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Innovative Coagulation Flocculation Strategies Using Chitosan-Based Hybrids for Heavy Metal and Organic Pollutant Removal

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Abstract

In Pakistan, freshwater resources are highly threatened by municipal and industrial effluents that are characterized by high contents of organic pollution and heavy metals, including lead (Pb) and cadmium (Cd). This experiment measured the performance of chitosan, polyacrylamide (PAM) and sodium alginate used as an individual and a combination of these at 25 and 50 mg L^{-1}, in removing BOD, COD, turbidity, total dissolved solids (TSS), electrical conductivity (EC) and heavy metals present in the sewage wastewater in Quetta. The experiments with the jar were carried out under the controlled conditions (pH 5, 30 °C, rapid mixing at 250 rpm, slow mixing at 50 rpm and then 1 h settling). The individual polymer of chitosan was most efficient in removal and recorded the following removals 86% BOD, 78.9% COD, 66% Cd, 73.5% Pb and 44.75 TDS at 50 mg L^{-1}. The removal was further increased by combined polymer treatments, whereby the PAM50 + Chit50 mixture gave a 98.13% BOD, 91.1% COD, 98.4% turbidity, and 91% heavy metal removal. This is explained by the fact that the complementary mechanisms are in the higher performance of combined treatments, chitosan neutralizes the charges, binds the metals and stabilizes the flocs, whereas PAM enhances the aggregation of particles by bridging. The removal of Pb was always greater than that of Cd because of the affinity of chitosan to Pb2+. The addition of extra polymer enhanced removal without floc destabilization, which showed the best treatment conditions. These findings indicate that biopolymer-based hybrid systems, especially chitosan-PAM and chitosan-alginate systems, represent long-term, cost-effective and biodegradable methods of municipal wastewater treatment and that it is a viable measure to improve the quality of water in the fast-developing cities.

Keywords: BOD, COD, Chitosan, Heavy metals, Polyacrylamide, Sodium alginate, TDS, Turbidity and Wastewater treatment.

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1. Introduction

The water quality crisis is rapidly escalating in Pakistan due to population pressure, fast urbanization and the extended industrialization (Tayyab et al., 2022). These alterations have placed tremendous pressure on freshwater resources, particularly in large industrial provinces like Punjab, where the volume of wastewater is growing by the year (Ishaque et al., 2024). Most of the peri-urban industrial areas release the untreated or partially treated effluents into the municipal drains, and this causes serious degradation of both the surface and groundwater systems (Bashir, 2021). The per-capita water resources in Pakistan have dropped significantly over the past few decades, when it used to be about 5,600 m^3 in the late 1940s, and currently it reaches extremely low values (Fida et al., 2023). It is estimated that such availability can drop to less than 700 m^3 in 2025, and the country will be deep into the water shortage range (Sly, 2022). This drastic reduction is not only due to the climate patterns but is also tightly connected with the fact of untreated municipal and industrial wastewater dumping into natural water resources (Balkhi et al., 2023).

Toxic organic and inorganic direct and indirect materials that are often found in industrial wastewater consist of dyes, suspended solids, pesticides, microbial pathogens and heavy metals (Pratap et al., 2023). In Pakistan, the textiles, leather and chemical production industries are key polluters that discharge significant amounts of these pollutants, most of which remain and accumulate in the soil and water environments (Ilyas et al., 2019). Sewage also increases the biological oxygen demand (BOD), chemical oxygen demand (COD), turbidity and nutrient contents, leading to eutrophication and ecological imbalance of rivers and lakes (Monoson et al., 2023). Heavy metals, including lead (Pb) and cadmium (Cd), are some of the most serious environmental and public health hazards among all other pollutants (Jabeen et al., 2020). They are non-biodegradable, extremely toxic, and can accumulate in tissues of humans and animals, causing neurological, renal and reproductive diseases (Jomova et al., 2025). According to recent environmental tests, the levels of Pb and Cd in industrial city wastewater are often more than national and WHO standards, which demonstrates the necessity to find effective removal technologies (Murtaza et al., 2022).

Despite the fact that there is a great variety of treatment technologies available, such as membrane filtration, adsorption, electrocoagulation, and oxidation, most modern systems cannot be actively implemented in developing areas because of the high costs of operation and technical demands (Goh et al., 2022). As a result, the implementation of the coagulation flocculation is still one of the most feasible and commonly used methods of wastewater treatment in reducing turbidity, organic load, suspended solids and heavy metals (Singh et al., 2022). It functions through destabilizing pollutants and allowing them to form larger flocs, which can be removed from the liquid phase (Ho et al., 2024). Alum and ferric salts are efficient traditional coagulants, but they are linked to major disadvantages such as excessive sludge generation, pH changes and possible residual toxicity (Diver et al., 2023). These and other restrictions have contributed to the growing popularity of natural biopolymers, including chitosan, polysaccharides and alginate that contain benefits like biodegradability, reduced toxicity and decreased chemical sludge

(Badawi et al., 2023). Polyacrylamide (PAM) polymers are also popular because of their good stability and flocculation (Sonal et al., 2021).

Recent studies have shown that hybrid systems based on the combination of biopolymers with synthetic polymers can be used to increase the ability of the system to remove contaminants, reduce turbidity and lower the level of COD and BOD (Alam et al., 2025) These systems have demonstrated future applications of enhancing the ability of the system to remove contaminants, reduce turbidity and lower the COD and BOD level making such systems a viable option of cost effective wastewater treatment in developing countries (Biswal et al., 2024). The freshwater systems in Pakistan are getting highly contaminated, and the present treatment processes are inadequate. This paper compares sodium alginate, chitosan and polyacrylamide as they are and in combination in removing heavy metals, organic pollutants and physicochemical contaminants in wastewater.

