

Comparative Analysis of the Treatment Potential of Cationic Starch and its Polyacrylamide Blend on Tannery and Sewage Effluents

https://doi.org/10.14233/ajchem.2025.34437

MONIKA AGARWAL*. RAJEEV KUMAR LOKESH KUMAR SAXENA ANKITA TRIPATHI and ROHIT SINGH*

Department of Chemistry, Dayanand Anglo-Vedic (P.G.) College (Affiliated to Chhatrapati Shahu Ji Maharaj University, Kanpur), Kanpur-208001, India

*Corresponding authors: E-mail: monikaagarwal_kn03@csjmu.ac.in; rohitsingh@iitdalumni.com

Received: 18 July 2025 Accepted: 19 September 2025 Published online: 30 September 2025 AJC-22138

The discharge of tannery and sewage wastewater is loaded with many toxic wastes, especially elevated levels of total dissolved solids (TDS) and suspended solids (SS) poses a significant environmental concern. This study reports the flocculation efficacy of cationic starch (CS) and its polymeric blend with polyacrylamide (CS-PAM) through the standard Jar Test method. Key operational parameters including polymer dosage, contact time and pH were optimized. Maximum solid removal efficiencies of 94% for tannery and 96% for sewage effluents were achieved at optimal dosages of 3.2×10^{-4} g/L and 1.6×10^{-4} g/L, respectively, under acidic (pH 4.0) and neutral (pH 7.0) conditions. X-ray diffraction analysis confirmed the interaction of flocs with the modified polymers. The results indicate that while cationic starch shows the substantial flocculation due to its inherent cationic nature, the CS-PAM copolymer exhibits enhanced performance. These findings highlight the potential of CS-based flocculants as sustainable, biodegradable and cost-effective alternatives to conventional synthetic flocculants for industrial and municipal wastewater treatment.

Keywords: Polyacrylamide, Flocculation, Tannery effluent, Wastewater treatment, Total dissolved solids, Suspended solids.

INTRODUCTION

Water pollution from wastewater is a significant environmental concern due to the high levels of total dissolved solids and suspended solids [1,2]. Effective treatment methods are essential to mitigate their impact on aquatic ecosystems and human health [3,4]. The escalating global challenge of wastewater management, propelled by industrial expansion, population growth and stringent environmental regulations, underscores the urgent need for innovative and sustainable treatment technologies [5,6]. Wastewater effluents laden with suspended solids, organic pollutants, pathogens and toxic heavy metals threaten aquatic ecosystems, human health and water security, necessitating advanced methods for contaminant removal [7]. Among these, coagulation-flocculation remains a cornerstone of wastewater treatment due to its simplicity, cost-effectiveness and adaptability to diverse contaminants [8]. However, conventional coagulants such as potassium aluminium sulfate (alum) and ferric chloride, while effective, generate voluminous sludge and pose risks of secondary pollution from residual metal ions [9]. Similarly, synthetic organic polymers like polyacrylamide (PAM) dominate industrial applications for their exceptional flocculation efficiency [10,11], but their persistence alone without any grafting or blending with other entities in eco-systems and potential release of neurotoxic acrylamide monomers during degradation have sparked environmental and health concerns [12-14].

In this context, biopolymers derived from renewable resources, such as starch, chitosan and cellulose, have emerged as eco-friendly alternatives [15-17]. Their inherent biodegradability, non-toxicity and abundance position them as ideal candidates for sustainable wastewater treatment [18]. Starch, a polysaccharide abundant in plants like corn, potatoes and cassava, has garnered particular interest [19,20]. Through chemical modification, such as cationization, starch can be tailored to enhance its interaction with negatively charged contaminants in wastewater [21,22] Cationic starch (CS), synthesized *via* the introduction of quaternary ammonium or tertiary amine groups, exhibits a strong positive charge density that promotes electrostatic attraction to anionic colloids, organic matter and metal ions [23,24]. This modification not only improves solubility and stability of starch in aqueous

This is an open access journal, and articles are distributed under the terms of the Attribution 4.0 International (CC BY 4.0) License. This license lets others distribute, remix, tweak, and build upon your work, even commercially, as long as they credit the author for the original creation. You must give appropriate credit, provide a link to the license, and indicate if changes were made.

systems but also amplifies its flocculation efficiency through mechanisms including charge neutralization, polymer bridging and sweep flocculation [25]. For instance, a report demonstrated that cationic starch reduced turbidity in textile wastewater by over 90%, outperforming alum in sludge volume reduction [26].

Despite these advantages, cationic starch faces limitations in mechanical strength and shear resistance compared to the synthetic polymers, particularly in high-turbidity or chemically complex wastewater streams [27]. To address this, researchers have explored hybrid systems that combine biopolymers with synthetic counterparts, aiming to synergize their strengths. Cationic starch-polyacrylamide (CS-PAM) blends, for example, leverage the biodegradability of starch and the high molecular weight of PAM to enhance floc formation, settling velocity and contaminant entrapment [28]. The cationic groups on starch improve colloidal destabilization, while the long-chain PAM reinforces floc structure via bridging, developing the dense aggregates that settle rapidly [29]. Such hybrid systems have shown promise in treating challenging effluents, such as mining wastewater and dye-laden textile discharges, achieving efficient removal of suspended solids and heavy metals [30].

However, critical gaps persist in the literature. First, comparative studies evaluating cationic starch and CS-PAM across diverse wastewater types such as municipal, industrial and agricultural effluents are sparse, limiting the understanding of their adaptability [30]. Secondly, the environmental trade-offs of hybrid systems remain understudied; while blending reduces synthetic polymer usage, the long-term ecological impacts of residual PAM in CS-PAM blends require scrutiny [31]. Furthermore, the cost-benefit analyses of scaling up starch-based flocculants are rare, hindering their commercialization despite laboratory success [32].

In present study, cationic starch and its blend with polyacrylamide has been investigated as efficient flocculants for the removal of TDS and suspended solids from wastewater. Cationic starch, a biodegradable and eco-friendly polymer, enhances coagulation and flocculation, while PAM improves floc strength and settling efficiency [33,34]. The combination of these polymers investigated to determine their synergistic effects in improving wastewater treatment performance. By integrating technical performance metrics with sustainability criteria, this research seeks to advance the development of starch based flocculants as scalable, green alternatives in wastewater treatment, aligning with the United Nations Sustainable Development Goals (SDG 6: Clean Water and Sanitation) and circular economy principles [35].

This study aims to address these gaps by systematically assessing the performance of cationic starch and CS-PAM blends in treating wastewater resources derived from tannery and sludge effluents. Key objectives of the present study include evaluating contaminant removal efficiency for turbidity, COD and organic matter under varying pH, polymer dosage and salinity conditions as well as floc morphology analysis (SEM). It is noteworthy, although there are numerous study concerned with the use of CS-PAM grafted polymers in wastewater treatment, but report on use of CS-PAM blend for effluent treatment is still warranted.

EXPERIMENTAL

The cationic starch obtained from Korchlite was used as such without further purification. The acrylamide monomer, obtained from E. Merck, Germany, was purified by recrystallization from methanol and dried in vacuum desiccator at room temperature. Analytical reagent grade methanol, ethanol, isopropanol and acetone were purified. Potassium persulphate and sodium metabisulfate were used as procured without further purification.

Instrumentation: Infrared absorption spectra of the polymers were recorded using a Bruker Vector-22 Spectrophotometer. For solid samples, spectra were obtained *via* the KBr pellet method. The viscosity was measured using an Oswald viscometer. Intrinsic viscosity was determined by extrapolating the intersection point of two plots: η_{sp}/C *vs.* C and η_{rel}/C *vs.* C to zero concentration. Here, *C* denotes the polymer concentration in g/dL and η_{sp}/C is expressed as $(\eta_{rel} - 1)/C$, where

$$\eta_{\rm rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0}$$

In this equation, t represents the flow time of the polymer solution (with viscosity η), while t_o corresponds to the flow time of the solvent (with viscosity η_0) during measurement. Powder X-ray diffraction (PXRD) analysis was conducted at room temperature using an ISO Reflux-2002 X-ray powder diffractometer (Rich & Scifert) equipped with Cu-Kα radiation. The obtained intensities were plotted against the diffraction angle. The pH of the wastewater was determined using the Systronics pH System-361 and the Microprocessor pH Meter-CP 931. The chemical oxygen demand (COD) and biological oxygen demand (BOD) were analyzed following the standard methods [36]. The turbidity of the effluent was measured using a Systronics Digital Nephelo-Turbidity Meter-132. The conductivity was assessed using the Systronics Conductivity Meter 306 and the Century Microprocessor Conductivity Meter CC 631. The colour of water in Platinum-Cobalt Units (Pt-Co) is measured using a UV-Vis spectrophotometer (e.g. Hach DR6000, Shimadzu UV-1800) or a Colorimeter (e.g. Lovibond PFX Series, Hach Colorimeter) at 455 nm wavelength. Calibration was performed using Pt-Co standard solutions ranging from 0 to 500 PCU, prepared by dissolving 500 mg potassium hexachloroplatinate (K₂PtCl₆) and 1 g cobalt chloride hexahydrate (CoCl₂·6H₂O) in 1000 mL distilled water.

