

RESEARCH ARTICLE

PERFORMANCE OF SHRIMP SHELL POWDER (SSP) AS BIOSORBENT FOR EFFICIENT TREATMENT OF PETROLEUM WASTEWATER

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ABSTRACT

Petroleum-contaminated wastewater is a significant environmental issue since it is harmful and possesses a complex composition. This study investigates the feasibility of shrimp shell powder (SSP) as a low-cost and environmentally friendly biosorbent to treat petroleum-contaminated wastewater. SSP was manufactured by collecting, washing, drying, and milling shrimp shells into powder. Physicochemical characteristics of SSP were established by Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD) to determine its functional groups and composition. Synthetic petroleum industrial wastewater was used and treated with varying dosages of SSP from 0.15 g to 1.0 g using sample size of 60 ml at natural pH (7.5) and shaking time of 60 minutes at 150 RPM. It was observed that SSP exhibited an optimum color removal efficiency of 94.11% and COD reduction of 91.68% with the optimal dose of SSP being equal to 0.6 g. At the dose of SSP, any increases in SSP dosage led to reductions in removal efficiencies by charge destabilization effects. Additionally, pH, electrical conductivity (EC), and total dissolved solids (TDS) were measured after treatment for determining the impact of SSP on treated effluent. With regards to, pH was increased from 7.8 to 9.0, Electrical Conductivity (EC) was increased from 500 to 780, and Total Dissolved Solids (TDS) was increased from 300 to 600 mg/L, as a result of calcium carbonate and chitosan-derived compounds dissolving. It means that SSP is effective and could be a viable, sustainable solution for wastewater treatment. This particularly applies to petroleum-derived pollutants. But there is a requirement for post-treatment filtration to be further improved. TDS accumulation has to be mitigated. The strength of this research is its potential of SSP as a cost-effective and environmentally friendly option for industrial wastewater treatment.

KEYWORDS

Shrimp Shell Powder, Petroleum Wastewater Treatment, Biosorption, Coagulation, Chitosan

1. INTRODUCTION

The oil sector is among the major economic drivers of world economic development. It generates vast quantities of wastewater from a variety of operations including exploration, production, refining, and petrochemical production. Oil wastewater contains a very large quantity of pollutants such as hydrocarbons, heavy metals, and other organic compounds that are extremely harmful to the environment and human health unless treated (Al Zarooni and Elshorbagy, 2006). Oil spill clean-up is being assisted by nanotechnology that is high-tech. Scientists have established that nanoparticles, namely graphene oxide and magnetic nanoparticles, are very effective in the removal of oil pollution from water bodies (Li et al., 2020; Wang et al., 2019). This translates to faster clean-up and less destruction of the environment because the nanoparticles are re-usable. It is required that wastewater be treated to prevent water body contamination, soil contamination, and poisonous effects on aquatic organisms and human health. The use of biological processes in oil-spill remediation techniques has gained popularity. Recent studies by researchers have explored the use of genetically engineered microorganisms with enhanced hydrocarbon-degrading efficiency, providing a sustainable and eco-friendly technique for remediation (Xu et

al., 2021 and Zhang et al., 2018). Riding on the biodegradation capability inherent in microbes, coupled with genetic modification for enhancing their performance, offers one promising avenue toward the development of efficient and directed bioremediation processes. Advances in treatment techniques have also contributed significantly in overcoming the challenge of crude oil-polluted seawater. One of the technologies is application of electrokinetic methods, where the application of electrical field enhances mobilization and extraction of oil pollutants in marine sediments (Chen et al., 2017). Electrokinetic methods not only make the cleanup faster but also minimize the perturbation of the local ecosystem. The application of absorbent materials with high oil-selective sorption capability has gained popularity. Researchers are also developing new absorbent materials such as aerogels and bio-materials, which have significant potential for the clean-up of oil spills. They absorb tremendous amounts of oil, and they have the potential to be engineered for specific kinds of oil and become more efficient (Cui et al., 2019; Yuan et al., 2021). These absorbents provide a cost-effective and versatile method of oil capture from seawater, and their renewable nature is in keeping with the increasing focus on green technology. Considerable progress has been made in the treatment of seawater that has been polluted by crude oil but there are still challenges to be overcome, and research and development must continue. Marine

