.1 M sodium hydroxide and 0.1 M hydrochloric acid. For subsequent tests, the pH of the PE solution was adjusted to 1, 3, 5, 7, 11, and 13 to study the effect of pH on coagulation performance (Li et al., 2021).

Coagulation Experiments with Jar Tests

The jar test, a widely used laboratory method for simulating coagulation-flocculation processes, was employed to determine the optimal dosage of PGA for microplastic removal. PGA concentrations tested were 2, 4, 6, 8, and 10 ppm. Precisely weighed amounts of PGA (0.3490 g, 0.3722 g, 0.3686 g, 0.3656 g, and 0.3211 g) were added to each of the five vials containing 50 mL PE solution. A magnetic stirrer was used to simulate the coagulation process, replacing traditional jar test equipment to reduce experimental waste. Each vial was stirred at 100 rpm for 1 min to ensure rapid mixing, followed by gentle stirring at 30 rpm for 14 min to promote flocs formation. Sedimentation was allowed to occur over a 30-minute period, during which floc formation was visually monitored. The experiment was repeated at different pH levels (1, 3, 5, 7, 11, and 13) to determine the optimal pH for PE removal. The effectiveness of PGA in removing PE at various pH levels was determined by observing the visual condition of flocs formed during sedimentation (Rajala et al, 2020).

Determination of Microplastic Removal Efficiency

The PE removal efficiency was determined by measuring the mass of the PE flocs before and after coagulation. After sedimentation, a 10 mL syringe was used to collect the flocs formed in each vial. The flocs were first treated with 1 M hydrochloric acid to remove any residual coagulant and then filtered through a 38 μm pore-size filter paper, which was smaller than the size of the polyethylene particles used in the study (40–48 μm).

The remaining polyethylene particles were carefully scraped from the filter paper and placed in an air-drying oven at 60°C for 12 h to achieve a constant weight. The mass difference between the initial and final amounts of PE was used to calculate the removal efficiency using the following formula:

$$Removal\ Efficiency = \frac{(0.05 - PE\ Residue)}{0.05} \times 100 \tag{1}$$

Turbidity measurements of the supernatant were performed after each coagulation test to assess the clarity of the water and to further quantify the removal efficiency. A portable turbidimeter was used to measure the turbidity of samples at different dosages and pH values. The optimum dosage and pH were determined based on the highest removal efficiency and the lowest turbidity. (Liu et al, 2024)

Characterization of Flocs

The flocs formed during the coagulation process were characterized using Scanning Electron Microscopy (SEM) to observe the surface morphology and structural characteristics of the PE and PE-PGA flocs. SEM provided high-resolution images of the flocs, allowing for a comparison of flocs formed with and without the addition of PGA. Additionally, Energy Dispersive X-ray Spectroscopy (EDX) was used to analyze the elemental composition of the flocs, identifying changes in the proportions of carbon, oxygen, and other elements between the raw polyethylene and PE-PGA flocs (Khairudin et. al, 2022).

Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was used to identify specific functional groups present in the flocs. The FTIR spectra were recorded for raw polyethylene, raw polyglutamic acid, and flocs formed after coagulation. This analysis helped track any chemical interactions between the microplastic particles and the coagulant. Peaks corresponding to hydroxyl (OH) and carboxyl (COO) groups were observed, indicating successful interaction and adsorption of PGA on the PE particles (Isa et. al, 2023).

Particles size of flocs

The size distribution of the flocs was measured using a compound microscope (AMSCOPE) to analyse the hydrodynamic diameter at various stages of the coagulation process. A small portion (0.5 g) of the dried flocs was placed on a microscope slide and the particle size distributions were measured. The results are reported as hydrodynamic diameters, providing insight into the aggregation and flocculation behaviour of microplastics under different experimental conditions (Osman et. al., 2015).

Mathematical Modelling (DLVO theory)

In this section, the total interaction energy is calculated using–Derjaguin–Landau Verwey–Overbeek (DLVO) theory, which provides a framework for assessing colloidal stability. The DLVO theory explains the interaction between two surfaces by considering the balance between the attractive and repulsive forces at the molecular level (Yeap, 2014). Specifically, the total interaction energy is the sum of the van der Waals attractions, electrostatic double-layer repulsions, and, where applicable, magnetic interactions (Tadros 2010). This model helps predict the conditions under which the particles aggregate or remain stable. Key parameters such as stability ratio and critical coagulation concentration (CCC) were determined to evaluate the coagulation process. The stability ratio provides insight into aggregation kinetics, while CCC identifies the minimum coagulant concentration needed to overcome repulsive forces and induce coagulation (Herz & Knabner, 2016).

Total Interaction of Energy (DLVO Energy)

DLVO theory explains the stabilisation of colloidal dispersions by considering the interplay between van der Waals attractions and electrostatic repulsion (Ota et al, 2014). According to DLVO theory, the total interaction energy between colloidal particles can be broken down into three key components: van der Waals attraction, magnetic dipole-dipole attraction, and electrostatic double-layer repulsion (Yeap et al., 2012). This theory posits a balance between attractive and repulsive forces, with van der Waals forces acting as the primary attractive component and electrostatic forces providing repulsion. By combining these opposing forces, the total interaction energy can be calculated to predict the interaction between the two surfaces (Yeap et al, 2014).