Samples collection: Tannery wastewater collected from the Tanneries situated at Jajmau, Kanpur (India) where vegetable and chrome tanning processes are used. Domestic wastewater collected from its source (main sewage collection point). The sequential sampling at fixed time intervals and flow-proportional sampling based on effluent discharge rates were used for variability studies. Samples were collected in pre-cleaned glass bottles, stored at 4 °C and preserved with appropriate chemicals depending on the target analytes.

Flocculation studies: Measurement of the flocculation were carried out using the standard Jar Test method [37]. Beakers of 1000 mL capacity each equipped with variable speed (0-100 rpm) agitators were used. A 500 mL wastewater (tannery and sewage) was added to the beaker and then the polymer solution was added into it by means of a syringe

(capacity 1-2 mL). The agitator was first adjusted to 100 rpm for 1 min and then continued for a total of 10 min at 50 rpm. The agitator was subsequently stopped and the wastewater was allowed to settle for 1 h. A measured volume of 20 mL of samples was taken to determine the solid content of the effluents before and after treatment with the polysaccharide. The suspended solid contents were calculated as per the literature [18].

In this work, the flocculation experiments were conducted using water-soluble cationic starch as well as a blended formulation of cationic starch and polyacrylamide, in tannery and sewage wastewater at room temperature. The study examined the influence of polymer dose, pH and contact time on flocculation efficiency. To determine the optimal polymer dosage for the solid waste removal, wastewater samples were treated with varying polymer concentrations. The effect of contact time was assessed by measuring suspended solids and total solids at different time intervals. Moreover, flocculation efficiency was evaluated at an optimal polymer dose under different pH conditions (4.0, 7.0 and 9.2). The pH of the solution was adjusted by adding 450 mL of a buffer solution with the required pH to 50 mL of wastewater.

Determination of total solid: Prior to analysis, crucibles were cleaned, heated at 100 °C for 1 h, cooled in a desiccator and then weighed. A measured volume of wastewater sample was transferred into the pre-weighed crucibles and evaporated in a drying oven at 100 ± 10 °C for 4-5 h. The dried samples were then cooled in a desiccator before being weighed again to determine total solids content.

The total solids were calculated as:

Total solids (mg/L) =
$$\frac{(A-B)\times 1000}{\text{Volume of sample (mL)}}$$

where A = weight of dried residue + crucible; B = weight of crucible.

Determination of total dissolved solids (TDS): A cleaned silica crucible was first heated at $100\,^{\circ}$ C, then cooled in a desiccator and weighed. This process was repeated until a constant weight was achieved. A measured volume of the sample was then filtered under vacuum and transferred into the pre-weighed crucible. sample was dried in an oven at $100\,^{\circ}$ C for 4 h before being weighed again.

The total dissolved solids (TDS) were calculated using the following equation:

Total dissolved solids (mg/L) =
$$\frac{(A-B)\times 1000}{\text{Volume of sample (mL)}}$$

where A = weight of dried residue + crucible; B = weight of crucible.

Determination of suspended solids: The suspended solids from the wastewater were determined by subtracting the total dissolved solids from the total solids present in the wastewater.

Synthesis of polyacrylamide and blend of cationic starch with polyacrylamide (CS-PAM): The polymer synthesis was conducted at 30 ± 10 °C using a redox initiation system comprising potassium persulfate and sodium metabisulfite. A 500 mL three-necked round-bottom flask employed as the reaction vessel, equipped with a stirrer, a condenser and

a gas inlet. The flask was initially charged with an aqueous solution of 0.104 mol acrylamide, along with the required initiators potassium persulfate (1.8×10^{-5} mol) and sodium metabisulfite (3.6×10^{-5} mol). To eliminate dissolved oxygen, a continuous flow of nitrogen gas was maintained throughout the reaction. The reaction vessel was immersed in a temperature controlled water bath, ensuring a stable environment for polymerization. The process proceeded under constant stirring for 2 h, during which nitrogen gas was continuously purged. Upon completion, the highly viscous polymeric mass was precipitated by introducing methanol (non-solvent) with vigorous stirring, using a reaction mixture to methanol ratio of 1:10. The resulting polyacrylamide was then dried in a vacuum oven at 50 °C for 12 h to remove residual solvents. For the synthesis of CS-PAM, 0.1 g sample of polyacrylamide was dissolved in 100 mL of distilled water in a beaker and stirred using a magnetic stirrer for 15 min to ensure thorough mixing. Subsequently, 0.1 g of cationic starch was added to the solution and the mixture (1:1 ratio) was stirred again to achieve uniform dispersion. The polymer solution was then precipitated by adding an excess of acetone and subsequently filtered using a sintered glass filter. The precipitated polymer was further slurried in acetone, followed by another filtration step. Finally, the purified polymer was dried in a vacuum oven at 40 °C to remove the residual solvent. Two more blends polymer with different cationic starch to PAM ratios (1:2 and 1:3) were also prepared for further investigations.

RESULTS AND DISCUSSION

FTIR studies: The FTIR spectra (Fig. 1) display the characteristic peaks of polyacrylamide (green), cationic starch (purple) and their blend (red), providing key structural insights into their composition and interactions. In pure polyacrylamide, the characteristic absorption bands appear around 3400-3300 cm⁻¹ due to N-H stretching, a strong peak near 1650 cm⁻¹ from amide C=O stretching (amide-I band) and another around 1600 cm⁻¹ for N-H bending (amide-II band), confirming the presence of amide functionalities. The purple spectrum, representing cationic starch, exhibits a broad and intense O–H stretching peak in the same 3400-3300 cm⁻¹ region, alongside a peak around 2900 cm⁻¹ from C-H stretching and strong C–O–C stretching vibrations between 1150-1000 cm⁻¹ indicative of the polysaccharide backbone; additional peaks near 1450 cm⁻¹ suggest the presence of quaternary ammonium groups introduced during cationization. The red spectrum, corresponding to the blend of polyacrylamide and cationic starch, shows a synergistic combination of these spectral features enhanced and broadened bands around 3300 cm⁻¹ indicate strong hydrogen bonding between -OH groups of starch and -NH₂ groups of PAM, while intensified peaks at ~1650 cm⁻¹ and 1450-1400 cm⁻¹ confirm the coexistence of amide and quaternary ammonium functionalities. The merged fingerprint region (1150-1000 cm⁻¹) and overall spectral broadening suggest physical or electrostatic interactions rather than covalent grafting, validating the successful formation of a functional polymer blend. This combination of properties supports its potential application in water treatment due to enhanced flocculation efficiency arising from the dual action of charge

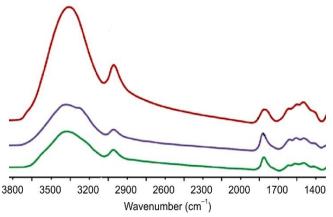


Fig. 1. FT-IR spectra of polyacrylamide (green), cationic starch (purple) and cationic starch-PAM blend (red)

neutralization (from cationic starch) and bridging (from polyacrylamide).

SEM studies: The scanning electron microscope (SEM) technique has been utilized to analyze the morphology of cationic starch and CS-PAM with varying mass ratios (1:1, 1:2, 1:3). The findings could help assess the relationship between void spaces (their number and size) and surface morphology in determining the efficiency of waste removal from effluents [33,34]. The distinct micromorphological changes in cationic starch and in CS-PAM with varying percentage compositions are observed (Fig. 2). The SEM images (Fig. 2a-b at 5K & 10K magnification) of cationic starch suggest the formation of a soft surface with weak flakes and pockets/gaps. Meanwhile, blending cationic starch with PAM in a 1:1 ratio (Fig. 2c-d) reveals marked changes in the internal micromorphology. The magnified SEM images suggest the presence of numerous void spaces, weakened crusts and regularly shaped grains (round and sub-round). The surface exhibits very few needle-like ettringite structures along with some smaller particles. Increasing the CS-PAM composition to a 1:2 ratio (Fig. 2e-f) further alters the internal micromorphological structure, with the formation of more prominent needle-like ettringite. The image suggests the development of irregularly shaped surfaces with large flakes and significant air gaps/pores, lacking any distinctive features. Interestingly, when the mass ratio of CS-PAM is further changed to 1:3 (Fig. 2g-h), the surface reveals the distinct porous structures and the formation of a dense surface with numerous pores/voids of varying sizes and well-defined walls. The finer particles from the former can fill the gaps between the latter's particles, resulting in improved particle size distribution and a more compact structure. Therefore, by adjusting the ratio of cationic starch and PAM, the sample can achieve enhanced waste removal efficiency for effluents.