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ecosystem complexity, type diversity of oil, and the need for large-scale application of these technologies are the challenges that require interdisciplinary solutions. Research directions of the future must be to optimize the existing technologies, create new material, and develop combined methods with consideration for the dynamic nature of marine ecosystems. Physical, chemical, and biological technologies are the conventional methods used to treat petroleum wastewater. Physical techniques like gravity settling and filtration are primarily utilized for suspended solids removal and free oil but are commonly not sufficient for dissolved contaminant removal (Hu et al., 2015; Elmobarak et al., 2021). Chemical treatments such as AOPs and coagulation-flocculation can break down organic contaminants but are costly to run and require the use of toxic chemicals, leading to secondary pollution (Jain et al., 2020). Organic substances can be biodegraded through microbial processes, but chemical toxicity from petroleum wastewater has the potential to inhibit microbial activities, and hence the efficiency of treatment would be low (Hu et al., 2015). In addition, traditional technologies have the potential to form huge quantities of sludge that is another type of disposal problem. Because traditional treatment technologies suffer from limitations, recent research work has been targeted towards the promotion of more sustainable and efficient technologies. Advanced oxidation technologies (AOPs) like Fenton and photo-Fenton reactions, H_2O_2 /UV, photocatalysis, and ozonation have been popularized as good options because they can efficiently degrade the overwhelming majority of petroleum wastewater organic pollutants (Jain et al., 2020; Elmobarak et al., 2021). They generate highly active species with the ability to mineralize contaminants into less toxic forms. However, AOPs need to be maximized with precautions in operational parameters for achieving optimum treatment efficiencies at the lowest possible cost. In addition, the integration of AOPs with biotreatment has also been researched in order to achieve maximum total performance by maximizing the strengths of both methods (Jain et al., 2020). Future studies continue to investigate the feasibility and scalability of such emerging treatments to tackle the complex nature of petroleum wastewater treatment. Conventional treatment technologies such as chemical coagulation, adsorption, and membrane filtration are usually expensive and generate secondary waste that needs further treatment (Lofrano and Brown, 2010). Hence, scientists are exploring alternative low-cost and sustainable methods, and one of them is the utilization of biowaste material for wastewater treatment. Utilization of seafood waste, and specifically shrimp shell waste, as an industrial wastewater treatment adsorbent has become more prominent because of its cheap abundance and high adsorptive capacity. Shrimp shells contain high concentrations of chitin. It is a biopolymer that has been widely studied due to its ability to adsorb heavy metals, dyes, and organic pollutants in wastewater (Bhatnagar and Sillanpää, 2009). The inherent porosity and functional groups in chitin and chitosan render them good biosorbents for the petroleum wastewater pollutants (Crini and Badot, 2008). Crab shells, fish scales and other seafood wastes are also effective for wastewater treatment. They contain high levels of calcium carbonate and biopolymers that increase their coagulation and adsorption capabilities (Zhang et al., 2022). It can be seen from studies that recycling seafood waste into adsorbents not only helps decrease environmental pollution but also supports the circular economy since organic waste is utilized to create beneficial products (Cooney et al., 2023). Though several technologies for treating petroleum wastewater exist, they are economically impractical, environmentally inadmissible, or technically complex for industrial application on a large scale. Low-cost, environmentally benign, and efficient alternatives that can remove contaminants without generating additional waste are still needed. To this end, seafood waste, particularly shrimp shells, offer a promising biosorbent with high chitin content and adsorption capacity. However, there are limited studies on the performance evaluation of shrimp shell powder (SSP) in the treatment of petroleum-contaminated wastewater. Therefore, the objective of this study is to evaluate the effectiveness of shrimp shell powder as a green biosorbent for the removal of color and Chemical Oxygen Demand (COD) from petroleum-contaminated wastewater. The study also aims to analyze the physicochemical properties of SSP through FTIR and XRD analysis, compare the influence of different dosages of SSP on treatment performance, and establish pH, electrical conductivity (EC), and total dissolved solids (TDS) change in the treated effluent. This study contributes to the formulation of green

