



## Coagulation and flocculation effects in the purification of tannery waste solutions

**Anatoliy Danylkovych**

Doctor of Technical Sciences, Professor  
Kyiv National University of Technologies and Design  
01011, 2 Mala Shyianovska Str., Kyiv, Ukraine  
<https://orcid.org/0000-0002-5707-0419>

**Olga Sanginova\***

PhD in Technical Sciences, Associate Professor  
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"  
01056, 37 Beresteiskyi Ave., Kyiv, Ukraine  
<https://orcid.org/0000-0001-6378-7718>

**Nataliia Tolstopalova**

PhD in Technical Sciences, Associate Professor  
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"  
01056, 37 Beresteiskyi Ave., Kyiv, Ukraine  
<https://orcid.org/0000-0002-7240-5344>

**Tetiana Obushenko**

Senior Lecturer  
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"  
01056, 37 Beresteiskyi Ave., Kyiv, Ukraine  
<https://orcid.org/0000-0003-0731-0370>

**Dmytro Yavorskiy**

Postgraduate Student  
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"  
01056, 37 Beresteiskyi Ave., Kyiv, Ukraine  
<https://orcid.org/0009-0003-3216-9740>

**Abstract.** Available methods of wastewater treatment of tanneries require improvement to ensure the desired efficiency of purification and regeneration of valuable components contained in the waste process solutions. The purpose of this study was to provide a comprehensive coagulation-flocculation treatment of liquid waste from tanneries using mathematical modelling methods. The study conducted experimental investigation of the effectiveness of coagulants – aluminium sulphate and iron (III) chloride – and flocculants: polyhexamethylene guanidine hydroxychloride and its acetate, as well as reagent P228. The effect of pH on the coagulation process was examined. The efficiency of the coagulation process was evaluated by an integral indicator - the degree of purification, which was determined considering the turbidity and optical density of the purified water samples. The study presented the findings on coagulation and flocculation effects that occur during the purification of samples of tannery waste process solutions after the filling-fattening and dyeing processes. The studied samples are characterised by high concentrations of sulphates (over 9,000 mg/dm<sup>3</sup>) and chlorides (over 1,500 mg/dm<sup>3</sup>), an increased content of suspended solids (over 845 mg/dm<sup>3</sup>) and metal ions: chromium (III), iron, and aluminium. According to the findings of the study, the aluminium-based coagulant is more efficient than the iron-based coagulant. Among the flocculants,

### Suggested Citation:

Danylkovych, A., Sanginova, O., Tolstopalova, N., Obushenko, T., & Yavorskiy, D. (2024). Coagulation and flocculation effects in the purification of tannery waste solutions. *Technologies and Engineering*, 25(6), 18-28. doi: 10.30857/2786-5371.2024.6.2.

\*Corresponding author



polyhexamethylene guanidine hydroxychloride is the most effective, while the pH value should be 10. The results of experimental studies were used to obtain a mathematical model that described the coagulation process with a sufficient degree of accuracy. The results of mathematical modelling can be used to calculate the optimum parameters of the coagulation process

**Keywords:** tannery wastewater; chemical precipitation; degree of purification; optimisation of the coagulation process

## Introduction

Leather production is characterised by multiple stages, using a considerable number of chemical reagents of various compositions, their high concentration in spent solutions, and a high degree of echogenicity. Notably, the content of pollutants in wastewater significantly depends on the specific features of technological processes at each stage of leather production. If, at the stage of preparatory processes, the spent solutions have a high content of insoluble organic and mineral substances, water-soluble proteins, and degraded keratin residues, then the following stages are characterised by a significant content of unreacted organic and mineral reagents. In this regard, the primary task of modern innovative production lies in minimising the environmental hazards of spent technological solutions, which is achieved by using a complex of mechanical, physicochemical, biological, and other treatment methods. For this, a wide range of chemical reagents is used – coagulants, flocculants, and other reagents of various chemical compositions. At the same time, developing effective methods of complex cleaning of spent solutions involves the study of the mechanism of their action, considering the features of the specific production technology.