The current paper presents the use of hybrid natural-synthetic polymer systems in the treatment of municipal wastewater under natural conditions of wastewater. In contrast with the traditional studies, which concentrate on a particular parameter, this paper is able to address organic load reduction, change in ionic strength, turbidity and heavy metal (Pb and Cd) removal to obtain a holistic picture of the performance of the treatment. Moreover, the paper measures synergistic effects between sodium alginate, chitosan and polyacrylamide to increase the removal efficiency without floc destabilization with increasing dosage, which indicates the practical application of polymer mixtures in developing countries to manage wastewater sustainably.

Research Objectives

1. To evaluate the individual and combined performance of chitosan, polyacrylamide, and sodium alginate in wastewater treatment
2. To determine optimal polymer dosages for maximum removal of organic pollutants and heavy metals
3. To assess the feasibility of biopolymer-based hybrid systems as sustainable treatment technologies

2. Materials and Methods

Municipal sewage wastewater, which was collected at the Wastewater Treatment Plant, Quetta, Pakistan, was used to carry out jar test experiments. The laboratory conditions, such as controlled pH, temperature, mixing and settling durations, were all under controlled conditions in the experiments. Nineteen treatments made up of a combination and a stand-alone administration of polyacrylamide, sodium alginate and chitosan in two dosage concentrations (25 and 50 mg L^{-1}) were randomly designed in a complete random design (CRD) with three repetitions. The analysis of physicochemical parameters and heavy metals was based on the standard parameters recommended by AOAC and National Environmental Quality Standards (NEQS). At the 5 percent probability level, the use of the Least Significant Difference (LSD) test was used to statistically compare the treatment means.

To determine the effectiveness of three polymers, polyacrylamide, sodium alginate and chitosan in the 25 and 50 mg/L dosage of sewage wastewater, a jar test was carried out to remove Pb, Cd, BOD, COD, TDS and turbidity of the wastewater. The samples were taken in the Wastewater Treatment Plant, Quetta, in

2025 (Fig. 2.1). The study was done at Takatu Campus, Quetta, Pakistan. The experiment involved 19 treatments that were repeated thrice.

2.1. Jar test

The experiment was conducted in 1L glass flasks with a 200 mL stock solution of sodium alginate and a 100 mL stock solution of chitosan and polyacrylamide. Two dosages (25 and 50 mg/L) were used separately and in combination, and the pH was maintained at 5.0 with the addition of HCl and NaOH. The mixture of the flasks was mixed at 250 rpm for 15 minutes, and then slowly mixed at 50 rpm for 30 minutes and then left to settle after 1 hour at 30°C. The samples were filtered using a 2.3 µm Whatman filter paper after settling. The filtrate was tested on COD, BOD, turbidity and concentrations of Pb and Cd.

2.2. Treatment Plan

T_1=Control	T_6= Chitosan (25 mg L^{-1})	T_{11}=PAM (50 mg L^{-1}) + Na-alginate (50 mg L^{-1})	T_{16}= Na-alginate (25 mg L^{-1}) + Chitosan (25 mg L^{-1})
T_2= PAM (25 mg L^{-1})	T_7- Chitosan (50 mg L^{-1})	T_{12}= PAM (25 mg L^{-1}) + Chitosan (25 mg L^{-1})	T_{17}= Na-alginate (25 mg L^{-1}) + Chitosan (50 mg L^{-1})
T_3= PAM (50 mg L^{-1})	T_8= PAM (25 mg L^{-1}) + Na-alginate (25 mg L^{-1})	T_{13}= PAM (25 mg L^{-1}) + Chitosan (50 mg L^{-1})	T_{18}= Na-alginate (50 mg L^{-1}) + Chitosan (25 mg L^{-1})
T_4= Na-alginate (25 mg L^{-1})	T_9= PAM (25 mg L^{-1}) + Na-alginate (50 mg L^{-1})	T_{14}= PAM (50 mg L^{-1}) + Chitosan (25 mg L^{-1})	T_{19}= Na-alginate (50 mg L^{-1}) + Chitosan (50 mg L^{-1})
T_5= Na-alginate (50 mg L^{-1})	T_{10}= PAM (50 mg L^{-1}) + Na-alginate (25 mg L^{-1})	T_{15}= PAM (50 mg L^{-1}) + Chitosan (50 mg L^{-1})	

2.3. Coagulant Preparation

The solutions of stock were made in the following way: 3g of chitosan substance, which was the product of chitin deacetylation, dissolved in 1ml acetic acid and 96mL of distilled water with magnetic stirring. Under acidic conditions, acetic acid increases the effectiveness of chitosan. Magnetic stirring was carried out to dissolve 2g of powder in 198mL of distilled water to create a sodium alginate solution. In the case of polyacrylamide, 3g PAM was dissolved in 197mL of distilled water and stirred in the same manner.

2.4. pH

pH of the effluents of the sewage was measured with a pH meter, which was previously calibrated against the standard buffer solutions electrodes of the meter were then rinsed with ultra-distilled water and then immersed in samples, and the pH was measured (Ishak et al., 2021).

2.5. Biological oxygen demand (BOD)

The oxygen needed by the microorganism to break down the organic matter in the wastewater was measured and calculated using Biochemical Oxygen Demand (BOD), which was measured using dissolved oxygen (DO) at the initial point and after 5 days of incubation, maintained in dark conditions at 25°C. The samples were incubated in BOD bottles when a potassium hydroxide solution was added to trap CO_2, and then incubated for five days. The increase in mercury in the manometric capillary tube indicated the presence of BOD (mg L^{-1}) (Lacalamita et al., 2024).

2.6. Electrical conductivity

An EC meter was used to measure the total salt concentration of wastewater. The meter was standardized using a 0.01M KCl solution (14121413 U/cm at 25°C), then the probe was washed and inserted through each wastewater sample, and a conductivity reading was recorded for each sample (Edori et al., 2021).