technologies in industrial wastewater treatment and highlights the potential of valorization of seafood waste in promoting a circular economy.

2. MATERIALS AND METHODS

2.1 Preparation of Shrimp Shell Powder

Shrimp shells were collected from a local fish market and thoroughly washed with tap water to remove any impurities. The cleaned shells were air-dried for 24 hours to remove surface moisture. Subsequently, they were oven-dried at 150°C for 60 minutes to eliminate any residual moisture and ensure their suitability for use as a biosorbent. The dried shrimp shells were then ground into a fine powder and stored in an airtight container for further experiments. The FTIR and XRD scans of the Shrimp Shell Powdered (SSP) provide important information about its molecular structure and mineral composition (Figure 1). In FTIR spectroscopy, FTIR peaks indicate chemical bond vibrations within the material. For shrimp shells, characteristic FTIR peaks are strong absorption bands at 1655 cm^{-1} and 1550 cm^{-1} , corresponding to amide I and amide II bonds, respectively. These bands also confirm the presence of chitin, one of the most vital organic compounds in shrimp shells, as chitin contains amide functional groups in its polysaccharide composition (Puvvada et al., 2012).

XRD analysis also completes this data by identifying the crystalline phases of the sample (Figure 2). Peaks at specific diffraction angles (2θ) in the XRD pattern of shrimp shell powder define the calcite. They represent the crystalline form of calcium carbonate. Classical peaks for calcite are present at about 29.5°. They are defined by characteristic d-spacing values in nanometers (nm) of calcium carbonate's lattice arrangement (Younes and Rinaudo, 2021). This calcite structure in the shrimp shells is crucial to provide stiffness and structural support (Fitriyana et al., 2024).