According to F. Chiampo *et al.* (2023), tannery wastewater may contain pathogenic microorganisms and toxic substances that cause disease and pose a health hazard to humans when ingested. B. Jiang *et al.* (2020) noted that liquid and solid wastes from the leather industry and tanneries, if not treated before being released into water bodies, create an increasing burden on the environment. According to N.M. Sivaram & D. Barik (2019), raw tannery wastewater can contain high levels of numerous pollutants, namely up to (mg/dm<sup>3</sup>): suspended substances – 10,000, sulphides – 300, surfactants – 250, chromium (III) ions – 150, wool – 50, fats – 600, chemical oxygen demand (COD) – up to 6000, biological oxygen demand-5 (BOD<sub>5</sub>) – 1500, the pH of the total effluent reaches 11.5.

A. Bhardwaj *et al.* (2023) studied various treatment methods such as membrane separation processes, advanced oxidation process (AOP), adsorption, biological treatment, and hybrid treatment technologies, which were found to be effective for treating tannery wastewater. It was noted that although these cleaning methods proved to be effective, they require further development and improvement to meet stricter regulatory standards. L. Sabliy *et al.* (2019) developed a technology for complex wastewater treatment from leather production, which involves biochemical treatment after mechanical cleaning and flotation in an anaerobic environment and a membrane

bioreactor. At the same time, wastewater enters the membrane bioreactor with reduced indicators of chemical and biological oxygen consumption by 8.8 and 17.0 times as a result of biological treatment.

M. Nigam *et al.* (2023) highlighted several conventional physicochemical (equalisation, coagulation, and adsorption) technologies, advanced approaches (Fenton oxidation, ozonation, cavitation), thermocatalytic, and biological wastewater treatment methods, and their integrative approaches. The researchers considered the conventional and oxidation methods suitable for pollutant degradation (70-99%). Due to membrane cost and contamination, membrane filtration processes are adequate but not used on an industrial scale.

S. Mim *et al.* (2023) proposed a coagulation-adsorption method for the pre-treatment of tannery effluents with a high content of sulphides, which provides 90-98% removal of suspended solids. The researchers provided a technological scheme of wastewater treatment of a tannery, which includes non-pressure filtration units, electrocoagulation-flotation devices, and dehydration of flotation sludge. S. Mim *et al.* (2024) offered the sorption method of cleaning spent solutions of leather and fur production. For this, natural aluminosilicate glauconite was used, containing (%): 44-56 SiO<sub>2</sub>, 3-22 Al<sub>2</sub>O<sub>3</sub>, 0-27 Fe<sub>2</sub>O<sub>3</sub>, 0-8 FeO, 0-10 MgO, up to 10 K<sub>2</sub>O, 4-10 H<sub>2</sub>O. The efficiency of treatment of spent solutions from chromium (III) compounds reached 80-95%, depending on the chemical composition of glauconite.

M.A. Aboulhassan *et al.* (2021) conducted Jar-Test experiments to evaluate the effectiveness of tannin-based polymer (TBP) in treating these tannery wastewaters. The findings showed that TBP is more effective than the classical ferric chloride coagulant, enabling it to remove over 60% and 96% of COD and colour from industrial wastewater, respectively. Compared to ferric chloride, TBP produces less sludge, has the highest dewatering efficiency, generates well-settable sludge, and allows for higher water recovery rates than FeCl<sub>3</sub>. Coagulation flocculation proved to be an effective method, while TBP can be used as a replacement for conventional coagulants in treating industrial wastewater.

B. Othmani *et al.* (2020) extensively investigated plant-based coagulants/flocculants for their effectiveness in removing various pollutants from water. Apart from safety and efficacy, the biodegradability of the substances under study is one of the exciting features that can promote the application of green products for water treatment as an alternative to persistent chemicals. To increase the

widespread use of the biocoagulant, the researchers recommended scaling up the laboratory research on pilot plants. According to A. Nath *et al.* (2021), the disadvantage of natural plant-based coagulants is the price, and therefore their use on an industrial scale is still ineffective compared to synthetic coagulants.

Therefore, the industrial effluents of leather production contain a wide range of pollutants of different chemical compositions, which depends on the specific features of the manufacturing technology of a particular type of leather material and the chemical reagents used at various stages. This necessitates the development of complex technologies for cleaning wastewater from leather production, which includes mechanical, physicochemical, and biological methods. The purpose of this study was to perform complex coagulation-flocculation cleaning of spent technological solutions after the filling, greasing, and dyeing processes of semi-finished chrome tanning for shoe uppers.