2.7. Total dissolved solids (TDS)

TDS was determined by using the following formula

Formula for TDS

$$TDS = \frac{EC\ x1000\ (Simply\ Hyddroponic, 2008)}{2}$$

2.8. Chemical oxygen demand (COD)

A colorimetric meter with medium-range vials of Hanna COD reagent was used to determine the Chemical Oxygen Demand (COD) of wastewater. Samples were homogenized, and 2mL was transferred into reagent vials and incubated in a COD reactor at 150 °C for 1-2h. COD values were determined after cooling and at 420 nm with a colorimeter, and blank samples were used to standardize the values (Chavhan et al., 2025).

2.9. Removal percentage (%)

The removal percentage of the respective samples was obtained by use of the formula: Removal (%) = $((C_0\text{-}C_e) / C_0) \times 100$. Here, C_0 and C_e are the preliminary and final concentrations of samples in wastewater, respectively.

2.10. Turbidity

Turbidity is the haze of the water due to the suspended material that was measured using a nephelometer. With the use of a standard turbidity solution, the turbidity filter data are indicated in Nephelometric Turbidity Units (NTU) (Matos et al., 2024)

2.11. Heavy metals

Cd and Pb were also studied with the Atomic Absorption Spectrophotometer (Hitachi Polarized Zeeman AAS, 2-8200, Japan) to treat the wastewater as per the settings established in the AOAC (1990). The same conditions that follow during the experiment presented in Table 2.1 lead to the determination of Cd and Pb.

2.12. Statistical interpretation and analysis.

Each and every treatment was done thrice. The data obtained were statistically analyzed with the completely randomized design (CRD), and the means of the treatments

were compared with the least significant difference (LSD) test at the 5% probability level (Joaquin et al., 2024).

Figure 2.1: Location map and study area at wastewater treatment plant, Takatu Campus, Quetta.

2.13. Physicochemical properties of wastewater

In sewage wastewater, COD, BOD, TDS, turbidity, lead and cadmium concentrations exceeded the permissible limits set by NEQS for municipal and industrial effluent discharge. In contrast, chromium (Cr) and copper (Cu) levels were within NEQS limits. The detailed wastewater properties are presented in Table 2.2.

Table 2.1 following functioning conditions are used to determine the Cadmium and lead by AAS.

Parameters	Set Value	
-	Cd	Pb
Wavelength (nm)	228.8	283.3
Slit Width (nM)	1.3	1.3
Lamp Current (mA)	7.5	7.5
Burner Head	Standard type	Standard type

Flame	Air-C_2H_2	Air-C_2H_2
Burner Height (mm)	5.0	7.5
Oxidant gas pressure (Flow rate) (kpa)	160	160
Fuel gas pressure (Flow rate) (kpa)	6	7

Table 2.2 Characteristics of wastewater and national environmental quality standards for municipal and industrial effluents

PARAMETERS	UNITS	DETECTED VALUE	STANDARDS NEQS
pH	-	6.03	6-10
EC	mS cm^{-1}	15	-
Turbidity	NTU	206	Less than 5
BOD	mg L^{-1}	560.13	80
COD	mg L^{-1}	712	150
TDS	mg L^{-1}	7500	3300
Cadmium	mg L^{-1}	0.95	0.1
Lead	mg L^{-1}	1.95	0.5
copper	mg L^{-1}	0.03	1.0
Chromium	mg L^{-1}	0.05	1.0

3. Result

This paper compared the ability of polyacrylamide, sodium alginate and chitosan at various concentrations to remove heavy metals Cd and Pb and reduce BOD, COD, EC, turbidity and TDS of sewage wastewater. In order to evaluate the efficiency of the polymers, the experimental conditions were maintained constant, that is, the temperature was maintained at 30 °C, pH 5, the time of settling was 1 hour, and mixing was 250 rpm for 15 minutes and then 50 rpm for 30 minutes. The following are the results which are discussed.

3.1. Impact of polymers and combinations of polymers on the reduction of BOD

Figure 3.1 demonstrates the impact of various polymers on the decrease in BOD of the wastewater. The BOD ranged from 560.13 to 80.00 mg L^{-1} and was much above the NEQS threshold of 80.00 mg L^{-1}. Chitosan, sodium alginate and polyacrylamide treatment at 25 mg L^{-1} resulted in a reduction of BOD to 83.35, 41.95 and 74.34, respectively, whereas a dosage of 50 mg L^{-1} led to a reduction of 86, 53.18 and 79.5. The individual polymer efficacies of chitosan were always high as compared to those of polyacrylamide and sodium alginate. The polymer usage improved the BOD removal even more, and Chit50+PAM50 attained the highest reduction of 98.13. Other mixtures like the PAM25+Chit50, PAM50+Chit25 and PAM25+SA25 had a reduction of 95.4%, 95.2 and 94.4 percent, respectively, and the sodium alginate and chitosan mixture saw a maximum of 92.4 percent reduction. The PAM50+Chit50 combination was better than the single applications and other combinations; it enhanced the removal of BOD by 14.10 and 23.43 percent with respect to the single application of Chit50 and PAM50. These findings have shown that chitosan and polyacrylamide, especially a combination of both, are most effective in the reduction of BOD in wastewater.