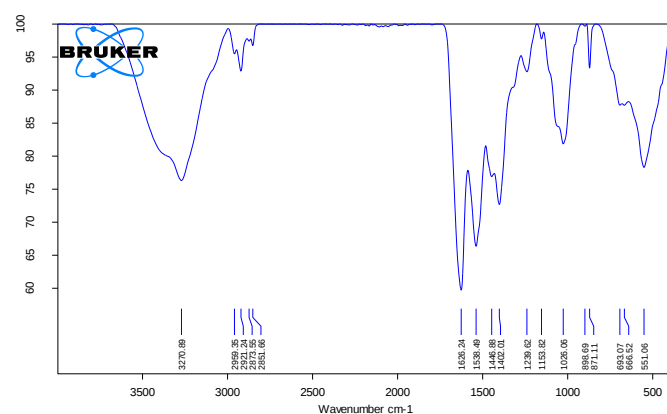


Figure 1: FTIR analysis for shrimp shell powder

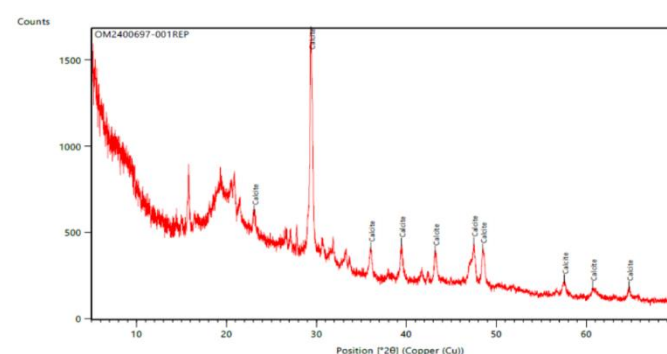


Figure 2: XRD analysis for shrimp shell powder

2.2 Experimental Procedure

Synthetic petroleum wastewater was prepared by dissolving 5 g of crude oil into 1000 g of tap water (w/w) under continuous stirring to ensure a homogeneous mixture. The solution was used as a test medium for evaluating the performance of shrimp shell powder in treating petroleum-contaminated water. The initial concentration for the physicochemical parameters of the synthetic sample is determined and summarized in Table 1. To evaluate the effectiveness of SSP for petroleum wastewater treatment, 60 ml of the synthetic petroleum wastewater sample was measured and transferred into 100 ml conical flasks. Different dosages of

SSP (e.g., 0.15 g, 0.2 g, 0.3 g, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 g) were added to the synthetic wastewater samples. The flasks were placed in an orbital shaker and agitated at 150 rpm for 1 hour at room temperature. After shaking, the samples were allowed to settle for 10 minutes, and the supernatant was carefully collected for analysis. Chemical Oxygen Demand (COD) and Color were tested before and after each run to evaluate the treatment efficacy. The level of Total Dissolved Solids (TDS), Electrical Conductivity (EC) and pH were measured after each run to evaluate the effect of SSP on physicochemical characteristics of the sample. The

influence of pH on the removal efficiency was investigated by adjusting the pH of the synthetic wastewater samples to different levels (e.g., pH 4, 6, 8, and 10) 3M form hydrochloric acid (HCl) or sodium hydroxide (NaOH) solutions before adding the SSP using the optimum dosage of SSP which determined in the previous experimental stage. To evaluate the influence of contact time on treatment efficiency, different shaking times between 30, 60, 90, and 120 minutes were performed Maintaining the optimum SSP dosage and pH. All experiments were conducted in triplicate, and the average values were reported to ensure the reliability of the results.

Table 1: The Initial Concentration of Physiochemical parameters for synthetic wastewater		
Industrial wastewater parameters	Units	results
pH	--	7.8
Color	Pt-Co	9000
TSS	mg/L	320
EC		580
COD	mg/L	19700
Ammonia-nitrogen NH ₃ -N	mg/L	42.8

3. RESULTS AND DISCUSSION

The results demonstrate that shrimp shell powder is highly effective in removing Chemical Oxygen Demand (COD) and color from petroleum wastewater. The removal efficiencies vary with the dosage of shrimp shell powder, showing a distinct trend that highlights the optimal dosage for maximum pollutant removal. At lower shrimp shell powder dosages (0.15–0.3 g), color removal efficiency steadily increases from 46.67% to 69.33% (Figure 3). The highest color removal (94.11%) is observed at 0.6 g, indicating that shrimp shell powder is highly effective in adsorbing and coagulating color-causing compounds. However, at higher dosages (0.7–1 g), color removal slightly decreases to around 74–89%, suggesting a saturation effect where excessive shrimp shell powder does not further enhance coagulation. A similar trend is observed in COD reduction, where the removal efficiency increases from 54.52% (0.15 g) to 91.68% (0.6 g) (Figure 4). The highest removal of COD is achieved at 0.6 g, after which further dosage increases lead to a slight decline in efficiency (76.5% at 1 g). This pattern indicates an optimal coagulation dosage, beyond which overdosing could result in destabilization of particles, reducing overall efficiency. Shrimp shell powder, primarily composed of chitin and its derivative chitosan, removes contaminants through. The positively charged amine groups in Chitosan bind to negatively charged pollutants, reducing repulsion and enhancing coagulation. The porous structure of shrimp shell powder absorbs organic matter and color-causing compounds, forming larger flocs. At optimal dosage levels, pollutant-laden flocs grow larger and settle more efficiently, enhancing removal efficiency. However, beyond the optimal dosage (0.6 g), excess coagulant can lead to charge reversal, causing flocs to redisperse, reducing removal efficiency. The study observed a similar dosage-dependent trend in COD removal from fish processing wastewater, emphasizing the existence of an optimal coagulation dosage for maximum effectiveness (Nouj et al., 2021).