To fulfil the purpose, the following tasks were set:

- ◆ to identify the factors affecting the process of coagulation cleaning of spent solutions of leather production after the stages of filling, greasing, and dyeing;
- ◆ to conduct experimental studies to determine the most effective coagulants and flocculants;
- ◆ to obtain an adequate mathematical model that describes the coagulation process and to investigate the coagulation-flocculation effects of the cleaning process of spent leather production solutions.

## Materials and Methods

For the study, a leather production solution was used after the filling-greasing and dyeing of semi-finished chrome tanning for shoe uppers. The characteristics of the solution under study are presented in Table 1. Wastewater samples were investigated in the Central Biochemical Laboratory “CBL” (n.d.), Kyiv.

**Table 1.** The Contribution of agroforestry practice to pesanggem household income

Water Quality Index	Value	Norm*	Regulatory document
pH	3.79	6.5-9.0	DSTU No. 4077-2001 (2003)
Suspended solids, mg/l	843	300	KND No. 211.1.4.039-95 (1995)
TS, mg/l	16,130	1,000	MVV No. 081/12-0109-03 (2004)
Sulphates, mg/l	9,513	380	MVV No. 081/12-0007-01 (2002)
Chlorides, mg/l	1,587	240	MVV No. 081/12-0004-01 (2002)
Ammonium, mg/l	39	20	DSTU ISO No. 7150-1:2003 (2004)
Fe total, mg/l	10	0.5	DSTU EN ISO No. 11885:2019 (2020)
Mn, mg/l	2.28	0.68	DSTU EN ISO No. 11885:2019 (2020)
Cu, mg/l	0.52	0.3	DSTU EN ISO No. 11885:2019 (2020)
Al, mg/l	10.79	2.72	DSTU EN ISO No. 11885:2019 (2020)
Cr total, mg/l	36.88	2.3	DSTU EN ISO No. 11885:2019 (2020)
COD, mgO/l	12,000	500	DSTU ISO No. 6060:2003 (2004)

**Note:** \*based on the Order of the Executive Body of the Kyiv City Council... (2011)

**Source:** developed by the authors of this study

As Table 1 shows, all the indicators of the sample of the used technological solution significantly exceed the normative values, especially for sulphates and COD, which are 25.0 and 24.0 times higher, respectively.

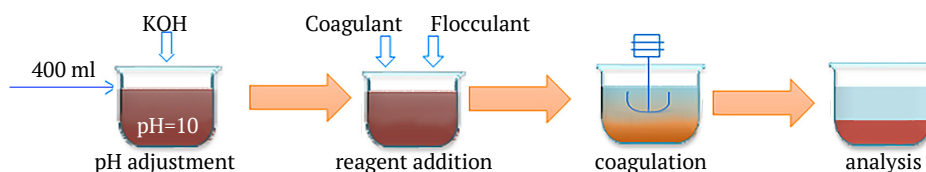
The research used:

- ◆ coagulants – 25% solutions of  $Al_2(SO_4)_3$  concentration and  $FeCl_3$ ;
- ◆ flocculants – 5% solutions of crystalline poly hexamethylene guanidine hydrochloride (PGMG-HC), its acetate (PGMG-A) and reagent F-PET, obtained in the laboratory of the Department of Organic Chemistry and Technology of Organic Production, National Technical University of

Ukraine “Igor Sikorsky Kyiv Polytechnic Institute” through sequential waste destruction polyethylene terephthalate under the action of monoethanolamine and glycerine at 180-200°C as a mixture of terephthalic acid oligomers and polyols with terminal ammonium groups;

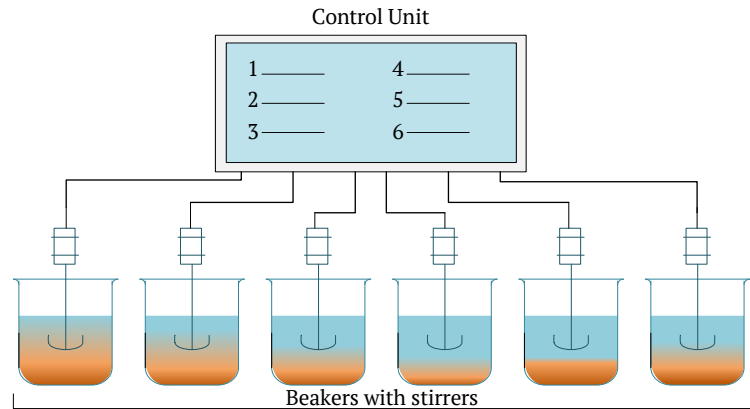
- ◆ pH regulator – 60% solution of crystalline KOH.