Annexure (A)

3.2. Effect of different polymers and their combinations on the reduction of COD

Figure 3.2 shows the effect of various polymers in reducing COD. The initial COD wastewater was 712.34 mg $L^{-1,}$ which was higher than the NEQS standard of 150 mg L^{-1}. Chitosan recorded the greatest individual polymer reduction, 78.9%, polyacrylamide 72% and sodium alginate 50.55% at 50 mg L^{-1} and less at 25 mg L^{-1}. Combined polymer treatments were more effective than single polymer treatment, where PAM50+Chit50 was the most effective with 91.1%, PAM25+Chit50 82.75% and PAM25+Chit25 82.2%. The combination of PAM+SA had the least reduction, as PAM25+SA25 was 71.5%. Alginate mixed with chitosan recorded to 87.9% SA50+Chit50. In general, polyacrylamide and chitosan mixtures outperformed other polymer mixtures and the greater the dosage, the higher the COD removal. Chitosan and PAM50+Chit50 combination better reduced COD by 6.5, 15.46, correlatively with its application alone.

Annexure (B)

3.3. Effect of different polymers and their combinations on Cd removal

The impact of the various polymers on cadmium removal is demonstrated in Figure 3.3. Initial Cd content of wastewater was 0.95 mg L^{-1}, which is more than the 0.1mg L^{-1} limit of NEQS. Before chitosan, sodium alginate, and polyacrylamide removed cadmium, it was 59, 40.1, and 56, respectively, at 25 mg L^{-1}, 50 mg L^{-1}, and 50mg L^{-1}. Chitosan was the most effective of single polymer applications, and polyacrylamide and sodium alginate were also the most effective. Combined polymer treatment also had an additional effect on the removal of cadmium. PAM50+Chit50 96.3% was the most efficient, and then PAM50+Chit25 93.55%, PAM25+Chit50 88.85% and PAM25+Chit25 83.95%, respectively. PAM+SA mixtures reflected less in removals, PAM25+SA25 had a 65.4 percent, and PAM50+SA50 had a 76.55 percent. Blends of SA and chitosan eliminated Cd to 82.5% SA50+Chit50. On the whole, PAM50+Chit50 was significantly better than any other combination and single treatment, removing at a maximum of 45 percent more than single polymer applications.

Annexure (C)

3.4 Effect of different polymers and their combinations on Pb removal

Figure 3.4 demonstrates how polymers and their combinations impact the reduction of lead in wastewater, and the initial concentration of lead stood at 1.95 $L^{-1,}$ much higher than the NEQS limit of 0.5 L^{-1}. Chitosan 73.5%, polyacrylamide 58.5% and sodium alginate 56% were the highest removers at 50 mg L^{-1}, but lower removals were observed at 25 mg L^{-1}. Chitosan would always perform well in singular use as compared to other polymers. Polymer treatments also enhanced the lead removal, with the most effective polymer treatment being PAM50 + Chit50 93.99 % then PAM50 + Chit25, 90.2 %, PAM25 + Chit50 87 % and PAM25 + Chit25, 79.9 %. Mixes of chitosan and sodium alginate removed achieve a high of 91.1% SA50+Chit50. Combinations of PAM+SA were less efficient than PAM25+SA25, which removed the least 72.8%. There was an augmentation of lead elimination with enhanced doses of polymer in all treatments. A combination of PAM50+Chit50 was the best, showing a 27.8% and 60.66 increase in removal compared to the chitosan and PAM individually. On the whole, chitosan and polyacrylamide solution proved to be the most effective in the lead removal, and other combinations of polymer solutions were less effective.

Annexure (D)

3.5 Effect of different polymers and their combinations on turbidity removal

The influence of various polymers on the turbidity removal is presented in Figure 3.5. Chitosan, sodium alginate and polyacrylamide reduced turbidity at 50mg L^{-1} by 80.1% and 77.4%, respectively and at 25mg $L^{-1,}$ the reductions were less. Chitosan has always recorded the greatest turbidity removal of individual polymers. A combination of the polymer treatments further increased the removal, with PAM50+Chit50 reaching the highest removal of 98.4%, with PAM50+Chit25 92.1% reaching the second highest removal, and PAM25+Chit25 82.75% reaching the third highest removal. Mixes of sodium alginate and chitosan eliminated turbidity to 91 percent SA50+Chit50. The combination of PAM25+SA25 71.7% is the least effective, had moderate removal, whereas the rest of the combinations with PAM+SA had moderate removal. The degree of turbidity reduction was dependent on polymer dosage in all the treatments. In general, the chitosan and polyacrylamide blend was the most efficient as compared to PAM+SA and SA+Chit. The removal was enhanced by Pam50+Chit50 by 22.8% and 25.31% over chitosan and polyacrylamide, respectively.

Annexure (E)

3.6. Effect of different polymers and their combinations on TDS reduction

The impact of various polymers on the reduction of TDS is presented in Figure 3.6. The wastewater had an initial TDS of 7500 mgL^{-1} which is above the NEQS limit of 3300 mg L^{-1}. Only 24.5% of PAM, 31.72 and 40.5% of sodium alginate and chitosan reductions took place at 25 mg L^{-1} and 27.5, 36.78 and 44.75 at 50 mg L$^{-1,}$ respectively. Chitosan was always the best polymer in terms of TDS removal. Increased reduction was shown in combined polymer applications, where the highest was 87.4% with SA50+Chit50, then 81.85% with SA25+Chit50 and 77.66% with SA25+Chit25. PAM+Chitosan combinations also significantly enhanced the TDS removal, with a PAM50+Chit50 having a higher removal of 72.4%, whereas PAM+SA showed lower removals ranging between 50.16% and 56.3%. The SA50+Chit50 combination was the most effective, with a reduction of 50.62% and 40.65% higher than when chitosan and sodium alginate were applied individually. All in all, chitosan and sodium alginate were the most efficient with regard to the removal of TDS.