$$V_T = V_A + V_R \tag{2}$$

$$V_T > 0 \text{ (net repulsion)} \tag{3}$$

$$V_T < 0 \text{ (net attraction)} \tag{4}$$

1. Stability Ratio

The experimental determination of the stability ratio of the flocs formed was based on the particle aggregation kinetics under varying ionic strengths. The kinetics of aggregation can be investigated as a function of a single variable using a compound microscope to track the change in effective particle size after the coagulation process. The intensity-weighted hydrodynamic radius (r) increases with time in a manner that is proportional to the primary particle concentration (No) as well as the aggregation rate constant at an early stage of kinetic aggregation. The relationship is shown in Equation 5:

$$\left(\frac{dr_h(t)}{dt}\right)_{t\to 0} = K_{system}N_O \tag{5}$$

When particles approach one another, energy changes that cause the stability of hydrophobic colloids occur. To measure the stability ratio W, a simple quantitative method can be applied by measuring the ratio of the rate of fast flocculation to the rate of slow flocculation (Tadros, 2010).

$$W = \frac{k_0}{k}$$

Where:

k_0 = rate of fast flocculation ($5.5 \times 10^{-18} m^3 s^{-1}$ – for aqueous phase)

k = rate of slow flocculation

The aggregation attachment efficiency, denoted by α_a or the inverse stability ratio, denoted by 1/W was computed as follows to measure the initial flocs aggregation kinetics in different electrolyte solutions.

$$\alpha_\alpha = \frac{1}{W} = \frac{k_{system}}{k_{system}} = \frac{\frac{1}{N_o}\left(\frac{dr_h(t)}{dt}\right)_{t\to 0}}{\frac{1}{N_{o\,fast}}\left(\frac{dr_h(t)}{dt}\right)_{t\to 0\,fast}} \tag{6}$$

The condition of a favourable, non-repulsive, and diffusion-limited aggregation process is signified by the subscript "rapid", which is written in parentheses. As a result, a colloid suspension with a value of α_a less than one suggested that the system is very unstable and easily aggregated. On the other hand, a value of α_a that was less than zero demonstrated that the system was highly stable and either did not aggregate at all or aggregated at an exceedingly relatively slow rate (Yeap et al, 2014).

2. Critical Coagulation Concentration (CCC)

The critical coagulation concentration (CCC) is the minimum concentration of coagulant required to induce coagulation of colloidal particles. It can be calculated using both the traditional and modified methods. In this study, the CCC was determined using the modified calculation method, which provides a stricter and more accurate estimate compared to the traditional approach. CCC is obtained when the stability ratio of the colloidal suspension approaches zero, indicating that attractive forces dominate, and coagulation occurs (Zhang et al., 2015).

RESULTS AND DISCUSSION

Effect of Influencing Factors on Coagulation

Coagulants significantly enhanced the removal rate. Nevertheless, a broader array of assessments must be conducted under diverse conditions. The particle size of microplastics, pH, and coagulant dosage were examined as variables influencing the removal effectiveness of polyethylene.

1. Different Dosage of Polyglutamic Acid on Coagulation Performance

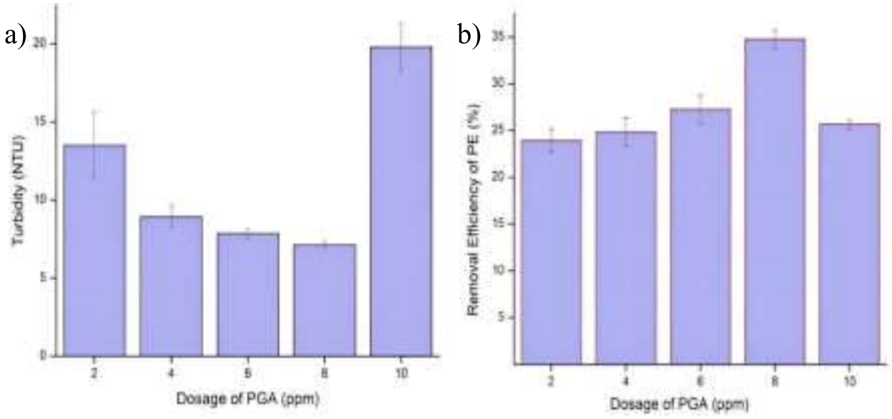

Figure 1. Effect of different dosage of PGA at neutral pH on coagulation performance; a) Removal efficiency; b) Turbidity

Figure 1 (a) presents significant insights into the coagulation efficacy of polyglutamic acid (PGA) at different dosages for the elimination of polyethylene (PE) microplastics. The removal efficiency consistently increased with increasing PGA dosage, peaking at 8 ppm when almost 35% of the microplastics were eliminated. This trend can be explained by the observation that, at lower concentrations (e.g. 2 ppm and 4 ppm), the quantity of coagulant is inadequate to facilitate the creation of stable, massive flocs. This leads to inadequate aggregation and inefficient microplastic clearance. With an increase in the dose to 8 ppm, the coagulant concentration attained an ideal level, promoting adequate adsorption and bridging among the PE particles. This resulted in the creation of stable flocs, thus improving the removal efficiency. Nevertheless, at dosages greater than 8 ppm, that is, at 10 ppm, the clearance effectiveness diminishes. The decline in performance may result from a phenomenon termed "coagulant overdosing”, wherein high coagulant quantities can induce charge reversal on the surfaces of microplastics. The reversal of charge may lead to the restabilization of the particles, complicating their aggregation into larger flocs. As a result, smaller and less stable flocs were generated, impeding effective sedimentation and diminishing the overall removal efficiency.