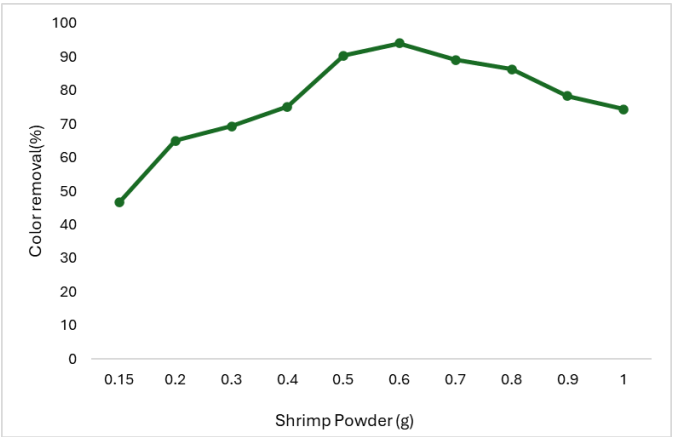


Figure 3: Performance of Shrimp Shell Powder for COD removal

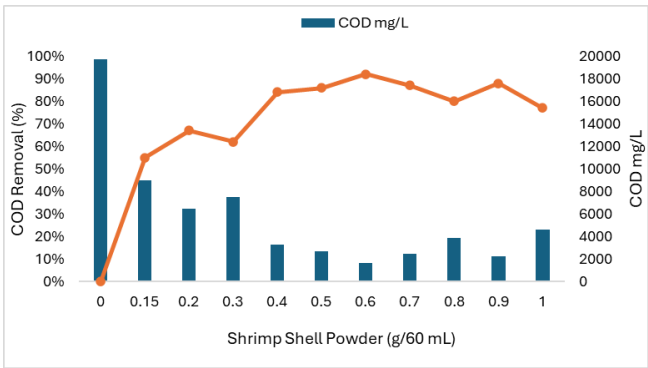


Figure 4: Performance of Shrimp Shell Powder for COD removal

XRD and FTIR analysis reveal the mechanisms for COD and color removal during petroleum wastewater treatment. As seen from FTIR analysis, chitin and chitosan, which are derivatives of chitin, are accountable for the removal of pollutants. The presence of amide I (1655 cm⁻¹) and amide II (1550 cm⁻¹) bonds suggest that the shrimp shell powder that is rich in chitosan adsorbs pollutants through hydrogen bonding and electrostatic attraction (Puvvada et al., 2012). The positively charged amine (-NH₂) groups of chitosan adsorb negatively charged organic pollutants and facilitate coagulation and flocculation activities (Nouj et al., 2021). XRD analysis confirms the presence of calcite (CaCO₃), which contributes to COD and color elimination by its function as a natural pH buffer and coagulant aid. Peaks at 29.5° are attributable to the calcite structure, which plays a significant function of charge neutralization and particle aggregation (Rinaudo, 2006). Dissolution of CaCO₃ releases carbonate and bicarbonate ions, which increase alkalinity, promoting the formation of larger flocs that settle better (Nazir et al., 2021). The synergistic effect of chitin adsorption and calcite coagulation is responsible for the superior removal efficiencies of COD (91.68%) and color (94.11%) at the optimal dosages. However, above the optimum dosage, excessive shrimp shell powder will lead to charge reversal, wherein flocs redisperse, and removal efficiency is diminished (Nouj et al., 2021). This behavior highlights that it is critical to maintain an optimum balance of adsorption and coagulation mechanisms for shrimp shell-based wastewater treatment systems.