Intrinsic viscosity: The intrinsic viscosity values of polyacrylamide (PAM), cationic starch and their blend indicate differences in molecular conformation, hydrodynamic volume and polymer-solvent interactions. PAM (1.88 dL/g) has the highest intrinsic viscosity due to its linear structure, high molecular weight and strong hydrogen bonding with water, leading to an expanded coil conformation. Cationic starch (1.62 dL/g) exhibits a lower intrinsic viscosity due to its more compact structure, partial branching and intramolecular hydrogen bon-

ding, which reduce its hydrodynamic volume. The blend of PAM and cationic starch (1.75 dL/g) shows an intermediate intrinsic viscosity, suggesting partial molecular interactions, such as electrostatic attraction between the cationic groups of cationic starch and the amide groups of PAM, leading to some conformational changes and entanglement effects. This trend, PAM > CS-PAM > CS, highlights the polymer interactions influence viscosity, with the blend not behaving as a simple additive system but rather showing moderate compatibility and interaction effects [36].

Flocculation studies

Removal of suspended solids from tannery and sewage effluents using CS-PAM blends: As shown in Fig. 3a-f, the effect of varying doses and blend ratios of a synthesized cationic starch–polyacrylamide (CS-PAM) copolymer can be observed on the percent removal of suspended solids from two industrially significant wastewaters viz. tannery effluent and municipal sewage. The polymer doses tested were 0.8, 1.2, 1.6, 2.4 and 3.2 mg/L, while the CS-PAM blends were formulated in starch-to-polyacrylamide mass ratios of 1:1, 1:2 and 1:3. These blend ratios allow a gradual increase in the contribution of PAM, a high molecular weight, water-soluble polymer known for its excellent bridging ability and flocculation efficiency. The objective of this experiment was to evaluate the synergistic performance of cationic starch and PAM in varying proportions and to assess the effect of dose and ratio on flocculation efficiency, particularly in removing suspended particulate matter that significantly contributes to turbidity and overall pollutant load in untreated effluents [33].

In Fig. 3a-c, the data trends for tannery effluent reveal that the removal efficiency of suspended solids improves progressively with increasing polymer dose, especially in blends containing higher proportions of PAM. The tannery effluent, which is generally characterized by a complex matrix of organic and inorganic pollutants including sulfides, chromium salts, proteins, fats and high loads of suspended solids, poses a significant challenge to the conventional treatment processes. The use of cationic starch alone, though environmentally benign and cost-effective, often suffers from limitations due to relatively lower molecular weight and less flexible chain length, which restrict its bridging capacity between colloidal particles. However, when blended with PAM, especially in increasing ratios from 1:1 to 1:3, the performance improves dramatically due to synergistic mechanisms involving charge neutralization, polymer bridging and the formation of larger, more settle-able flocs. However, in the 1:1 CS-PAM blend (Fig. 3a), the polymer matrix is relatively balanced between natural and synthetic components. At lower doses (0.8-1.2 mg/L), the removal of suspended solids is moderate, indicating initial surface adsorption and some charge neutralization. As the dose increases to 1.6 and 2.4 mg/L, a significant improvement is observed, likely due to increased polymer chain availability for bridging mechanisms and higher interaction with suspended particles. Also, at 3.2 mg/L, the efficiency either plateaus or slightly decreases, which may be attributed to overdosing. Overdosing can lead to the saturation of available binding sites on the particle surface, resulting in repulsion between excess polymer chains or re-stabilization of particles due to charge reversal.

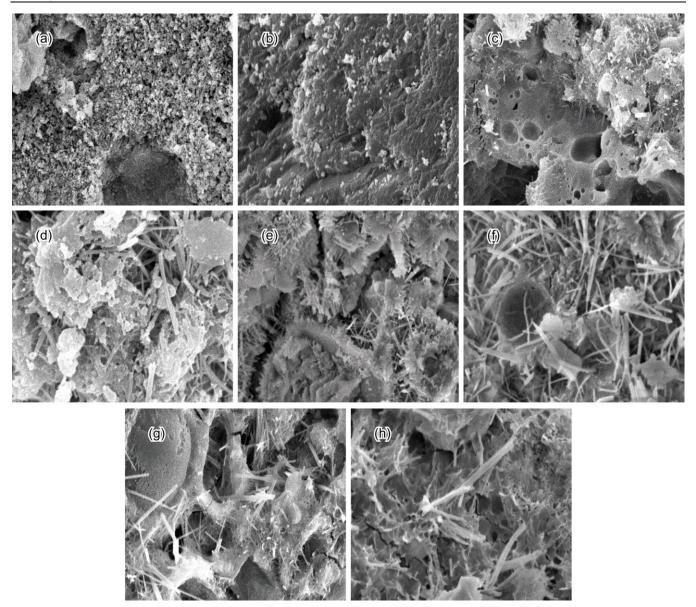


Fig. 2. SEM images of CS (a,b) and CS-PAM (c,d, at 1:1 ratio; e,f at 1:2 ratio; g,h at 1:3 ratio); magnification 5000X (left) and 10000X (right)

The 1:2 CS-PAM blend (Fig. 3b) demonstrates improved flocculation performance across all doses compared to the 1:1 ratio. The higher PAM content introduces longer chain segments and more active sites, enhancing the polymer's ability to interact with a greater number of suspended particles simultaneously. This results in stronger interparticle bridges and denser floc structures, which settle more efficiently. The removal percentage shows a steeper rise between 1.2 and 2.4 mg/L, indicating an optimal dose range where flocculation is maximized without adverse effects from overdosing. Notably, the response curve appears more linear in this ratio, suggesting a more controlled and predictable interaction between the polymer and the effluent matrix. Nevertheless, the most striking performance is observed in the 1:3 CS-PAM blend (Fig. 3c), which contains the highest PAM content. This blend exhibits near-complete removal of suspended solids (approaching 100%) at 2.4 mg/L and even at 1.6 mg/L, removal efficiency is significantly high. The enhanced performance at lower doses in this blend can be explained by the dominance of PAM's properties like high molecular weight, flexibility and extensive functional group density-leading to superior floc formation through mechanisms such as charge patching and sweep flocculation. However, even in this case, the trend begins to plateau at 3.2 mg/L, once again highlighting the importance of optimizing the polymer dose to avoid overdosing effects such as polymer saturation or steric stabilization, which can inhibit further aggregation.

Fig. 3d-f present the corresponding removal trends for municipal sewage effluent, which differs from the tannery effluent in composition and pollutant profile. Sewage typically contains a mixture of biodegradable organics, nutrients (*e.g.*, nitrogen and phosphorus compounds), microbial matter and suspended solids of both organic and inorganic origin [38]. The particle size distribution is generally more uniform and less complex than that of tannery effluent, which can lead to differences in polymer interaction and floc formation. In the

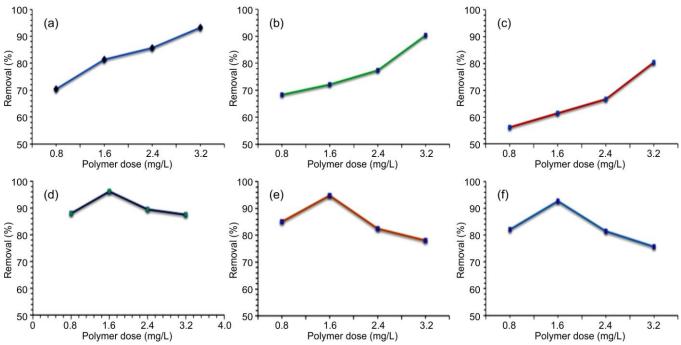


Fig. 3. Percent removal of suspended solids *versus* polymer dose for CS-PAM ratios of 1:1 (a,d), 1:2 (b,e) and 1:3 (c,f), applied to tannery effluent (a-c) and sewage effluent (d-f), respectively