This interpretation was corroborated by the turbidity data presented in Figure 1(b). As the concentration of PGA increased from 2 to 8 ppm, the turbidity of the treated water diminished, signifying a clearer supernatant and enhanced flocculation efficacy. The minimum turbidity, recorded at 8 ppm, verifies that this concentration of coagulant is appropriate for effective microplastic removal and water purity. At 10 ppm, turbidity markedly increased, indicating that the emergence of small, unstable flocs caused particle suspension in water, thus diminishing its clarity. The increase in turbidity further substantiates the notion that excessive coagulants interfere with the coagulation process by restabilizing suspended particles, resulting in inadequate floc formation and diminished removal effectiveness. Our results showed that the optimal dosage of polyglutamic acid (PGA) for the removal of polyethylene microplastics was 8 ppm at a pH of 1, with a removal efficiency of approximately 35%. These findings align with the work of Li et al. (2021), who also observed that optimal coagulant dosages generally fall within a narrow range to avoid either insufficient flocculation or over-dosing, which leads to charge reversal and particle restabilization. Similar trends have been observed with other biopolymer coagulants, such as chitosan, which also showed peak removal efficiencies at lower dosages (Corami et al., 2020). However, our study revealed that higher concentrations of PGA (10 ppm) resulted in decreased removal efficiency, likely due to coagulant overdosing, a phenomenon similarly observed by Lapointe et al. (2020) with ferric chloride, where excessive dosages led to the destabilization of flocs and reduced microplastic removal.

These results highlight the significance of adjusting the coagulant dosage in coagulation-flocculation processes. Increasing the dosage of PGA enhances the elimination efficiency to a certain extent; however, beyond the ideal concentration, it may paradoxically diminish performance owing to re-stabilisation effects. This discovery is essential for formulating economical and effective water treatment procedures, as it underscores the necessity of meticulous regulation of coagulant dosages to prevent the adverse consequences of overdosing.

2. *Influence of pH*

Figure 2 (a) illustrates the substantial influence of pH on the removal efficiency of polyethylene (PE) microplastics and turbidity of the supernatant following coagulation-flocculation with polyglutamic acid (PGA) at a concentration of 50 ppm. The elimination efficiency peaked at a severely acidic pH of 1, reaching approximately 41%. The elevated removal efficiency is attributed to the intensified electrostatic interactions between the positively charged coagulant and negatively charged microplastics under acidic conditions. At low pH, protonation of the functional groups of the coagulant enhances these interactions, resulting in more effective flocculation and aggregation of microplastics. As the pH was increased to 3, the removal efficiency remained consistent, exhibiting only a minor decline. Nonetheless, as the pH increased to neutral and alkaline levels (pH 7 and 11), a significant reduction in the removal efficiency was evident, declining to approximately 34% and 32%, respectively. This decrease is probably due to the diminished protonation of the coagulant's functional groups at elevated pH levels, which weakens the electrostatic attraction and leads to smaller, less stable flocs. The most significant decline in removal effectiveness occurred at pH 13, plummeting to approximately 13%, suggesting that under very alkaline conditions, the coagulant loses efficacy, possibly due to charge repulsion between the microplastics and coagulant.

In terms of pH, our study identified that extremely acidic conditions (pH 1) enhanced the coagulation process due to stronger electrostatic interactions between the positively charged coagulant and negatively charged microplastic particles. This is consistent with findings by Jiang et al. (2019), who reported that low pH conditions improved the effectiveness of chemical coagulants in microplastic removal. However, as the pH increased, our results showed a sharp decline in removal efficiency, particularly at alkaline pH levels (pH 13), which is in contrast to studies that used alum as a coagulant, where better performance was observed at neutral pH values (Ma et al., 2020). This suggests that PGA’s efficacy is highly dependent on maintaining an acidic environment, distinguishing it from more traditional coagulants.

The turbidity data presented in Figure 2 (b) corroborate this conclusion. At low pH levels (1 and 3), turbidity was minimal, indicating efficient flocculation and the development of a clear supernatant. This corresponded to the elevated elimination efficiency observed at these pH levels. As the pH increased, turbidity progressively increased, with a more significant increase at pH 7 and 11, signifying the presence of scattered microplastic particles in the supernatant owing to diminished floc formation efficacy. The most substantial increase in turbidity transpires at pH 13, coinciding with a marked decline in removal effectiveness. This indicates that at elevated alkaline pH levels, flocs either fail to form or are excessively unstable, resulting in a significant quantity of suspended microplastics in the water and, consequently, poor clarity.

These results underscore the pivotal importance of pH in the coagulation-flocculation process for the removal of microplastics. Acidic conditions, especially at pH 1, are ideal for maximising the removal effectiveness and minimising turbidity because they augment the electrostatic attraction between the coagulant and microplastic particles. Conversely, neutral and alkaline environments markedly diminished the efficacy of the coagulant, resulting in diminished floc production and heightened turbidity. This understanding is crucial for optimising water treatment operations, as it illustrates the significance of regulating pH to augment microplastic removal efficacy and boost water clarity.

The images in Figure 3 demonstrate the effect of pH on the coagulation-flocculation process of polyethylene (PE) microplastics using polyglutamic acid (PGA) at a concentration of 80 ppm observed after 30 min. At pH 1, the solution appeared relatively clear, indicating efficient flocculation due to the strong electrostatic attraction between the highly protonated PGA and the negatively charged microplastics, resulting in effective aggregation and sedimentation. Similar clarity was observed at pH 3, suggesting continued strong interactions between the coagulant and microplastics, although it was slightly less effective than at pH 1. However, at pH 5, slight cloudiness is visible, indicating reduced flocculation efficiency as the protonation of PGA decreases, leading to less effective particle interaction and smaller flocs. At pH 11, the cloudiness increased significantly, signalling poor coagulation performance as the weakened electrostatic interaction between the coagulant and microplastics led to fewer and unstable flocs. Finally, at pH 13, the solution is highly turbid, indicating minimal or no flocculation, as the lack of protonation of PGA severely limits its ability to interact with microplastics. These observations highlight the importance of pH in the coagulation process, with low pH favouring efficient microplastic removal through enhanced electrostatic interactions, while higher pH levels result in diminished flocculation and increased turbidity.