Figure 1 schematically represents the experiment procedure. To determine the optimum consumption of coagulant and flocculant, the test coagulation method was used using a modified laboratory setup with 6 beakers, each containing 1,000 ml. Figure 2 schematically represents the setup.



**Figure 1.** Scheme of experimental research

**Source:** developed by the authors of this study

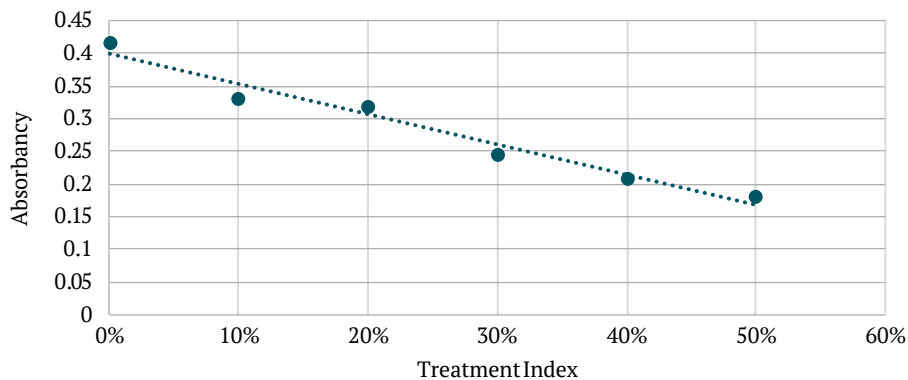


**Figure 2.** Laboratory setup

**Source:** developed by the authors of this study

To prepare the studied samples, 400 ml of each spent technological solution was diluted in a ratio of 1:10, the pH was adjusted within 9-10, while coagulants and flocculants were combined with the selected sample. Subsequently, the resulting solution was stirred for one minute, stirred slowly for 20 minutes, and settled for 10 minutes. A stationary CyberScan WL Turbidimeter TB1000 (USA) turbidimeter was

used to investigate the turbidity of solutions. The optical density of the samples of the treated solution was analysed on a spectrophotometer ULAB 101 (China). The treatment index was the selected indicator of the quality of the coagulation process. It was calculated based on the optical density measured by a spectrophotometer and is determined by the graph presented in Figure 3.



**Figure 3.** Graph of dependence of the optical density of water samples on the treatment index

**Source:** developed by the authors of this study based on the findings of experimental research

Experimental studies were performed according to the plan of a full factorial experiment (Volokyta & Selivanov, 2022). Statistical processing of the obtained findings was performed as follows:

- ◆ the effectiveness of coagulants and flocculants was assessed by the closeness of the correlation between the dose of flocculant/coagulant and the treatment index; the value of the correlation coefficient was calculated according to known formulas (Bondarenko et al., 2024);

- ◆ the adequacy of the mathematical model was evaluated using the built-in tools of the STAR system (Mathematical and computer..., n.d.) by the following indicators: standard deviation, correlation ratio, F-ratio.

The STAR system was used to model the coagulation process and assess the adequacy of the obtained models.

## Results and Discussion

The study of the effect of coagulants and flocculants was divided into 4 stages. At each of the stages, the influence of individual parameters on the treatment index was investigated.

Stage 1: Study of the effect of coagulant  $Al_2(SO_4)_3$  and flocculant PGMG-HC.

Stage 2: Study of the effect of coagulant  $Al_2(SO_4)_3$  and PGMG-HC flocculant.

Stage 3: Study of the effect of coagulant  $Al_2(SO_4)_3$  and flocculant PGMG-A.