The effects of different dosages of shrimp shell powder (0–1 g) on pH, Electrical Conductivity (EC), and Total Dissolved Solids (TDS) during the treatment of petroleum wastewater have notable trends with respect to the chemical structure and coagulation properties of shrimp shell powder. The initial pH of raw wastewater was found to be 7.8, which indicates a weak alkalinity to neutrality. With the gradual increase in shrimp shell powder from 0.15 g to 1 g, pH also rose step by step, reaching a plateau between 8.6 and 9.0 (Figure 5). A sharp increase in pH (from 7.8 to 8.6) was observed at a 0.15 g dosage, suggesting rapid dissolution of calcium carbonate (CaCO₃) and release of alkaline ions. The pH remained relatively stable (8.9–9.0) for dosages between 0.2–1.0 g, indicating saturation where additional shrimp shell powder did not significantly impact pH. The presence of CaCO₃ in shrimp shells contributes to the alkaline shift (Rinaudo, 2006). The dissolution releases carbonate (CO₃²⁻) and

bicarbonate (HCO_3^-) ions, which react with H^+ ions, reducing acidity and increasing pH (Khiari et al., 2010). Chitosan (the deacetylated form of chitin) possesses amine functional groups ($-\text{NH}_2$), which interact with wastewater constituents and contribute to pH stabilization (Younes and Rinaudo, 2015). As a analysis also reported that shrimp shell-based coagulants increased pH in fish processing wastewater from 7.2 to 8.8, consistent with the findings in this study (Nouj et al., 2021). The EC of untreated wastewater was 580 $\mu\text{S}/\text{cm}$. As shrimp shell powder dosage increased, EC progressively rose, reaching 1400 $\mu\text{S}/\text{cm}$ at 1 g dosage. A moderate increase was observed at lower dosages (0.15–0.3 g), with EC ranging between 830–920 $\mu\text{S}/\text{cm}$. A steeper increase was noted beyond 0.4 g, where EC values exceeded 1000 $\mu\text{S}/\text{cm}$, indicating higher ionic activity. Release of dissolved ions: Shrimp shells contain calcium (Ca^{2+}), magnesium (Mg^{2+}), and trace minerals, which dissolve into the wastewater, increasing ionic strength (Guibal, 2004). Chitosan facilitates adsorption of negatively charged contaminants while simultaneously releasing cations (Suyambulingam et al., 2023). Chitosan and protein residues contribute to dissolved organic matter, further increasing EC levels (Roussy et al., 2005). Observed a similar 50–120% increase in EC when shrimp shell derivatives were used in industrial effluent treatment, highlighting the release of ionic compounds (Vishali et al., 2018). The Noted that shrimp shell-based adsorbents increase EC due to the presence of amino acids and calcium salts, supporting the trends observed in this study (Rech et al., 2019). The TDS of untreated wastewater was 290 ppm. With increasing shrimp shell powder dosage, TDS steadily rose, reaching 700 ppm at 1 g dosage. A gradual increase was observed between 0.15–0.3 g, with TDS values between 420–460 ppm, indicating moderate ion release. A sharp rise occurred from 0.4 g onwards, where TDS exceeded 500 ppm, peaking at 700 ppm at 1 g dosage. The breakdown of shrimp shell components contributes to an increase in both inorganic and organic dissolved solids (Rinaudo, 2006). Some chitosan molecules form soluble fragments, increasing TDS levels (Roussy et al., 2005). While shrimp shell powder effectively removes contaminants, it also releases small soluble compounds, contributing to the net TDS increase (Renault et al., 2009). The researcher observed a 30–60% increase in TDS when shrimp shell coagulants were used in fish processing wastewater treatment, consistent with our findings (Nouj et al., 2021). The ideal range for effective pH adjustment and stable EC/TDS levels appears to be 0.3–0.6 g. Higher dosages (>0.6 g) cause excessive ion release, increasing TDS significantly. Since shrimp shell powder increases EC and TDS, additional filtration (e.g., activated carbon or reverse osmosis) may be required if stringent water quality standards must be met (WHO, 2017). Shrimp shell-based coagulants offer a sustainable and cost-effective alternative for industrial wastewater treatment, reducing reliance on chemical coagulants. pH increases (from 7.8 to 9.0), enhancing coagulation efficiency. EC and TDS increase, indicating ion release from shrimp shell dissolution. Higher dosages (>0.6 g) result in an excessive TDS increase, suggesting an optimal dosage range.