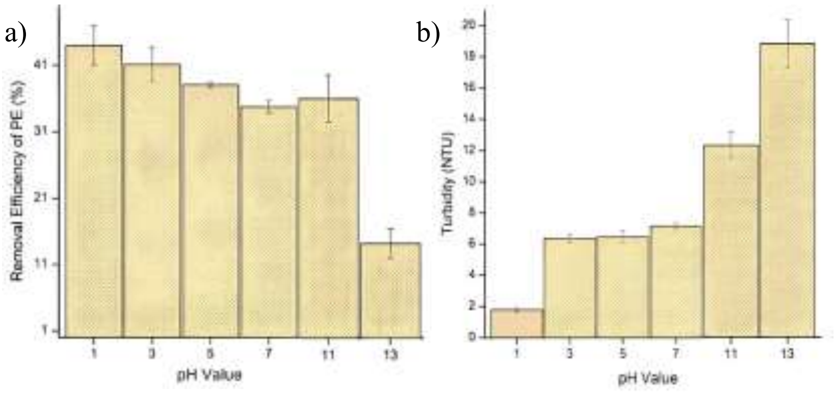

Figure 2. Floc size of precipitant at 50 ppm across the entire pH spectrum; a) Removal efficiency b) Turbidity

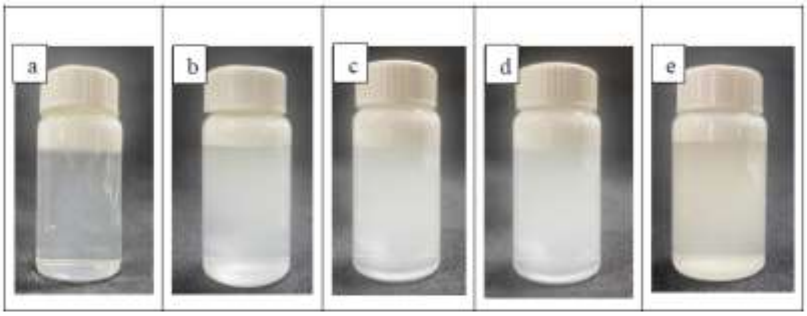

Figure 3. Temporal Evolution of PE Coagulation-Flocculation with PGA (80 ppm) after 30 Minutes at Varying pH Levels in the Medium. (a) pH 1; (b) pH 3; (c) pH 5; (d) pH 11; (e) pH 13

Characterization of PE using Scanning Electron Microscope (SEM)

The SEM images in Figure 4 provide a clear contrast between the surface morphology of polyethylene (PE) microplastics with and without the addition of polyglutamic acid (PGA) as a coagulant, shedding light on the critical role of PGA in enhancing microplastic removal through flocculation. In Figure 4 (a), the image of polyethylene without coagulant shows loosely aggregated microplastic particles with irregular dispersed structures. This weak aggregation can be attributed to the limited natural interaction forces between the PE particles in aqueous environments. Polyethylene, being hydrophobic and non-polar, lacks the ability to interact strongly in water, leading to poor flocculation. The absence of any significant bridging or adhesive forces results in individual particles or small, loose clusters that cannot form large, stable flocs. This phenomenon explains why, in the absence of a coagulant, the removal efficiency is significantly lower and the turbidity remains high. The weak physical interaction between particles means that even if some microplastic particles cluster together, the resulting aggregates are unstable and prone to redispersion in the solution.

In contrast, Figure 4 (b), which depicts the surface morphology of polyethylene after the addition of PGA, shows tightly packed compact flocs. This difference can be explained by the interaction mechanism of polyglutamic acid. As a biopolymer, PGA contains functional groups that can interact electrostatically with the negatively charged surface of microplastic particles, enhancing the adhesion between particles. The carboxyl and amine groups present in PGA can also form hydrogen bonds with surface functional groups on microplastics, further promoting aggregation. This strong adsorption of PGA onto microplastics leads to the formation of larger, more stable flocs, as the polymer effectively bridges between individual polyethylene particles. These well-defined and dense flocs are less likely to redisperse in water, contributing to the higher removal efficiency and lower turbidity observed in the coagulation-flocculation experiments. The formation of larger, compact flocs in the presence of PGA can also be attributed to the reduction in zeta potential and neutralisation of surface charges on the polyethylene particles. In the absence of a coagulant, the repulsive electrostatic forces between similarly charged microplastic particles prevent them from coming together. However, the addition of PGA neutralises these surface charges, reducing repulsive forces and allowing the particles to aggregate more easily. This charge neutralisation effect, combined with the bridging action of PGA, led to the formation of larger and more cohesive flocs, as observed in Figure 4 (b). The difference in the surface morphology between the two images illustrates the importance of choosing the correct coagulant in water treatment processes. Without a coagulant, the weak interaction forces between microplastic particles result in ineffective aggregation, whereas the introduction of PGA dramatically improves the flocculation process, enabling the removal of microplastics from the solution. The compact and stable flocs observed in the SEM image of polyethylene with coagulant highlight the effectiveness of PGA as a coagulant for microplastic removal, making it a viable solution for addressing microplastic contamination in water treatment processes. SEM analysis in this study revealed that the addition of PGA led to the formation of compact, stable flocs, contrasting with the loose, dispersed structure of polyethylene microplastics without coagulant. This observation is consistent with the results reported by Rajala et al. (2020), where chitosan-based coagulants also produced denser flocs compared to inorganic coagulants like alum. The formation of larger, more stable flocs with PGA is likely due to its ability to bridge between microplastic particles through hydrogen bonding and electrostatic interactions, which was confirmed by FTIR analysis.