Stage 4: Study of the effect of coagulant  $Al_2(SO_4)_3$  and flocculant F-PET.

For each stage, a separate plan of a full factorial experiment was drafted, considering the ranges of variations presented in Table 2.

**Table 2.** Variation ranges of the studied parameters by stages

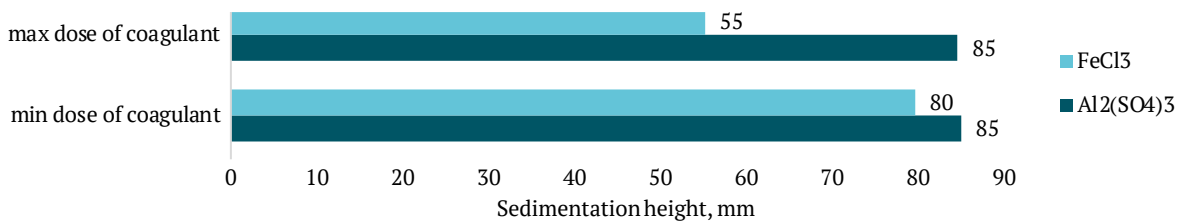
Stage 1		
Range of variation	Parameter, units and notation	
	Coagulant $Al_2(SO_4)_3$	Flocculant PGMG-HC
	ml	ml
	$x_1$	$x_2$
$x_{min}$	0	4
$x_{max}$	10	10
Stage 2		
	Coagulant $FeCl_3$	Flocculant PGMG-HC
	ml	ml
	$x_5$	$x_2$
$x_{min}$	0	4
$x_{max}$	10	10
Stage 3		
	Coagulant $Al_2(SO_4)_3$	Flocculant PGMG-A
	ml	ml
	$x_1$	$x_3$
$x_{min}$	0	2
$x_{max}$	10	6
	Coagulant $Al_2(SO_4)_3$	Flocculant F-PET
	$x_1$	$x_4$
	ml	ml
$x_{min}$	0	2
$x_{max}$	10	6
$x_{min}$		
$x_{max}$		

**Note:** the pH value ( $x_6$ ) varied within 9-10

**Source:** developed by the authors of this study

Figure 4 presents a comparative analysis of two coagulants: aluminium sulphate and ferric chloride, in the presence of the same dose (500 mg/dm<sup>3</sup>) of the PGMG-HC flocculant. The maximum dose of the coagulant corresponds

to 1000 mg/dm<sup>3</sup>, and the minimum dose corresponds to the process without adding the coagulant. The results show that aluminium sulphate is more effective (85%) for the maximum dose than ferric chloride (55%).



**Figure 4.** Degree of wastewater treatment depending on the type of coagulant

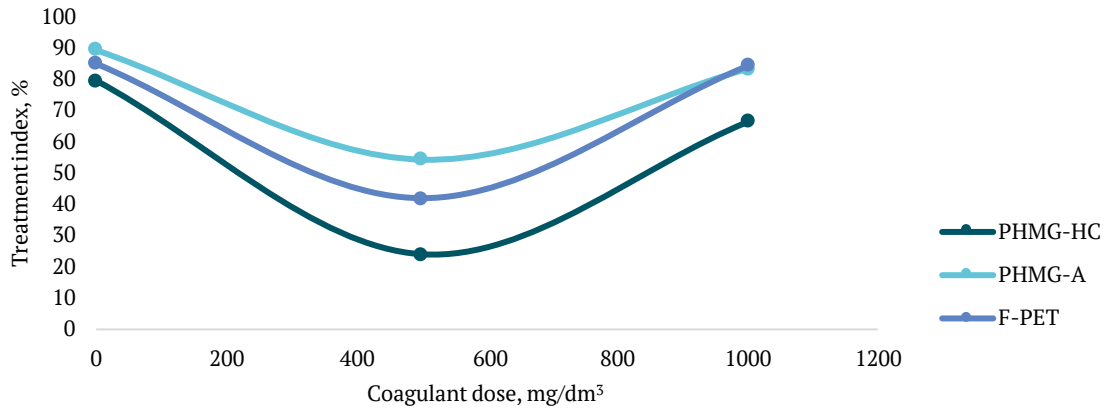
**Source:** developed by the authors of this study based on the findings of experimental research