1:1 CS-PAM blend for sewage effluent (Fig. 3d), the removal trend mirrors that seen in tannery effluent, but the efficiency at lower doses is slightly better, likely due to the more homogeneous nature of the suspended matter. Flocculation improves steadily with increasing dose, peaking around 2.4 mg/L, beyond which overdosing effects again become apparent. The 1:2 blend (Fig. 3e) shows improved performance, with significant suspended solids removal observed even at intermediate doses. The extended chains of polymer and improved flexibility allow better coverage of the particle surfaces and more effective floc formation. This indicates that for sewage effluent, an increased PAM ratio enhances removal without the need for excessively high doses, which is advantageous in terms of economic and environmental sustainability. However, the 1:3 blend (Fig. 3f) performs exceptionally well, with removal efficiencies exceeding 90% at just 1.6 mg/L and nearing complete the removal at 2.4 mg/L. The high PAM content again proves beneficial due to its ability to form robust, interconnected floc networks that effectively entrap suspended solids. However, as with tannery effluent, the highest dose (3.2 mg/L) does not yield further improvement and may suggest a saturation point beyond which flocculation becomes inefficient or counterproductive. From a mechanistic standpoint, the observed trends across both effluent types can be attributed to the interplay of three primary flocculation mechanisms: (i) charge neutralization, wherein cationic groups on starch and PAM neutralize the negatively charged particles; (ii) polymer bridging, where long-chain polymers adsorb onto multiple particles to form aggregates; and (iii) sweep flocculation, where flocs are enmeshed within a polymer matrix and settle rapidly. The enhanced performance of higher PAM content blends is consistent with the properties of PAM like high molecular weight, extended chain conformation and strong interaction with colloidal surfaces. Furthermore, the presence of starch in all blends contributes to the biodegradability and eco-friendliness of the copolymer, which is crucial from a sustainability perspective. While PAM alone may raise concerns related to residual monomer toxicity, its partial substitution with natural starch helps mitigate environmental risks, making CS-PAM blends a promising alternative for large-scale wastewater treatment applications.

In summary, Fig. 3a-f provides the clear evidence that both polymer dose and blend ratio significantly influence the efficiency of suspended solids removal in wastewater treatment. The optimum performance was consistently observed at a dose of 2.4 mg/L for the 1:3 CS-PAM blend in both tannery and sewage effluents. These results underscore the importance of fine-tuning polymer formulations to match the specific physico-chemical characteristics of the target effluent, thereby maximizing treatment efficiency while minimizing chemical consumption and environmental impact [39].

Time-dose interaction study of CS-PAM blends: The treatment of wastewater containing high concentrations of suspended solids is critical to environmental sustainability and public health. Polymer-assisted flocculation remains one of the most efficient and scalable methods for solid-liquid separation [34]. In this context, Fig. 4a-f illustrates a comparative and comprehensive time-dose interaction study involving different CS-PAM blend ratios (1:1, 1:2 and 1:3), applied at polymer doses of 0.8-3.2 mg/L and contact times ranging from 1 to 5 h, for two types of wastewater: tannery and sewage effluents. The results offer valuable insights into flocculation kinetics, optimal dose determination and the role of polymer composition in treatment efficiency.

Tannery effluent is typically rich in organic matter, inorganic salts (especially chromium), fats and suspended solids. The behaviour of this effluent under different CS-PAM treatments is demonstrated in Fig. 4a-c, corresponding to blend

ratios of 1:1, 1:2 and 1:3, respectively. In Fig. 4a (1:1 blend), the removal of suspended solids shows a positive correlation with both increasing polymer dose and contact time. At the lowest dose of 0.8 mg/L, removal is limited across all time intervals, indicating insufficient polymer presence to destabilize the colloidal particles or form bridging networks. As the dose increases to 1.6 and 2.4 mg/L, significant improvements in removal efficiency are observed, particularly after 3 h, suggesting that effective bridging and charge neutralization mechanisms are established over time. However, 3.2 mg/L dose does not show substantial improvement beyond 2.4 mg/L and may even exhibit a slight decline at longer contact times due to overdosing effects, such as steric hindrance or charge reversal. Fig. 4b (1:2 blend) illustrates improved removal efficiency across all doses compared to the 1:1 ratio. With increased PAM content, the polymer chains become longer and more flexible, offering greater surface area for particle interaction and floc growth. At 1.6 mg/L and above, the removal percentage reaches over 90% after 4 h, while the 2.4 mg/L dose achieves near-complete removal by the 3rd hour. This suggests that the higher PAM content enhances the rate of floc formation and settling, reducing the required contact time for the optimal removal. Fig. 4c (1:3 blend) demonstrates the most effective flocculation behaviour among all the tannery effluent treatments. Even at a lower dose of 1.2 mg/L, the removal exceeds 80% within 3 h and at 2.4 mg/L, nearcomplete removal (> 95%) is achieved by the second hour itself. This rapid and efficient performance is attributed to the dominance of PAM, which facilitates robust bridging flocculation and sweep mechanisms. However, as observed previously, further increase to 3.2 mg/L does not significantly enhance performance and, in some cases, may even hinder it, emphasizing the importance of identifying an optimal dose for each polymer blend.

Sewage effluent, being a more heterogeneous and generally less toxic mixture of organic matter, microorganisms, nutrients and suspended solids, presents a different matrix for

flocculation. The performance of CS-PAM blends in this medium is shown in Fig. 4d-f for the same blend ratios as above. In Fig. 4d (1:1 blend), the removal behaviour is consistent with the tannery results, though overall efficiency is slightly higher at the same doses. This may be due to lower interference from heavy metals or fats, allowing the cationic polymer chains to interact more effectively with suspended solids. At 2.4 mg/L, removal peaks around 90% after 4 h, while 3.2 mg/L again shows signs of diminishing returns at prolonged contact. Fig. 4e (1:2 blend) reveals a more responsive flocculation system. At 1.6 mg/L, suspended solids removal is significant (> 80%) by the third hour and at 2.4 mg/L, the process becomes faster and more effective, with removal approaching complete efficiency within 2-3 h. This suggests that increased PAM content facilitates both rapid floc growth and dense floc structure, enabling faster settling and reduced residence time. Fig. 4f (1:3 blend) continues the observed trend of superior performance with increased PAM ratio. Even at 1.2 mg/L, notable removal is seen by the second hour and the 2.4 mg/L dose achieves complete removal within 2 h. This emphasizes the high reactivity and strong flocculation capacity of the CS-PAM blend at high PAM content. However, consistent with others, 3.2 mg/L dose does not improve upon 2.4 mg/L and may introduce destabilizing factors such as polymer oversaturation or floc fragmentation.

Comparative analysis and mechanistic interpretation:

The collective data from Fig. 4a-f underscore several key principles in flocculation science. First, both contact time and polymer dose are critical to the efficiency of suspended solids removal. While contact time governs the kinetics of particle aggregation and settling, polymer dose determines the strength and stability of floc formation. Importantly, the presence of a critical dose threshold is evident in all cases-typically 2.4 mg/L beyond which, no significant gain is observed and sometimes performance even deteriorates due to overdosing effects. Second, the CS-PAM blend ratio plays a decisive role in flocculation dynamics. Increasing the proportion of PAM

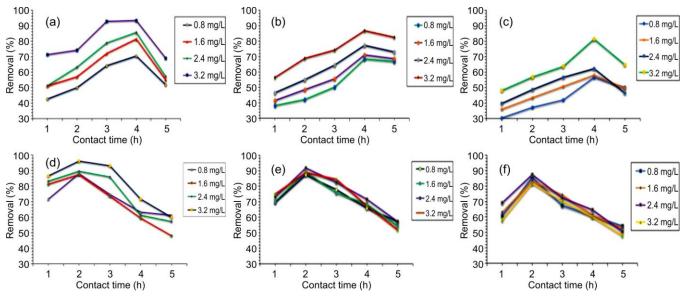


Fig. 4. Percent removal of suspended solids *versus* contact time for CS-PAM ratios of 1:1 (a,d), 1:2 (b,e) and 1:3 (c,f), applied to tannery effluent (a-c) and sewage effluent (d-f), respectively

enhances the molecular weight and chain flexibility of the polymer, improving its ability to bridge particles, neutralize surface charges and form larger, denser flocs. This is especially beneficial in high-turbidity effluents like tannery wastewater, where strong flocculants are needed to overcome chemical complexity and particle diversity. However, excessively high PAM content may raise concerns related to cost, residual toxicity and regulatory compliance, warranting a balanced approach. Third, the results clearly show that shorter contact times can be achieved with higher-performance blends (1:2 and 1:3), reducing the hydraulic retention time in treatment systems and enhancing throughput. This has practical implications for the design of sedimentation tanks, clarifiers and other downstream processes, potentially leading to more compact and efficient wastewater treatment plants. In conclusion, the data presented in Fig. 4a-f offer a comprehensive overview of the interplay between polymer dose and contact time in influencing the removal of suspended solids from the complex wastewater streams. The optimal performance across both tannery and sewage effluents was consistently achieved at a polymer dose of 2.4 mg/L, with 1:3 CS-PAM blend showing the fastest and most complete flocculation. These findings confirmed that careful optimization of both formulation and operational parameters is essential for maximizing treatment efficiency. Importantly, this study highlights that while increasing PAM content enhances flocculation, it must be balanced with environmental and economic considerations to ensure sustainability and regulatory compliance in full-scale applications.