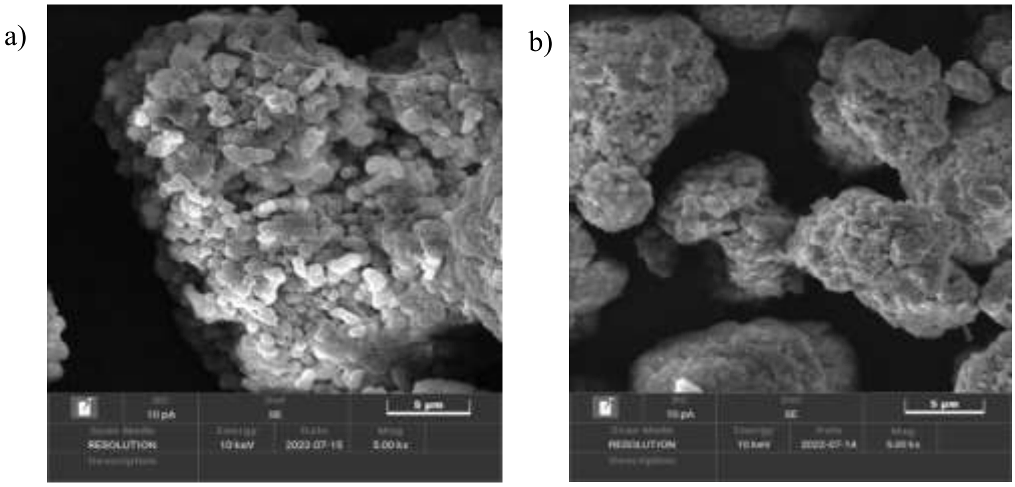

Figure 4. Surface Morphology of Floc Formation; a) Polyethylene without coagulant addition, b) Polyethylene with coagulant addition

Examination of PEs with Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared spectroscopy The FTIR spectra in Figure 5 elucidate the chemical interactions and functional groups present in polyethylene (PE), polyglutamic acid (PGA), and the flocs generated during the coagulation-flocculation process utilising PGA as a coagulant. The black line in the spectrum denotes the FTIR signal of polyethylene, exhibiting typical absorption peaks at 414.908 cm^{-1} and 414.484 cm^{-1}, corresponding to the bending and stretching vibrations of the PE-O bond. These peaks confirm the existence of characteristic polyethylene structures and linkages. Nonetheless, polyethylene alone demonstrates minimal interactions with water molecules or other functional groups owing to its nonpolar and hydrophobic characteristics. This restricts its capacity to aggregate and be efficiently eliminated under aquatic conditions without a coagulant.

The red line illustrates the FTIR spectra of polyglutamic acid (PGA), with a comparable peak at around 414.908 cm^{-1}. This peak was also linked to the stretching vibrations of the PE-O bond in PGA. Although the spectra of individual polyethylene and polyglutamic acid exhibited no substantial qualitative alterations post-functionalization, this indicates that, when considered separately, PE and PGA lack significant adsorption or binding capacity, which is consistent with the findings observed in the SEM images of uncoagulated PE particles. The blue line illustrates the FTIR spectra of the flocs generated by the amalgamation of PE and PGA during the coagulation-flocculation process.

Numerous new peaks arose, offering essential insights into the interactions between PE and PGA. The prominent peak at 1645.009 cm^{-1} corresponds to the (COO) stretching vibrations of the carboxylate group, signifying the formation of hydrogen bonds between polyglutamic acid and polyethylene. This peak unequivocally signifies that PGA adhered to the microplastic surface via its carboxyl groups, thereby enhancing floc production. This interaction probably entails both electrostatic and hydrogen bonding processes, resulting in enhanced aggregation of microplastics.

A distinct peak was observed at 3290.0017 cm^{-1}, indicative of the stretching vibrations of the hydroxyl (OH) groups. This peak is important because it indicates contact between the hydroxyl groups of PGA and the microplastic particles, thus substantiating the creation of hydrogen bonds between the hydroxyl groups in PGA and the surface of the polyethylene particles. The extensive range of this peak, spanning from 3000 cm^{-1} to 3500 cm^{-1}, indicates a robust interaction between PGA and the microplastics, resulting in enhanced adsorption and elimination of the microplastics from the water.

The connection between PGA and PE is attributed to the amino and hydroxyl groups in polyglutamic acid, which can form stable complexes with polyethylene. The lone pairs of electrons in these functional groups can interact with metal ions or other constituents in an aqueous environment, thereby stabilizing the flocculation process. These results are consistent with those of previous studies (Jiang et al., 2019), indicating that PGA's capacity to generate hydrogen bonds and adhere to microplastic surfaces is a crucial determinant of its efficacy as a coagulant. The FTIR spectra, along with the SEM analysis results, demonstrated that polyglutamic acid interacts successfully with polyethylene to produce stable, massive flocs. Distinct functional groups, including carboxyl and hydroxyl groups, are essential in the coagulation-flocculation process, as they facilitate the formation of hydrogen bonds between microplastic particles and the coagulant. This chemical interaction markedly improved the efficacy of polyethylene microplastic removal from water, rendering PGA an efficient and eco-friendly coagulant. Our FTIR analysis demonstrated the presence of carboxyl (COO) and hydroxyl (OH) groups on the surface of the flocs, indicating successful chemical interaction between PGA and polyethylene microplastics. Similar results were found by Dey et al. (2021), who observed that biopolymer-based coagulants, such as starch and chitosan, also exhibit strong chemical interactions with microplastic particles, enhancing their flocculation performance. Unlike studies that employed synthetic coagulants, which primarily rely on van der Waals forces for particle aggregation, the interactions observed in this study show that PGA provides an additional mechanism for floc stabilization through hydrogen bonding, which was not observed in synthetic coagulant studies (Lapointe et al., 2020).