Annexure (F)

3.7: Effect of different polymers and their combinations on Electrical conductivity

Figure 3.7 indicates how the concentration of various polymers affects electrical conductivity reduction with an initial EC of wastewater of 15 mS cm^{-1}. Reduction of EC was more with an increase in the dose of polymer, and the greatest with chitosan in individual polymers, followed by sodium alginate and PAM. At 25 mg L$^{-1,}$ the percentage reductions were 24.5, 31.72 and 40.5 percent. At 50 mg L$^{-1,}$ they were 27.5, 36.78 and 44.75 percent, respectively. The further increase was in combined treatments, where SA50+Chit50 87.4%, SA50+Chit25 77.6%, SA25+Chit25 72.55% and SA25+Chit50 71.67%. A combination of PAM and Chitosan was also beneficial in EC removal, with the PAM50+Chit50 getting 72.4% elimination, whereas the PAM+SA had lower efficacy of 50.1656.3% of elimination. The SA50+Chit50 showed the greatest reduction, which was 6.78-14.9 percent greater than all the other treatments and 50.62 percent and 40.65 percent greater than PAM and chitosan applications, respectively. In general, chitosan with sodium alginate was the best in EC reduction.

Annexure (G)

4. Discussion

The findings of this research reveal a consistent and evident trend in which chitosan, polyacrylamide, and sodium alginate, either as single agents or as a combination of the three agents, help in enhancing the level of physicochemical quality of sewage wastewater collected in Quetta by a significant margin. Chitosan was the most effective single polymer in the reduction of BOD, COD, turbidity, TSS, EC and heavy metals, and its mixtures with polyacrylamide and sodium alginate increased the effectiveness of the treatment. These results confirm the increasing popularity of biopolymers as sustainable, highly reactive wastewater treatment agents based on their functional groups, electrostatic interactions and bridging mechanisms (Cui et al., 2025). One of the primary results of this study was the superior performance of the PAM50+ Chit50 mixture that recorded the highest percentage removal of BOD 98.13%, COD 91.1%, turbidity 98.4%, Cd 96.3% and Pb 93.99%. The fact that Pb is preferentially removed over Cd is possibly due to variations in ionic properties and their affinity with functional groups of the polymeric system. The related reasons are that Pb ions are more attracted to the negatively charged and electron-giving sites because they are more polarizable and have a larger ionic radius, form stronger complexes, and bind to the surface (Brezonik et al., 2022). Conversely, Cd exhibits relatively weaker interactions with functional groups, which means that it has a lower removal efficiency (Dhokpande et al., 2024). The positive effect of the hybrid treatment system also indicates a synergistic process according to which adsorption, charge neutralization, and polymer bridging combine to enhance the effect of metal sequestration (Wang et al., 2023). These mechanisms act synergistically, leading to the growth of richer and more resistant aggregates and resulting in higher removal efficiency than in the case of individual treatment processes (Chen et al., 2024). This synergistic interaction must be due to complementary processes. Polyacrylamide is used in bridging and aggregation of particles, which are considered to be the main processes, but chitosan offers good charge neutrality, affinity to metals and stability of floc. The same synergistic effects have been documented with hybrid polymeric coagulants, where the higher the floc density and surface activity, the higher the pollutant adsorption (Abujazar et al., 2022). The noticeable enhancement of the BOD and COD removal is indicative of the fact that the dual polymer matrix formed smaller flocs, which were capable of entrapping the dissolved organic material, whereas the augmented surface activity led to the adsorption of the metal ions and suspended solids.

Chitosan alone was always found to be better in all parameters of removal as compared to sodium alginate and polyacrylamide. It can be explained by the fact that it has both amino and hydroxyl functional groups and thus it protonates more under acidic pH 5.0, enhancing the binding to negatively charged particles and metal ions (Giri and Badwaik, 2024). The strong ability of chitosan to remove metals is consistent with the results that show that the biopolymer belongs to the most effective natural chelating agents (Zanbili et al., 2024). Conversely, sodium alginate demonstrated moderate removal in the majority of the parameters, probably because its charge density is low and its floc strength is less, although its performance was significantly better when used with chitosan. The pattern of TDS and EC was a little different in that the SA50+Chit50 was the best in terms of reduction. This finding indicates that the affinity of alginate to multivalent ions is high, and the gel-like networks form by the ionic cross-linking of the polysaccharide, especially in the presence of divalent metals found in sewage (Wang et al, 2024). As TDS and EC are parameters of ionic content dissolved, the ionic binding capacity of alginate was probably a source of its dominance in the specified parameters. The gelation adsorption process with chitosan produced vast and stable flocs that were able to remove both soluble and colloidal species, and this explains the unusually high reductions of 87.87 percent on TDS and EC.

The performance of Cd and Pb heavy metals in this experiment also indicates the superiority of the chitosan-based treatments (Ling et al., 2025). The greatly greater elimination of Pb than Cd in the majority of treatments is consistent with the previously established high affinity of amino groups of chitosan to Pb^{2+} rather than Cd^{2+} based on differences in ionic radius, electronegativity and stability of complexations (Radha et al., 2025). The intermediate metal extraction capacities of polyacrylamide agree with the existing literature, where the main task of PAM is to enhance the floc but not to bind the metal (Othman et al., 2024). This is the reason why PAM was not performing effectively as compared to chitosan, but when the two polymers were combined, it performed better. In every parameter, the dosage of 50 mg L^{-1} was always better than the dosage of 25 mg $L^{-1,}$ which validates that increased concentrations of polymer increase charge neutralization, adsorption and bridging flocculation. Nevertheless, a high amount of polymer may lead to the destabilization of particles; the lack of it in this study indicates that the dosages were within the optimum range (Karam et al., 2021). In current research, the results revealed that there was a higher reduction in the BOD, COD, turbidity and lead and cadmium when the polymers were used in combination than when they were used separately. A combination of chitosan with polyacrylamide was found to give maximum Cd and Pb removal, and the minimum percentage of removal was found in sodium alginate. Optimal reduction of TSS and EC was recorded in mixtures of sodium alginate and chitosan, and the lowest reduction was recorded in the sole use of polyacrylamide. Chitosan has a plethora of properties that render it curious, such as a nontoxic nature, biocompatibility and biodegradability (Kumari et al., 2020).