Figure 5 shows the effect of the coagulant dose on the degree of treatment at a constant dose of flocculants (500 mg/dm<sup>3</sup>). In the absence of the coagulant, high purification degrees were observed: 89% for PGMG-A, 85% for F-PET, and 80% for PGMG-HC. The following purification degrees were obtained for an aluminium sulphate dose of 500 mg/dm<sup>3</sup>: 54% for PGMG-A, 42% for F-PET, and 24% for PGMG-HC. The following treatment degrees were obtained for an aluminium dose of 1,000 mg/dm<sup>3</sup>: 84% for

PGMG-A, 84% for F-PET, and 66% for PGMG-HC. It was found that the highest treatment index is achieved using PGMG-A flocculant, and a high degree of treatment can be achieved without adding coagulants. Figure 6 shows the effect of the flocculant dose on the purification degree at a constant coagulant dose (1,000 mg/dm<sup>3</sup>). For a flocculant dose of 250 mg/dm<sup>3</sup>, the following treatment degrees were obtained: for PGMG-A 85%, for F-PET 83%, for PGMG-HC 40%. For a flocculant dose of 500 mg/dm<sup>3</sup>, the following

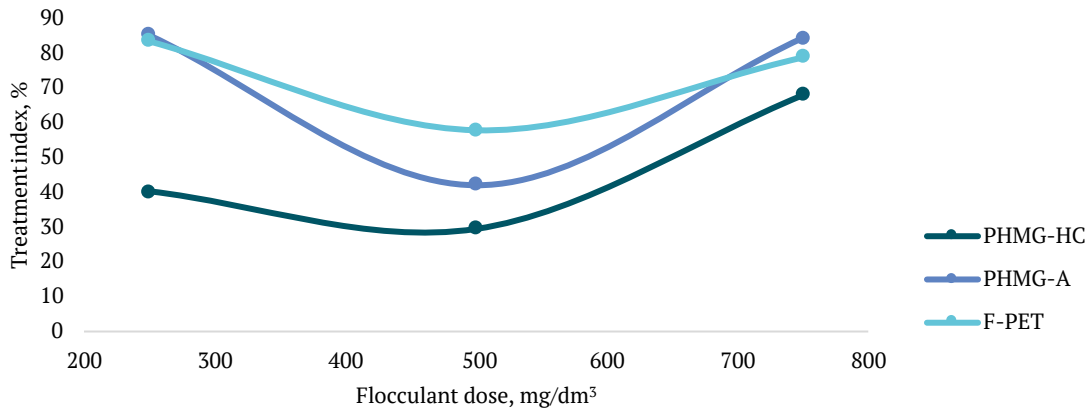
treatment degrees were obtained: for PGMG-A 42%, for F-PET 58%, for PGMG-NS 29%. The following treatment

degrees were obtained for a dose of 750 mg/dm<sup>3</sup>: for PGMG-A 84%, for F-PET 79%, for PGMG-NS 68%.



**Figure 5.** Degree of wastewater treatment depending on the dose of coagulant and type of flocculant

Source: developed by the authors of this study based on the findings of experimental research



**Figure 6.** Degree of wastewater treatment depending on the flocculant dose

Source: developed by the authors of this study based on the findings of experimental research

As Figure 6 shows, the flocculant dose variation affects the treatment index of the samples under study. The mathematical model that best describes the coagulation process is as follows:

$$\begin{cases} y_1 = 91.48 - 2.06x_1 - 88.06x_2 - 1.58x_6 \\ y_2 = 1.95 - 0.16x_1 - 0.76x_2 - 5.6 \cdot 10^{-2}x_6, \end{cases} \quad (1)$$

where  $y_1$  is the turbidity of the spent solution sample after coagulation (NOK),  $y_2$  is the absorbency of the sample under study (at  $\lambda = 400$  nm).

Characteristics of the received model:

- ◆ standard deviation for each equation, respectively:

$$\sigma_1 = \pm 1.7 \text{ NOK}, \sigma_2 = \pm 0.22\%;$$

- ◆ correlation ratio for each equation, respectively:

$$r_1 = 0.91; r_2 = 0.89;$$

- ◆ F-ratio for each equation, respectively:  $F_1 = 10.4;$

$$F_2 = 9.7.$$

Based on the obtained characteristics, the obtained mathematical model accurately describes the experimental data. The most effective are the coagulant  $Al_2(SO_4)_3$  and the flocculant PGMG-A. Table 3 presents a comparative analysis of a sample of the spent solution before and after treatment. The coagulation-flocculation method provides deep treatment from all pollutants.