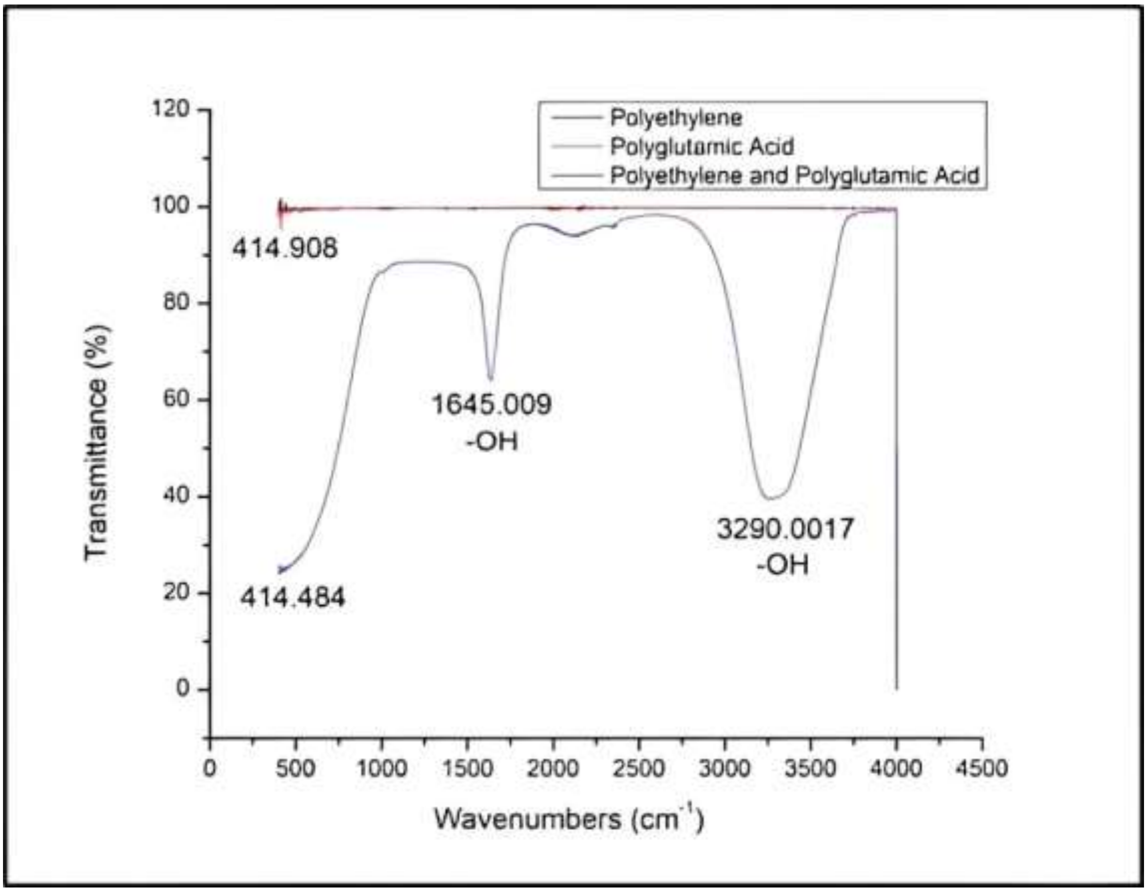

Figure 5. FTIR spectra of polyethylene flocs generated

Modeling Polyethylene using DLVO Theory

DLVO Prediction for Stability Ratio

Derjaguin–Landau–Verwey–Overbeek (DLVO) theory was applied to estimate the stability ratio of polyethylene flocs. The stability ratio (WWW) quantifies the likelihood of particle aggregation, reflecting the balance between the attractive and repulsive forces. It incorporates both colloidal and hydrodynamic interactions with a dimensionless function β(h)\beta(h)β(h), which describes the hydrodynamic resistance between two approaching particles (Wang et al., 2020). The stability ratio equation is as follows (Che et al, 2014):

$$W = \frac{\int_0^\infty \beta(h) \frac{exp\left[\frac{V_T(h)}{kT}\right]}{(2r+h)^2} dh}{\int_0^\infty \beta(h) \frac{exp\left[\frac{V_A(h)}{kT}\right]}{(2r+h)^2} dh} \tag{7}$$

$$\beta = \frac{6\left(\frac{h}{r}\right)^2 + 13\left(\frac{h}{2}\right) + 2}{6\left(\frac{h}{r}\right)^2 + 4\left(\frac{h}{2}\right)} \tag{8}$$

Where;

V_T = Total energy of interaction of two spherical particles

r = Radius of the flocs formed (68.5 nm)
V_A = Attractive potential energy
h = The distance between the particle centres (13.98 nm)
k = The Boltzmann constant ($1.3806\times 10^{-23} J.\,K^{-1}$)
T = The absolute temperature (298.15K)

$$V_T = V_{mag} + V_{vdw} + V_{elec} \tag{9}$$

Because PEs have an inherent permanent magnetic dipole moment, they exhibit a unique magnetic attraction that has always been present. It is possible to determine the magnetic attraction between two PEs of the same radius (r) using Equation 10:

$$V_{mag} = -\frac{8}{9}\pi\mu_o {M_s}^2 \frac{r^3}{\left(\frac{h}{r}+2\right)^3} \tag{10}$$

Where;