The residual polymers in treated effluents must be given due attention with the aim of reducing the possible ecological impacts, and their long-term environmental performance needs to be tracked (Knap-Bałdyga et al., 2023). When using polymer-assisted and hybrid treatment systems, metal-containing sludge is formed where heavy metals are immobilized via adsorption and flocculation, then controlled handling and disposal are necessary to avoid secondary contamination (Cainglet et al., 2020). The remaining efficiency of treated effluents is set to be minimal because of their integration into flocs, yet it is impossible to exclude the presence of traces, which underscores the value of proper post treatment management (Maćczak et al., 2020). Although the economic analysis was not within the scope of this study, the lowered dosage level of the chemicals and the increased efficiency of the removal in the hybrid system give reasons to believe that there are positive implications for the operational costs of the large-scale applications.

Although the current results indicate high removal rates and distinct synergistic interactions between the analyzed polymers in controlled laboratory settings, the relevant research should be developed to test the effectiveness of the systems with prolonged operation time and under a diversified wastewater structure. Further research dedicated to the properties of sludge, the stability of the floc in the long-term and the pilot-scale experience would contribute to the further understanding of the feasibility of the hybrid polymer systems at the large scale. Moreover, the determination of nutrient and microbial pathogen elimination and the possibility of using treated effluents would also enhance the usefulness of these polymers in sustainable wastewater management models.

5. Conclusion

The use of chitosan proved to be the most efficient in removing BOD, COD, turbidity and heavy metals individually in sewage wastewater, and its combination with polyacrylamide or sodium alginate even increased the efficacy of the treatment. This was especially good in the combination of the PAM50+Chit50, which has up to almost 100 percent removal of organic pollutants and heavy metals, demonstrating the synergism in charge neutralization, metal binding and bridging of the floc. The presence of sodium alginate in chitosan reduced TDS and EC because of the cross-linking and gelation qualities of sodium alginate. The findings affirm that hybrid polymer treatments are superior to single application and the optimal doses of polymers play an important role in ensuring that the maximum number of contaminants is collected with minimal destabilization of the flocs. These results justify the actual implementation of bio-based coagulation systems using biopolymers as an effective and sustainable solution to the enhancement of the quality of wastewater in the urban parts of Pakistan.

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Annesure (A)

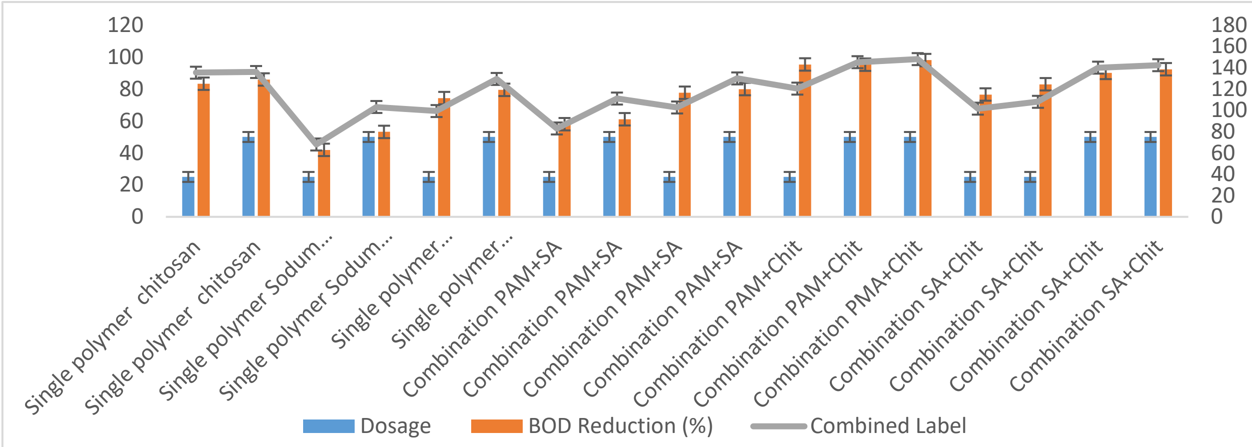


Figure 3.1. Effect of different polymers and their combinations on the reduction of BOD

Annexure (B)

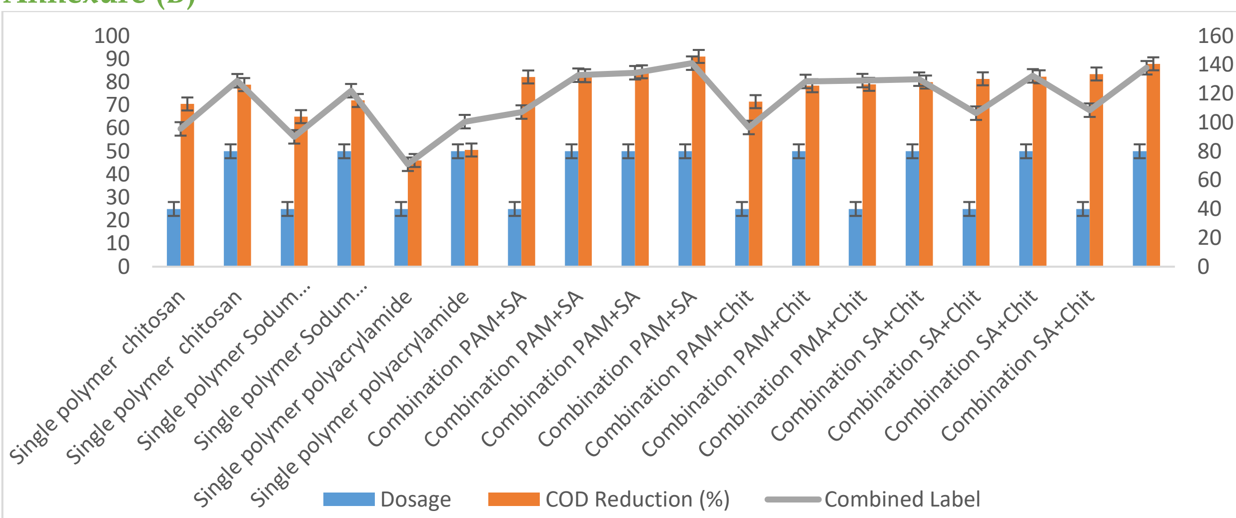


Figure 3.2. Effect of different polymers and their combinations on the reduction of COD