**Table 3.** Comparative analysis of the spent solution sample before and after treatment

Water Quality Index	Before Treatment	After Treatment	Degree of Contaminant Removal, %
pH	3.79	9.14	--
Suspended solids, mg/l	843	< 5	99
TS, mg/l	16,130	970	94

Table 3. Continued

Water Quality Index	Before Treatment	After Treatment	Degree of Contaminant Removal, %
Sulphates, mg/l	9,513	438	95
Chlorides, mg/l	1,587	110	93
Ammonium, mg/l	39	21.7	44
Fe total, mg/l	10	0.02	100
Mn, mg/l	2.28	< 0.01	100
Cu, mg/l	0.52	< 0.01	98
Al, mg/l	10.79	0.11	99
Cr total, mg/l	36.88	< 0.01	100
COD, mgO/l	12,000	466	96

**Source:** developed by the authors of this study based on the findings of experimental research

The study proved that coagulation is the most widely used physical and chemical purification method to reduce turbidity and suspended substances. Disadvantages of chemical coagulants include the formation of difficult-to-decompose sediments, prohibitive cost, and, most importantly, aluminium residues in treated water. W.L. Ang & A.W. Mohammad (2020) reviewed studies to assess the potential of using natural coagulants as alternatives to synthetic chemicals. However, S. Gautam & G. Saini (2020) noted that despite being an economical and environmentally friendly alternative, natural coagulants are inferior to chemical coagulants in wastewater treatment, especially on a large scale. Lack of sources for mass availability, the low shelf life of such coagulants, and high operating costs are some of the obstacles to their large-scale application.

The study findings of the quality indicators of the spent solution sample showed a significant improvement in the treated water quality in all indicators, except for the content of aluminium and sulphates. Aluminium sulphate may provide better results, as Figure 4 shows, since its coagulant properties contribute to denser sedimentation of organic compounds and suspended particles. This is particularly important for tanneries, where wastewater contains a large amount of organic matter. Despite its more comprehensive pH range, ferric chloride may be less effective in treating specific organic contaminants and may form smaller flocs, reducing its performance. Furthermore, tannery wastewater may contain large amounts of dissolved salts and metals. Iron ions ( $Fe^{3+}$ ) from ferric chloride may compete with other metals for precipitation, reducing coagulation efficiency.

When using aluminium sulphate, flocs are formed more slowly but are usually more stable and larger. This facilitates their subsequent removal from water (e.g., by settling or filtration). Ferric chloride forms flocs faster but can be smaller and less stable, which may complicate their separation from water. W.L. Ang & A.W. Mohammad (2020) showed that aluminium sulphate works better in a narrower pH range (usually 5-7), often found in wastewater. At the same time, N. Nomanifar *et al.* (2024) pointed out that ferric chloride can work on a broader pH range, including more acidic environments (pH 4-6). However, its effectiveness may decrease in slightly acidic and neutral waters. Thus,

aluminium sulphate may be more effective in wastewater with a pH close to neutral. These findings are consistent with the results obtained by Z. Bingül *et al.* (2021), who investigated the pH effect of tannery wastewater obtained from a local tannery on XPC removal and turbidity.

The study of the effect of the coagulant dose on the degree of purification at a constant dose of flocculants (Fig. 5) showed that PGMG-A coagulant provides a higher degree of treatment. The large amount of suspended substances in the examined samples of the spent solution can explain the obtained findings. The nature of the change in the degree of treatment is comparable for all the flocculants studied. The value is lower for a lower coagulant dose than a higher dose. When an excess amount of coagulant is added, the particles can begin to recharge. Instead of neutralising the negative charges of the colloids, excess aluminium ions can give the particles a positive charge, which again causes them to repel each other. This leads to destabilisation of the flocs and deterioration of their adhesion, which reduces the purification efficiency. An excessive amount of small flocs can also be formed, which are more difficult to remove from the water than large ones. With a further increase in the coagulant dose, a transformation of stable flocs can occur, because the excess coagulant again begins to bind with the remaining charged particles or small flocs. The flocculant helps in the aggregation and formation of large and heavy flocs, increasing the purification degree. This effect may be due to the coagulant beginning to precipitate smaller and remaining contaminants, and the flocculant stabilizes new flocs, improving the final filtration. The findings of A.K. Tolkou & A.I. Zouboulis (2020) are consistent with this conclusion: it was found that the coagulant, both with and without the addition of flocculant, can provide better performance for the coagulation/flocculation process than conventional coagulants.