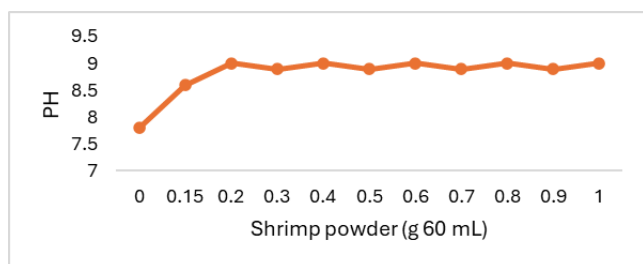


Figure 5: The effect of SSP on pH level of petroleum wastewater sample

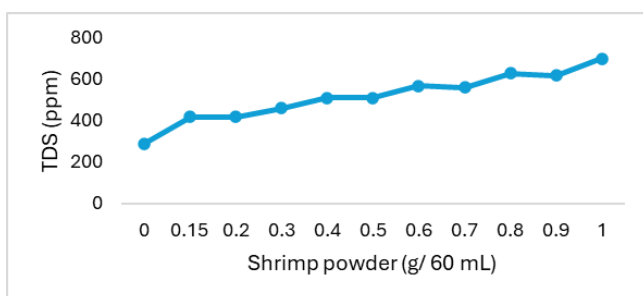


Figure 6: The effect of SSP on TDS level of petroleum wastewater sample

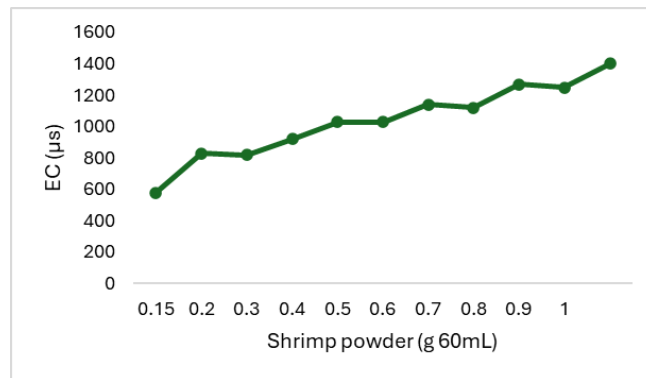


Figure 7: The effect of SSP on EC level of petroleum wastewater sample

4. CONCLUSION

The study demonstrated that shrimp shell powder (SSP) is an effective biosorbent for petroleum-contaminated wastewater treatment. The optimal dosage of SSP (0.6 g) resulted in significant reductions in color (94.11%) and COD (91.68%), indicating strong coagulation and adsorption properties. FTIR and XRD analyses confirmed the presence of chitin and calcium carbonate, which contributed to the observed treatment efficiencies. However, higher dosages (>0.6 g) led to increased Total Dissolved Solids (TDS) and Electrical Conductivity (EC), suggesting a saturation threshold beyond which pollutant removal efficiency declined. The study also highlighted the pH-modulating effect of SSP, increasing pH from 7.8 to 9.0, which enhanced coagulation mechanisms. Despite these promising results, additional post-treatment methods, such as activated carbon filtration or reverse osmosis, may be required to meet stringent water quality standards. The findings underscore the potential of SSP as a sustainable, cost-effective alternative to chemical coagulants in wastewater treatment, contributing to environmentally friendly waste management and pollution control strategies. Future research should explore field-scale applications and long-term stability assessments to further validate the practical implementation of SSP in industrial wastewater treatment processes.

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