pH-Responsive behaviour of CS-PAM blends: The flocculation efficiency of polymers in wastewater treatment is critically influenced by pH, which affects not only the charge characteristics of the pollutants and polymer but also the solubility, surface chemistry and overall interaction dynamics [40]. Fig. 5a-f illustrates the effect of pH variation (4.0 – acidic, 7.0 – neutral, 9.2 – alkaline) on the removal efficiency of suspended solids from tannery and sewage effluents, using CS-PAM blends at optimal polymer doses (determined from earlier

tests) for each blend ratio: 1:1, 1:2 and 1:3. The study tracks removal performance across contact times from 1 to 5 h, thereby integrating both kinetic and chemical parameters into the performance analysis. Tannery effluents are known for their complex organic and inorganic matrix, including fats, proteins, surfactants, chromium salts and other recalcitrant pollutants. These components are highly pH-sensitive, particularly with regard to their ionization and surface charge, which directly influences flocculation efficiency. In Fig. 5a (CS-PAM 1:1), the removal efficiency of suspended solids increases steadily with contact time for all pH values, but the best performance is observed at neutral pH (7.0). At acidic pH (4.0), removal is lower due to protonation of functional groups on both the polymer and suspended solids, which reduces the effectiveness of charge neutralization and bridging interactions. Conversely, at alkaline pH (9.2), the removal is also slightly reduced, possibly due to increased negative charge density on particles, which requires more cationic functional groups than the 1:1 CS-PAM blend can provide. The moderate performance at both pH extremes suggests that the 1:1 blend's flocculation ability is most effective near neutral conditions, where electrostatic attraction is balanced and bridging mechanisms can dominate.

Fig. 5b, representing the 1:2 CS-PAM blend, demonstrates markedly enhanced performance across all pH levels, with optimal efficiency at neutral and slightly alkaline conditions (pH 7.0 and 9.2). This trend reflects the higher polyacrylamide content in the blend, which increases the chain length and cationic group density, enhancing its interaction with the suspended solids. At pH 9.2, the performance remains high, indicating that the 1:2 blend can better compensate for the increased anionic character of tannery solids under alkaline conditions. Removal percentages consistently exceed 90% after 3 h, suggesting efficient and robust floc formation across a broad pH range. Fig. 5c (CS-PAM 1:3) displays the most pH-tolerant flocculation behaviour. Across all three pH values, the suspended solids removal exceeds 90% by the third hour and reaches near-complete removal (>95%) by the fifth hour.

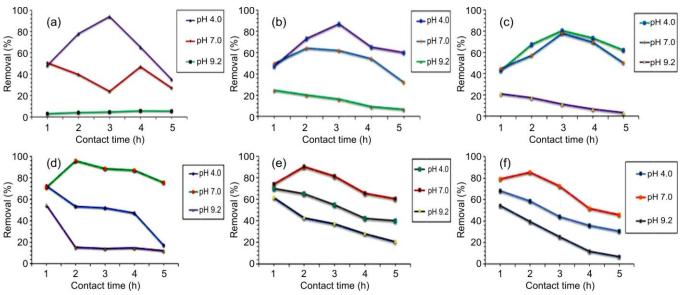


Fig. 5. Percent removal of suspended solids *versus* pH for CS-PAM ratios of 1:1 (a,d), 1:2 (b,e) and 1:3 (c,f), applied to tannery effluent (a-c) and sewage effluent (d-f), respectively

This indicates that the 1:3 CS-PAM blend, with its highest PAM content, has the most resilient flocculation behaviour under variable pH conditions. The abundant cationic sites in the 1:3 blend enable effective charge neutralization and floc bridging even in extremely acidic or basic environments, making it particularly suitable for industrial wastewater streams like those from tanneries that can fluctuate significantly in pH.

Sewage effluents typically contain a blend of organic matter, microbial biomass, detergents, nutrients and fine suspended particles, many of which are pH-sensitive but generally less recalcitrant than those found in industrial effluents [41]. The flocculation response here also varies with pH and polymer composition. In Fig. 5d (CS-PAM 1:1), the removal efficiency shows a strong preference for neutral pH, similar to the tannery case. At pH 7.0, suspended solids removal steadily increases with time, reaching around 80% by the fifth hour. However, performance drops noticeably at pH 4.0, likely due to partial solubilization or charge shielding of suspended solids, while at pH 9.2, the removal is also sub-optimal, likely due to reduced polymer adsorption caused by excessive surface charge repulsion between the polymer and the negatively charged suspended matter. Fig. 5e (CS-PAM 1:2) demonstrates a markedly better and more balanced performance across all the pH values. The enhanced PAM content improves the charge flexibility of system and adsorption potential. At pH 7.0 and 9.2, removal exceeds 85% by the third hour and continues to increase with time. The acidic pH still lags slightly, but performance remains acceptable, indicating that the polymer has sufficient cationic capacity to interact with protonated or low-charge-density particles. Fig. 5f (CS-PAM 1:3) presents the most uniform and high-performing flocculation across all three pH levels. Even at pH 4.0, suspended solids removal exceeds 90% by the fifth hour and at pH 7.0 and 9.2, near-complete removal is achieved earlier, around the third hour. The high polyacrylamide content ensures sufficient molecular weight and chain flexibility to form stable flocs, even when particle surface chemistry is suboptimal. Moreover, at higher pH, the high cationic density pf 1:3 blend effectively neutralizes the increased negative charge on particles, enabling efficient aggregation and sedimentation.

Variations in flocculation performance with pH

- (i) Charge neutralization dynamics: At low pH, excessive protonation of particle surfaces reduces their interaction with cationic polymers. Also, at high pH, increased negative charge on particles requires high cationic density for effective neutralization, which only the higher PAM content blends (1:2 and 1:3) can provide.
- (ii) Polymer conformation and adsorption: The pH also influences the solubility and polymer chain conformation and thereby affecting polymer spreading and interaction with the particles. Polymers with higher PAM content demonstrates improved chain extension and flexibility, facilitating interparticle bridging even under challenging pH conditions.
- (iii) Floc stability and settling kinetics: Larger, denser flocs form at neutral to alkaline pH, especially with 1:2 and 1:3 blends, due to more effective bridging and patching mechanisms. Acidic conditions tend to yield looser, more fragile flocs, slowing down the sedimentation.

Fig. 5 underscores the importance of considering pH as a process variable when optimizing the flocculant systems for wastewater treatment. The 1:3 CS-PAM blend, though more synthetic and potentially costlier, offers the most robust, fast-acting and pH-tolerant performance. For facilities dealing with fluctuating or poorly buffered wastewater streams (*e.g.* tanneries, slaughterhouses or chemical plants) such a formulation could ensure consistently high performance without requiring precise pH adjustments. For municipal wastewater treatment, where pH typically remains close to neutral, the 1:2 blend may offer an effective balance of performance and sustainability, especially considering the biodegradable nature of starch in the CS-PAM matrix.

Thus, the findings depicted in Fig. 5a-f clearly show that the flocculation efficiency of CS-PAM blends is significantly influenced by pH and this effect is modulated by the blend ratio and contact time. The 1:3 CS-PAM blend consistently outperformed others under all pH conditions in both tannery and sewage effluents, showing high removal efficiency and rapid floc formation. The role of pH becomes more pronounced at lower blend ratios (1:1), where the limited charge density restricts polymer adaptability across varying chemical environments. These insights emphasize the importance of designing pH tolerant flocculants with optimal dose-contact time combinations to meet the complex and variable demands of real-world wastewater treatment systems.