Annexure (C)

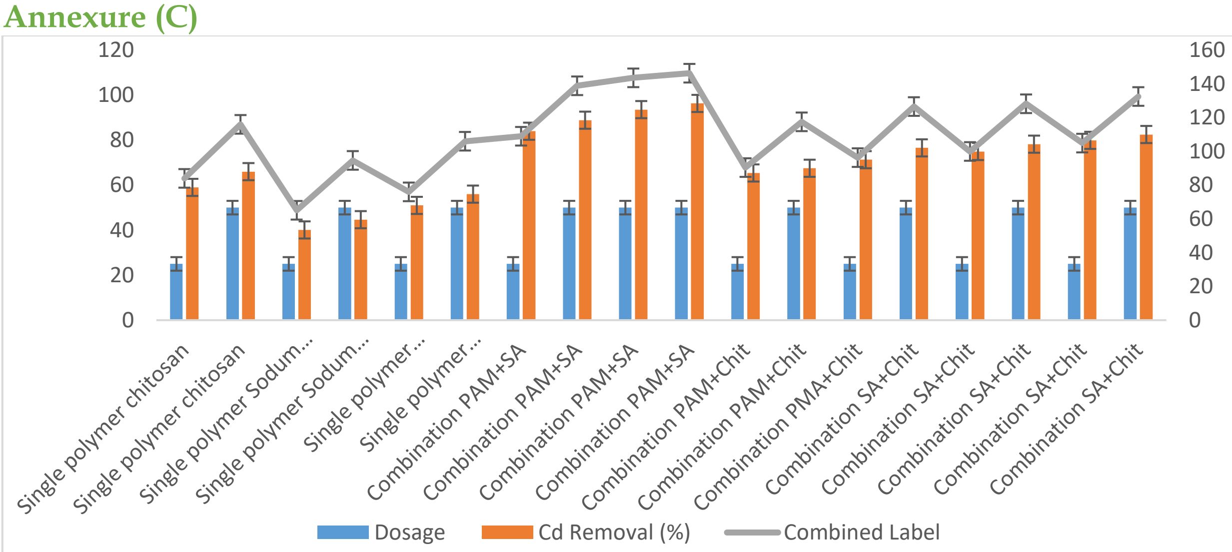


Figure 3.3. Effect of different polymers and their combinations on Cd removal

Annexure (D)

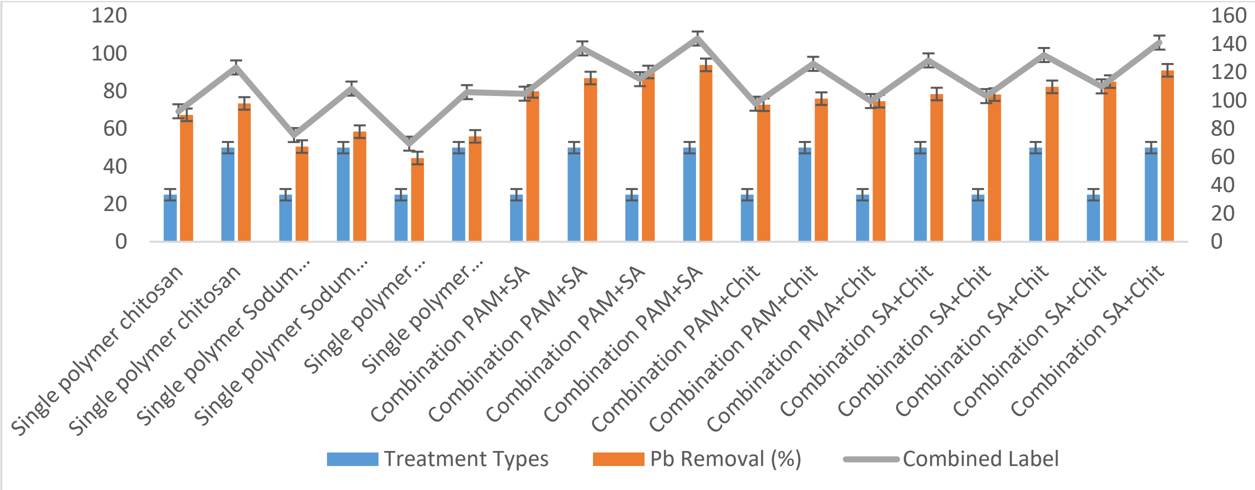
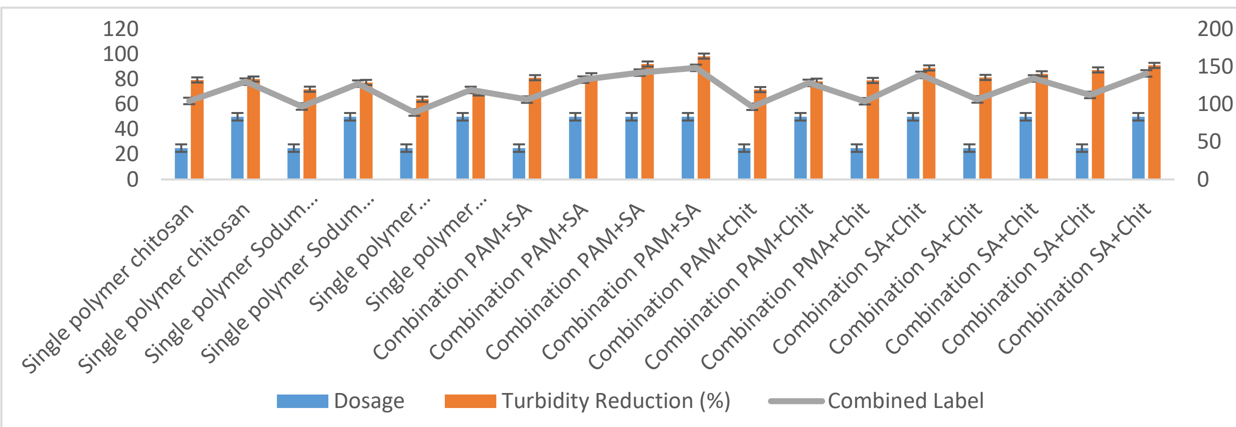