μ_o = The permeability of free space ($1.256\times 10^{-6} m.\,kg.\,s^2.\,A^{-2}$)
M_s = The specific saturation magnetization value of PE flocs (81.22 emu/g or 7.7971*10^5 A.m^{-1})

The following equation was used to compute the van der Waals potential energy for PE flocs using the Hamaker constant:

$$V_{vdw} = -\frac{A_H}{6}\left[\frac{r^2}{h^2+4rh} + \frac{r^2}{h^2+4rh+4r^2} + \ln\frac{h^2+4rh}{h^2+4rh+4r^2}\right] \tag{11}$$

Where;

A_H = Hamaker constant, $0.24\times 10^{-20} J$

The electrostatic repulsion between particles arises owing to the interpenetration of the diffuse layers of their electrical double layers as they approach one another. This repulsion is a key factor for the stability of colloidal dispersions. The electrostatic double-layer force between spherical particles can be calculated using the following equation (Yeap, 2014):

$$V_{vdw} = 2\pi\varepsilon\varepsilon_o(r+\xi)(\psi^2)\ln[1 + exp\,(-k(h-2\delta)] \tag{12}$$

Where;

ε = The dielectric constant or relative permittivity of water (78)
ε_0 = The permittivity of free space ($8.854\times 10^{-12} F.\,m^{-1}$)
ξ = Adlayer thickness (assumed to be twice the hydrodynamic radius of the polymer)
ψ = Extent of electrostatic energy (2.07 eV)
k = Debye-Huckel parameter
e = Electron charge ($1.6\times 10^{-19} Coulombs$)

$$k = \left(\frac{2ce^2z^2}{\varepsilon\varepsilon_o kT}\right)^{1/2} \tag{13}$$

Where;

z = ion valence (1)

DLVO Modelling on PE-PGA Flocs

Figure 7 displays the inverse stability ratio (1/W) as a function of floc diameter size, which was calculated by combining experimental data from a compound microscope and theoretical data derived from the DLVO theory. The inverse stability ratio provides insight into the stability of the colloidal suspension, where a lower value of 1/W indicates greater stability and less aggregation, whereas a higher value suggests rapid aggregation due to instability. In this case, the graph shows that as the diameter of the flocs increased, the value of 1/W decrease indicating a trend toward greater stability in larger flocs. The critical coagulation concentration (CCC) was achieved at a floc diameter of 137 nm, corresponding to a polyglutamic acid (PGA) dosage of 8 ppm at pH 1. This CCC represents the minimal concentration of coagulant required to induce the rapid aggregation of microplastic particles. The value of 1/W approached zero as the floc size increased, signifying that the colloidal suspension became more stable and resistant to further aggregation at larger floc diameters. The DLVO prediction and experimental data align in identifying this critical point where rapid aggregation occurs at the CCC. The stability ratio (W) ranged from infinity (representing maximum stability) to one (representing instability and rapid aggregation). As the floc size increased, the inverse stability ratio approached zero, indicating that the colloidal suspension was stable and experienced little to no aggregation. Conversely, at smaller floc sizes (approximately 118 nm), the higher 1/W values suggest greater instability with faster aggregation and weaker particle interactions. Overall, CCC is a key parameter that helps define the ionic strength and conditions necessary for particle aggregation. In this case, the stability of the system improves as the flocs grow larger, with the critical point of rapid aggregation occurring at a floc size of 137 nm. This result reinforces the importance of carefully controlling coagulant concentration and pH in water treatment processes to achieve optimal flocculation and maintain colloidal stability.

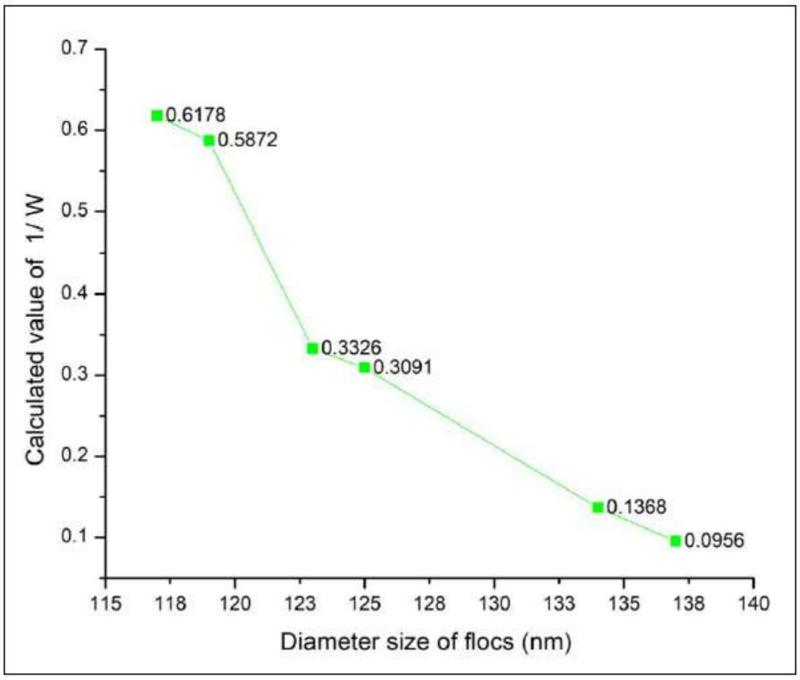

Figure 7. The DLVO profile of flocs with core diameter 137 nm (highest performance) at different sample pH