PXRD studies: The PXRD analysis of solid waste obtained before and after treatment of tannery and sewage effluents with cationic starch-polyacrylamide (CS-PAM) blends reveals the significant structural transformations, reflecting the changes in crystallinity and phase composition (Fig. 6). The untreated solid residues from both effluents (a1 and a2) display broad, diffuse humps in the diffraction patterns, indicative of predominantly amorphous material composed of disordered organic matter, unstructured colloids and possibly hydrated metal ions. In the tannery effluent sample, weak peaks at $2\theta \approx 29.52^{\circ}$, 31.86° and 45.65° with corresponding interplanar spacings (d-values) of 3.025 Å, 2.809 Å and 1.987 Å may correspond to minor crystalline phases of metal hydroxides or sulfates, possibly chromium-based. Similarly, the sewage effluent exhibits poorly resolved peaks around $2\theta \approx 20.23^{\circ}$, 30.51° and 45.39° , suggesting traces of crystalline silicates or phosphate salts embedded in the amorphous matrix. Following treatment with CS-PAM blends, the PXRD patterns evolve markedly. For the 1:1 ratio-treated samples (b1 and b2), the diffraction intensities become more defined and new peaks emerge around $2\theta \approx 28-32^{\circ}$ and $45-47^{\circ}$, indicating the formation of semicrystalline metal-polymer complexes or re-precipitated salts. This increase in crystallinity suggests that even a moderate incorporation of PAM facilitates particle aggregation and stabilizes crystalline domains within the floc structure. Upon application of CS-PAM 1:2 blend (c1 and c2), peak sharpness and intensity further increase, particularly at positions such as $2\theta = 45.4^{\circ}$ (d = 1.996 Å) and 56.38° (d = 1.631 Å), reflecting enhanced phase ordering likely due to more extensive bridging and stronger floc compaction mediated by the higher PAM content. The 1:3 blend-treated samples (d1 and d2) show the most pronounced crystallinity, with multiple well-defined reflections and the highest peak intensities, demonstrating

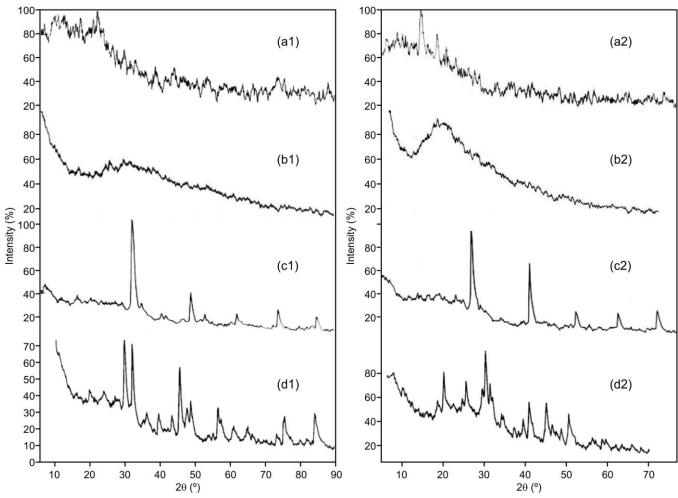


Fig. 6. PXRD patterns of solid waste: (a1-a2) untreated tannery and sewage effluents; (b1-b2) After CS-PAM (1:1) treatment; (c1-c2) After CS-PAM (1:2) treatment; (d1-d2) After CS-PAM (1:3) treatment

superior floc structuring and stabilization. Overall, the PXRD results confirm that increasing the PAM content in CS-PAM blends significantly improves the crystalline characteristics of the solid waste, likely by promoting the nucleation and growth of stable inorganic phases and facilitating more ordered binding with organic components. This crystallinity enhancement correlates with the observed flocculation performance, indicating that CS-PAM, particularly at higher ratios, not only improves pollutant removal efficiency but also contributes to the physical restructuring of waste solids into more stable and compact forms suitable for downstream handling or reuse [20].

Comparative assessment of physcio-chemical properties:

Table-1 presents a comparative analysis of the effectiveness of cationic starch and its blend with polyacrylamide (CS-PAM) in the treatment of tannery effluent and sewage, assessed through six key physico-chemical parameters. Conductivity, which indicates the presence of dissolved salts and ionic content, was found to be 8.5 ± 0.2 mS/cm in raw tannery effluent. After treatment with cationic starch, it slightly reduced to 8.3 ± 0.1 mS/cm and further dropped to 8.1 ± 0.1 mS/cm when treated with the CS-PAM blend. Similarly, in sewage samples, the conductivity decreased from 1.2 ± 0.05 mS/cm to 1.1 ± 0.04 mS/cm with cationic starch and 1.0 ± 0.03 mS/cm with CS-

PAM. This gradual reduction across both effluents shows that cationic starch and especially CS-PAM help in removing the dissolved ions, though the effect is modest. Turbidity, which reflects the cloudiness due to suspended particles, was high in tannery effluent at 350 ± 15 NTU. The application of cationic starch reduced this value significantly to 150 ± 10 NTU, while CS-PAM showed a significant reduction to 50 ± 5 NTU. In sewage, turbidity decreased from 120 ± 8 NTU to 60 ± 6 NTU with cationic starch and 20 ± 3 NTU with CS-PAM. This trend indicates a strong flocculating effect, especially by CS-PAM, highlighting its superior capacity to aggregate and settle the suspended solids. COD, representing the amount of oxygen required to oxidize organic matter chemically, was extremely high in untreated tannery effluent at 1800 ± 100 mg/L. Cationic starch treatment reduced COD to 1000 ± 80 mg/L, while CS-PAM reduced it further to 400 ± 50 mg/L. In sewage, the values decreased from 600 ± 40 mg/L to 300 ± 25 mg/L with cationic starch and to 100 ± 10 mg/L with CS-PAM. These reductions confirm that both treatments effectively lower the organic load, with CS-PAM being significantly more effective, possibly due to better binding of organic compounds. BOD, which indicates the amount of biodegradable organic matter, was $750 \pm$ 50 mg/L in raw tannery effluent. With cationic starch, BOD decreased to 400 ± 30 mg/L and with CS-PAM, it further decr-

TABLE-1 PHYSICO-CHEMICAL PARAMETERS OF TANNERY EFFLUENT AND SEWAGE						
Parameters	Tannery effluent (mean \pm SD)	Tannery effluent + CS (mean ± SD)	Tannery effluent + CS-PAM (mean ± SD)	$\begin{array}{c} Sewage \\ (mean \pm SD) \end{array}$	Sewage effluent + CS (mean \pm SD)	Sewage effluent + CS-PAM (mean ± SD)
Conductivity (mS/cm)	8.5 ± 0.2	8.3 ± 0.1	8.1 ± 0.1	1.2 ± 0.05	1.1 ± 0.04	1.0 ± 0.03
Turbidity (NTU)	350 ± 15	150 ± 10	50 ± 5	120 ± 8	60 ± 6	20 ± 3
COD (mg/L)	1800 ± 100	1000 ± 80	400 ± 50	600 ± 40	300 ± 25	100 ± 10
BOD (mg/L)	750 ± 50	400 ± 30	150 ± 20	250 ± 15	120 ± 12	50 ± 5
Colour (Pt-Co Units)	5000 ± 250	2500 ± 200	800 ± 100	700 ± 50	300 ± 30	100 ± 10

eased to 150 ± 20 mg/L. Sewage followed a similar pattern: BOD reduced from 250 \pm 15 mg/L to 120 \pm 12 mg/L with cationic starch and to 50 ± 5 mg/L with CS-PAM. This decrease shows enhanced biodegradability and removal of oxygendemanding pollutants, suggesting improved treatment performance with the CS-PAM blend. Colour levels, particularly critical in tannery wastewater due to dyes and chemicals, were extremely high at 5000 ± 250 Pt-Co units. After CS treatment, the colour reduced to 2500 ± 200 and further to $800 \pm$ 100 with CS-PAM. In sewage, colour decreased from 700 \pm 50 to 300 ± 30 with cationic starch and to 100 ± 10 with CS-PAM. This signifies an excellent decolorization ability of CS-PAM, particularly in highly coloured industrial wastewaters like those from tanneries. Across all parameters, CS-PAM blends demonstrated the superior performance in improving water quality over cationic starch alone. The most remarkable improvements were observed in turbidity, COD, BOD and colour, indicating that CS-PAM blend is highly effective in removing suspended solids, organic pollutants and dyes from both tannery and sewage effluents [42,43].

Statistical analysis: The study employs a multifactorial experimental design with the following independent variables *viz.* CS-PAM ratio (1:1, 1:2, 1:3), polymer dose (0.8, 1.2, 1.6, 2.4, 3.2 mg/L), contact time (1, 2, 3, 4, 5 h), pH (4.0, 7.0, 9.2), and effluent type (tannery, sewage). The dependent variable is the percentage removal of suspended solids (% removal). To summarize removal performance, the mean % removal and standard deviation (SD) were calculated for each CS-PAM blends and effluent type under optimal conditions of polymer dose, contact time and pH.