Figure 3.4. Effect of different polymers and their combinations on Pb removal

Annexure (E)



3.5. Effect of different polymers and their combinations on turbidity removal

Annexure (F)

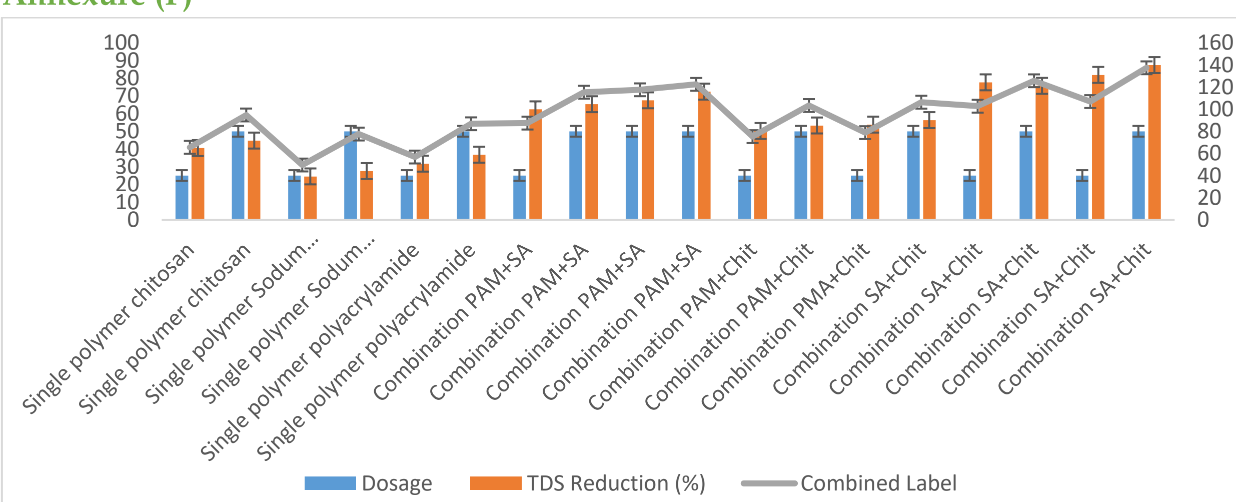


Figure 3.6. Effect of different polymers and their combinations on TDS reduction

Annexure (G)

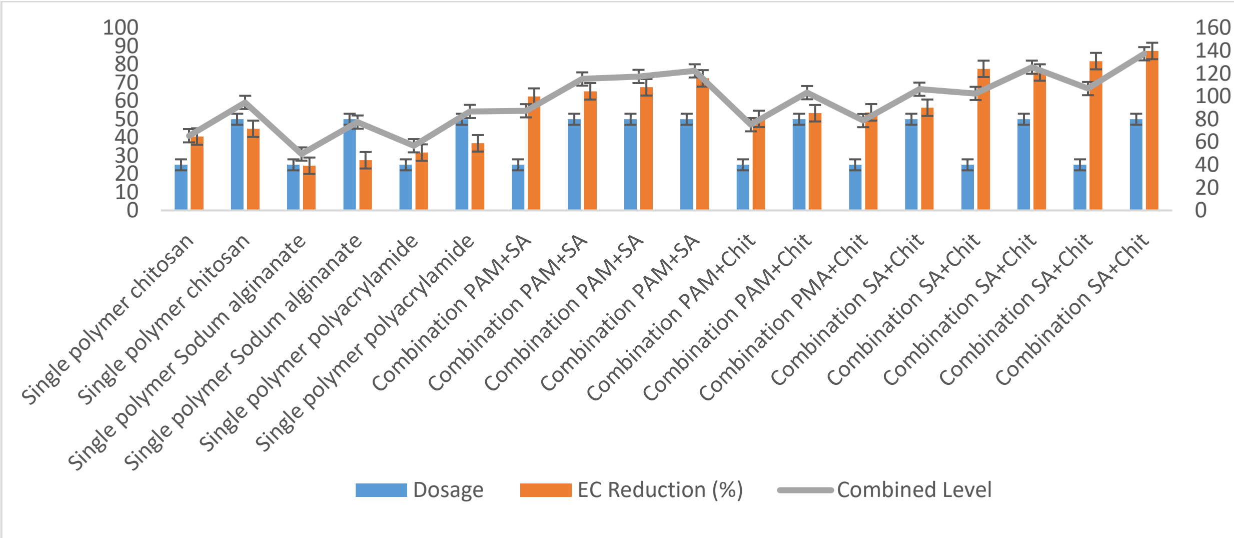


Figure 3.7. Effect of different polymers and their combinations on Electrical conductivity