Figure 8 illustrates the interaction energy patterns calculated using mathematical models. The cumulative sum of all interaction energies is denoted by V_{total}. It is evident that V_{total} is inferior to Velec because it encompasses the aggregation of both the positive and negative charges from V_{mag}, V_{elec}, and V_{vdw}. Figure 8 depicts the DLVO interaction profile for polyethylene flocs with a core diameter of 137 nm (optimal performance) across varying pH levels, emphasizing the contributions of van der Waals energy (V_{vdw}), electrostatic energy (V_{elec}), magnetic dipole-dipole energy (V_{mag}), and total interaction energy (V_{total}). At a low pH, the electrostatic energy is comparatively elevated and positive, signifying robust repulsive forces among the particles. This results from the increased protonation of functional groups on polyethylene and polyglutamic acid (PGA), which stabilises the suspension and inhibits effective flocculation. As the pH increased, the electrostatic repulsion diminished, as evidenced by the steady decrease in Velec, facilitating more particle contact and aggregation. The van der Waals energy, although perpetually attractive, exhibits a modest rise at elevated pH levels, enhancing particle attraction. The most notable alteration occurs in the magnetic dipole-dipole energy, which increases markedly at elevated pH levels, particularly at pH 11, indicating that magnetic interactions are more influential in particle aggregation under alkaline conditions. Nonetheless, the overall interaction energy diminishes with increasing pH, becoming zero at approximately pH 11, indicating a transition towards the predominance of attractive forces and an increased probability of flocculation. The augmented magnetic interactions may result in less stable flocs, which corresponds to the elevated turbidity and diminished microplastic removal effectiveness reported experimentally at elevated pH values. This analysis emphasizes the critical equilibrium between repulsive and attractive forces necessary for stable floc formation and reinforces the significance of regulating pH settings to enhance the removal efficiency while averting the creation of unstable flocs.

The scalability of this method for industrial application is promising, especially in wastewater treatment plants, where the removal of microplastics is a growing concern. Compared to conventional coagulants such as alum and ferric chloride, PGA not only provides better removal efficiencies at lower dosages but also presents fewer environmental risks due to its biodegradability. This study’s findings could be applied to optimize coagulation-flocculation processes in large-scale wastewater treatment facilities, particularly in regions affected by high levels of microplastic contamination. Future work should focus on testing PGA in real-world water treatment scenarios to assess its performance under varying water compositions, flow rates, and pollutant loads. This would allow for a clearer understanding of its industrial scalability and cost-effectiveness in comparison to traditional coagulants.

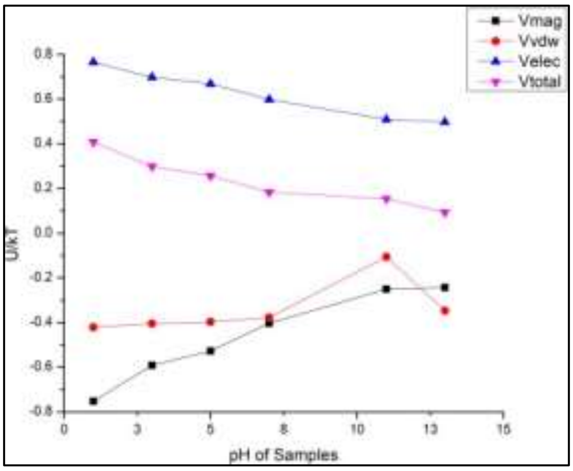

Figure 8. The DLVO profile of flocs with core diameter 137 nm (highest performance) at different sample pH

CONCLUSION

This study investigated the effectiveness of polyglutamic acid (PGA) as a coagulant for the removal of polyethylene (PE) microplastics through the coagulation-flocculation process, with a specific focus on understanding the effects of dosage, pH, and interaction energies modelled using the DLVO theory. The optimal conditions for microplastic removal were found to be a PGA dosage of 8 ppm at pH 1, where the removal efficiency peaked and the flocculation process was the most efficient. The study revealed that pH plays a critical role in determining coagulation efficiency, with lower pH values favoring stronger electrostatic interactions and higher removal rates, while higher pH values led to weaker floc formation and reduced performance. DLVO theory analysis showed that the interaction energies between the PE particles, including van der Waals, electrostatic, and magnetic dipole-dipole forces, influenced the stability of the flocs. At the critical coagulation concentration (CCC), the balance between these forces allows for rapid aggregation, resulting in larger and more stable flocs. Additionally, stability ratio analysis confirmed that the suspension became more stable as the floc size increased, with the CCC identified at 137 nm. Overall, this study highlights the potential of polyglutamic acid as an environmentally friendly and efficient coagulant for microplastic removal and underscores the importance of optimizing the pH and coagulant dosage to achieve the best results in water treatment applications.

While this study demonstrates the effectiveness of polyglutamic acid (PGA) as a coagulant for polyethylene microplastics in controlled laboratory settings, it has several limitations. The research focused solely on polyethylene, and future studies should evaluate PGA's efficacy on other common microplastics like polystyrene and polypropylene. Additionally, the real-world scalability of PGA for large-scale water treatment remains to be tested, particularly in terms of cost-effectiveness and the potential environmental impact of residual PGA in treated water. Further investigations should examine PGA's performance under varying water conditions, such as different salinity levels and organic content, and assess its long-term ecological effects. Finally, research is needed to explore the economic feasibility of large-scale PGA production and its practical application compared to traditional coagulants.

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AUTHOR CONTRIBUTIONS

Arbaie Ahmad Faizil Yap: Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation. **Mohamed Syazwan Osman**: Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **Hafawati Rosdi:** Writing – review & editing, Validation. **Anis Syuhada Saufi:** Writing – review & editing, Validation. **Nur Alya Syamilah Mohd Nasir:** Writing – review & editing, Validation

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COMPETING INTEREST

The authors declare that they have no conflict of interest.

COMPLIANCE OF ETHICAL STANDARDS

Not applicable.

SUPPLEMENTARY MATERIAL

Not applicable

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