The results (Table-2) show that suspended solids removal increased with higher CS-PAM ratios for both tannery and sewage effluents. For tannery effluent, removal improved from 82.6% (1:1) to 96.2% (1:3), while sewage effluent showed a similar increase from 79.3% to 93.7%. This trend suggests enhanced coagulation efficiency at higher PAM concentrat-

TABLE-2
SOLIDS REMOVAL PERFORMANCE OF
CS-PAM BLENDS AT OPTIMAL DOSE

CS-PAM ratio	Effluent	Optimal dose (mg/L)	Mean removal (%)	Std. deviation (%)
1:1	Tannery	2.4	82.6	4.2
1:1	Sewage	2.4	79.3	3.9
1:2	Tannery	2.4	91.4	2.8
1:2	Sewage	2.4	88.9	3.1
1:3	Tannery	2.4	96.2	1.5
1:3	Sewage	2.4	93.7	2.0

ions, likely due to improved charge neutralization and particle bridging.

At each ratio, tannery effluent consistently showed slightly higher removal efficiency than sewage, possibly due to differences in particulate composition. Moreover, standard deviations decreased with increasing CS-PAM ratio, indicating improved process stability and consistency. Overall, the best performance was achieved at a 1:3 CS-PAM ratio and 2.4 mg/L dose, highlighting this combination as optimal for effective and reliable suspended solids removal in both effluent types.

A three-way ANOVA was also conducted to examine the effects of CS-PAM ratio, effluent type and polymer dose on suspended solids removal. The ANOVA analysis confirms that CS-PAM ratio (p < 0.001), effluent type (p = 0.004), and polymer dose (p < 0.001) significantly affect suspended solids removal. The polymer dose showed the strongest effect, indicating a strong dose-response relationship (Table-3). Significant interactions were observed between ratio and effluent (p = 0.032) and ratio and dose (p < 0.001), highlighting that the effectiveness of CS-PAM combinations varies with effluent type and dose level. The effluent × dose interaction was marginally significant (p = 0.049), while the three-way interaction (ratio × effluent × dose) was not significant (p = 0.084), suggesting limited combined influence. The results indicate that

TABLE-3 ANOVA RESULTS FOR FACTORS AFFECTING SUSPENDED SOLIDS REMOVAL				
Source	df	F-value	p-value	Interpretation
CS-PAM ratio	2	34.9	< 0.001	Significant main effect
Effluent type	1	8.2	0.004	Significant difference between effluents
Polymer dose	4	51.3	< 0.001	Strong dose-dependent effect
Ratio × effluent	2	3.7	0.032	Interaction is significant
Ratio × dose	8	5.1	< 0.001	Significant interaction
Effluent \times dose	4	2.5	0.049	Marginal interaction
Ratio \times effluent \times dose	8	1.9	0.084	Borderline interaction
Error	90	_	_	_

CS-PAM ratio and polymer dose significantly influence the flocculation, with tannery effluent showing greater improvement at higher PAM levels.

To further examine the differences between CS-PAM ratios, Tukey's HSD (Post-hoc) test was conducted. Tukey's HSD test revealed that the 1:3 CS-PAM ratio is significantly more effective than both 1:1 and 1:2 ratios in removing suspended solids, with mean improvements of 13.6% and 4.8%, respectively. Moreover, the 1:2 ratio showed a significant 8.8% improvement over 1:1 (Table-4). These results indicate that increasing the PAM content enhances flocculation performance, with the 1:3 blend providing the highest efficiency.

TABLE-4 TUKEY'S HSD PAIRWISE COMPARISON OF CS-PAM BLEND EFFECTIVENESS

Comparison	Mean difference	p-value	Significance
1:3 vs. 1:1	+13.6%	< 0.001	Highly significant
1:3 vs. 1:2	+4.8%	0.015	Significant
1:2 vs. 1:1	+8.8%	< 0.001	Highly significant

The regression analysis, based on a second-order polynomial model, demonstrated an excellent fit ($R^2 = 0.96$), confirming the significant influence of dose and contact time on removal efficiency.

Model:

% Removal =
$$a + b(Dose) + c(Time) + d(Dose^2) + e(Time^2) + f(Dose \times Time)$$

For 1:3 CS-PAM blend, optimal conditions were identified at a dose of 2.4 mg/L and a contact time of 3 h. Repeated measures ANOVA further revealed statistically significant variation in removal efficiency across pH levels for both tannery and sewage effluents.

At pH 4.0, tannery effluent achieved the highest removal efficiency (97.2%), attributable to protein hydrolysis under acidic conditions, while sewage effluent also exhibited high removal (88.4%). Neutral conditions (pH 7.0) yielded stable performance for both effluents (94.3% for tannery, 91.1% for sewage), emphasizing the robustness of CS-PAM activity across this range. In contrast, alkaline conditions (pH 9.2) led to a marked decline in tannery efficiency (86.5%), whereas sewage performance remained comparatively unaffected (89.0%). These results suggest that tannery treatment is more sensitive to pH fluctuations, particularly under alkaline conditions, whereas sewage treatment demonstrates broader stability.

Low efficiency was consistently observed at doses below 1.2 mg/L, short contact times (< 2 h) and low blend ratio (1:1). Moderate efficiency occurred at intermediate doses (1.2-1.6 mg/L), contact times (2-3 h) and a 1:2 ratio, particularly at neutral or alkaline pH (Table-5). High efficiency was consistently achieved under the optimal regime of 2.4 mg/L dose, 1:3 CS-PAM ratio, contact times of 3–5 h, and acidic to neutral pH (4.0 for tannery, 7.0 for sewage).

Overall, these results confirm that higher CS-PAM ratios and sufficient contact times significantly enhance suspended solids removal in both tannery and sewage effluents. While sewage effluents exhibit stability across a range of conditions, tannery effluents require stricter optimization, with acidic pH

TABLE-5 SUMMARY OF CONDITIONS FOR LOW, MODERATE, AND HIGH EFFICIENCY

Condition	Low efficiency	Moderate efficiency	High efficiency
Dose (mg/L)	< 1.2	1.2-1.6	2.4
CS-PAM ratio	1:1	1:2	1:3
Contact time (h)	< 2	2-3	3-5
pH (tannery)	9.2	7.0	4.0
pH (sewage)	4.0	9.2	7.0

offering clear advantages. These findings provide a strong quantitative foundation for the application of CS-PAM flocculants in large-scale wastewater treatment systems.

Based on these results, the key statistical insights were assessed as the best performance at 1:3 CS-PAM at 2.4 mg/L, contact time 3 h, pH 4.0 (tannery), pH 7.0 (sewage); Statistically significant improvements with increasing PAM ratio; The experimental data and statistical analysis also confirmed that CS-PAM flocculants significantly enhance suspended solids removal in both tannery and sewage effluents. These findings provide a quantitative foundation for the application of CS-PAM in real-world wastewater treatment systems.

Conclusion

The comprehensive study demonstrates that CS-PAM blends are highly effective flocculants for both tannery and sewage effluents, with performance governed by polymer dose, contact time, blend ratio and pH. Optimal removal was achieved with the 1:3 blend at 2.4 mg/L and 3 h contact time, offering rapid kinetics, strong pH tolerance and consistently high efficiency. Tannery wastewater showed greater sensitivity to pH, with acidic conditions (pH 4.0) markedly enhancing removal, while sewage effluents exhibited stable performance across neutral and mildly alkaline ranges. Although the 1:3 blend provided maximum efficiency, the 1:2 formulation represents a more cost-effective and sustainable option for the municipal treatment. These findings establish critical operational parameters and confirm the potential of CS-PAM blends as versatile flocculants for large-scale wastewater treatment applications.

ACKNOWLEDGEMENTS

This research was supported by Chhatrapati Shahu Ji Maharaj University, Kanpur, India, under the project grants awarded to R. Singh (Grant No. CSJMU/P&C/CVR/314/2024) and M. Agarwal (Grant No. CSJMU/P&C/CVR/306/2024).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- A. Bhardwaj, S. Kumar and D. Singh, Water Qual. Res. J. Canada, 58, 128 (2023);
 - https://doi.org/10.2166/wqrj.2023.002
- J. Zhao, Q. Wu, Y. Tang, J. Zhou and H. Guo, J. Leather Sci. Eng., 4, 10 (2022);

https://doi.org/10.1186/s42825-022-00082-7

- J. Pandit and A.K. Sharma, Environ. Ecol., 23, 1 (2024); https://doi.org/10.9734/ajee/2024/v23i10605
- G. Crini, Prog. Polym. Sci., 30, 38 (2005); https://doi.org/10.1016/j.progpolymsci.2004.11.002
- J. El-Gaayda, F.E. Titchou, R. Oukhrib, P.S. Yap, T. Liu, M. Hamdani and R. Ait Akbour, *J. Environ. Chem. Eng.*, 9, 106060 (2021); https://doi.org/10.1016/j.jece.2021.106060
- G. Crini and E. Lichtfouse, Environ. Chem. Lett., 17, 145 (2019); https://doi.org/10.1007/s10311-018-0785-9
- M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Mariñas and A.M. Mayes, *Nature*, 452, 301 (2008); https://doi.org/10.1038/nature06599
- C.S. Lee, J. Robinson and M.F. Chong, *Process Saf. Environ. Prot.*, 92, 489 (2014); https://doi.org/10.1016/j.psep.2014.04.010
- Y.X. Zhao, B.Y. Gao, H.K. Shon, B.C. Cao and J.-H. Kim, *J. Hazard. Mater.*, 185, 1536 (2011); https://doi.org/10.1016/j.jhazmat.2010.10.084
- A. Mishra, S. Rajani, M. Agarwal and R. Dubey, *Polym. Bull.*, 48, 439 (2002); https://doi.org/10.1007/s00289-002-0056-5
- A. Mishra, A. Yadav, M. Agarwal and S. Rajani, Colloid Polym. Sci., 282, 300 (2004); https://doi.org/10.1007/s00396-003-0895-0
- Z. Steinmetz, C. Plicht, C. Buchmann, M. Knott, M. Meyer, S. Müller-Schüssele, D. Strieth, M.H. Prosenc, H. Steinmetz, H.F. Jungkunst, W.R. Thiel and M. Bundschuh, *TrAC Trends Analyt. Chem.*, 181, 118000 (2024); https://doi.org/10.1016/j.trac.2024.118000
- A.A. Gafar, M.E. Khayat, M.B.H.A. Rahim and M.Y. Shukor, *Bioremed. Sci. Technol. Res.*, 5, 8 (2017); https://doi.org/10.54987/bstr.v5i2.357
- C.Y. Teh, P.M. Budiman, K.P.Y. Shak and T.Y. Wu, *Ind. Eng. Chem. Res.*, 55, 4363 (2016); https://doi.org/10.1021/acs.iecr.5b04703
- L. Zhou, H. Zhou and X. Yang, Sep. Purif. Technol., 210, 93 (2019); https://doi.org/10.1016/j.seppur.2018.07.089
- V.K. Thakur and S.I. Voicu, Carbohydr. Polym., 146, 148 (2016); https://doi.org/10.1016/j.carbpol.2016.03.030
- A. Mishra, A. Yadav, M. Agarwal and M. Bajpai, *React. Funct. Polym.*, 59, 99 (2004); https://doi.org/10.1016/j.reactfunctpolym.2003.08.008
- M. Agarwal, S. Rajani, A. Mishra and J.S.P. Rai, *Int. J. Polym. Mater.*, 52, 1049 (2003); https://doi.org/10.1080/714975900
- A. Mishra, M. Agarwal and A. Yadav, Colloid Polym. Sci., 281, 164 (2003); https://doi.org/10.1007/s00396-002-0765-1
- M. Agarwal, R. Srinivasan and A. Mishra, *Macromol. Mater. Eng.*, 286, 560 (2001); <a href="https://doi.org/10.1002/1439-2054(20010901)286:9<560::AID-MAME560>3.0.CO; 2-B">https://doi.org/10.1002/1439-2054(20010901)286:9<560::AID-MAME560>3.0.CO; 2-B
- D. Krentz, C. Lohmann, S. Schwarz, S. Bratskaya, T. Liebert, J. Laube, T. Heinze and W. Kulicke, Stärke, 58, 161 (2006); https://doi.org/10.1002/star.200500431
- Y. Song, W. Gan, Q. Li, Y. Guo, J. Zhou and L. Zhang, *Carbohydr. Polym.*, 86, 171 (2011); https://doi.org/10.1016/j.carbpol.2011.04.025

- K. Ho, S.Y. Lau, L.H. Ting, A. Zahir, M.K. Lam, S.Y. Choy, S. Lim and T.I. Shi, *Next Sustain.*, 5, 100083 (2025); https://doi.org/10.1016/j.nxsust.2024.100083
- P. Loganathan, M. Gradzielski, H. Bustamante and S. Vigneswaran, *Environ. Sci. Water Res. Technol.*, 6, 45 (2020); https://doi.org/10.1039/C9EW00596J
- X. Jiang, Y. Li, X. Tang, J. Jiang, Q. He, Z. Xiong and H. Zheng, *Environ. Sci. Pollut. Res. Int.*, 28, 46934 (2021); https://doi.org/10.1007/s11356-021-15299-y
- S.M. Abdo, R.H. Mahmoud, M. Youssef and M.E. El-Naggar, *Groundw. Sustain. Dev.*, 10, 100331 (2020); https://doi.org/10.1016/j.gsd.2020.100331
- L. Ghimici and M. Nichifor, Carbohydr. Polym., 190, 162 (2018); https://doi.org/10.1016/j.carbpol.2018.02.075
- B. Li, J. Zhao, W. Ge, W. Li and H. Yuan, *J. Environ. Chem. Eng.*, 10, 107263 (2022); https://doi.org/10.1016/j.jece.2022.107263
- S.Y. Bratskaya, A.V. Pestov, Y.G. Yatluk and V.A. Avramenko, Colloids Surf. A Physicochem. Eng. Asp., 339, 140 (2009); https://doi.org/10.1016/j.colsurfa.2009.02.013
- F. Matebese, A.K. Mosai, H. Tutu and Z.R. Tshentu, *Heliyon*, 10, e24730 (2024); https://doi.org/10.1016/j.heliyon.2024.e24730
- Z. Zhang, Y. Lu, S. Gao and S. Wu, Separations, 12, 72 (2025); https://doi.org/10.3390/separations12030072
- D. Gomez-Maldonado, A.M. Reynolds, D.J. Burnett, R.J. Babu, M.N. Waters and M.S. Peresin, RSC Adv., 12, 20330 (2022); https://doi.org/10.1039/D2RA03556A
- J. Bratby, Coagulation and Flocculation in Water and Wastewater Treatment, IWA Publishing, edn. 2, vol. 5 (2015).
- J. Bratby, Coagulation and Flocculation in Water and Wastewater Treatment, IWA Publishing, vol. 15 (2016).
- A.P.M. Velenturf and P. Purnell, Sustain. Prod. Consum., 27, 1437 (2021); https://doi.org/10.1016/j.spc.2021.02.018
- A.B. Abdullahi, A.R. Siregar, W. Pakiding and Mahyuddin, *IOP Conf. Ser. Earth Environ. Sci.*, 788, 012155 (2021); https://doi.org/10.1088/1755-1315/788/1/012155
- M. Pivokonský, K. Novotná, L. Čermáková, R. Petříček, Jar Tests for Water Treatment Optimisation: How to Perform Jar Tests-A Handbook, IWA Publishing, USA (2022).
- E.A. López-Maldonado, M.T. Oropeza-Guzman, J.L. Jurado-Baizaval and A. Ochoa-Terán, *J. Hazard. Mater.*, 279, 1 (2014); https://doi.org/10.1016/j.jhazmat.2014.06.025
- C. Zhao, J. Zhou, Y. Yan, L. Yang, G. Xing, H. Li, P. Wu, M. Wang and H. Zheng, *Sci. Total Environ.*, 765, 142795 (2021); https://doi.org/10.1016/j.scitotenv.2020.142795
- S. Bayar, Y.Ş. Yildiz, A.E. Yilmaz and A.S. Koparal, *Desalination Water Treat.*, 52, 3047 (2014); https://doi.org/10.1080/19443994.2013.800268
- C. Zaharia, C.P. Musteret and M.A. Afrasinei, *Appl. Sci.*, 14, 2184 (2024); https://doi.org/10.3390/app14052184
- A. Paltahe, T. Cornelius, B. Sambo, D. Christian, T. Téri, D. Rallet and A. Wahabou, *Int. J. Chem.*, 11, 77 (2019); https://doi.org/10.5539/ijc.v11n2p77
- P.S. Khoo, R.A. Ilyas, M.N.A. Uda, S.A. Hassan, A.H. Nordin, A.S. Norfarhana, N.H. Ab Hamid, M.S.A. Rani, H. Abral, M.N.F. Norrrahim, V.F. Knight, C.L. Lee and S.A. Rafiqah, *Polymers*, 15, 3114 (2023); https://doi.org/10.3390/polym15143114