The nonlinear dependence of the purification degree with a change in the flocculant dose and a constant dose of aluminium sulphate, presented in Figure 6, is associated with the features of the interaction between the flocculant, coagulant, and colloidal particles in wastewater. The efficiency of the flocculant depends on its concentration, the chemical properties of the water, the coagulant dose, and the structure of the formed flocs. At low flocculant doses,

the flocs formed by the coagulant are still too small and unstable to settle effectively. As the flocculant dose increases, its polymer chains bind small flocs, forming larger aggregates that are easier to settle and remove. This leads to an improvement in the purification degree since the flocculant helps stabilise the particle aggregation process. If the flocculant dose is too high, the system may become oversaturated with polymer chains. Instead of binding the particles, the flocculant starts to act oppositely – it coats the floc surfaces and makes them too “slippery” for further aggregation. This may cause ruptures of existing flocs or prevent the formation of large stable aggregates. As a result, the particles become smaller again and are more difficult to settle, reducing the cleaning efficiency. With a further increase in the flocculant dose, the particles become coarser again, because the polymer chains of the flocculant can start to connect the remains of small particles and form larger and more stable aggregates. In this phase, the flocculant starts to bind the remaining small flocs, creating larger flocules, improving the cleaning efficiency. This effect may depend on the type of flocculant and its molecular structure (e.g., linear or branched chains). A constant dose of aluminium sulphate creates coagulation flocs, but their size and stability depend on the flocculant. Without the optimum amount of flocculant, the flocs may still be too small or unstable for effective treatment. In the first phase, the flocculant binds small flocs, improving their sedimentation. However, if there is too much flocculant, the excess chains can “shield” the particles, preventing further aggregation.

Thus, the correct dosage of coagulant and flocculant is a key factor in effective wastewater treatment. The correct coagulant dosage ensures neutralisation of colloid charges and the formation of primary flocs. The obtained findings correlate with those of Junaidi *et al.* (2023). In the cited study, a wastewater sample was tested by jar test with the addition of polyaluminium chloride (PAC) coagulant. The test results gave the optimum coagulant dose of 3,000 mg/l; it can remove 77% of COD, 33% of BOD, 92.68% of TSS, 33% of total chromium, and 98% of colour. PAC forms flocs faster than conventional coagulants, such as  $Al_2(SO_4)_3$ . PAC coagulant is one of the most effective since it leads to rapid water coagulation with different turbidities, forms less sludge, and leaves less aluminum residue in purified water. The dose of the proposed coagulant is higher than in the present study, while the degree of purification is lower. S. Haydar & J.A. Aziz (2009) investigated the purification of tannery wastewater using the coagulation-flocculation-sedimentation method. Alum with cationic and anionic polymers was used as a coagulant. The findings were compared to a study where only alum was used for treatment. The study results showed that the combination of alum with the cationic polymer C-492 resulted in 97% removal of wastewater turbidity, 93.5% removal of total suspended solids (TSS), 36.2% removal of COD, and 98.4% removal of chromium. The removal rate achieved after treatment of tannery wastewater using the PA-HE coagulant-flocculant combination demonstrated high

efficiency, with values reaching approximately 100% for TSS, 98.71% for BOD<sub>5</sub>, 99.93% for COD, 98.88% for  $NH_4^+$ , 98.21% for  $NO_3^-$ , 90.32% for  $NO_2^-$ , 93.13% for  $SO_4^{2-}$ , 95.44% for  $PO_4^{3-}$ , and 60% for total chromium as shown in the study by G.E. Mouhri *et al.* (2024).

Thus, the correct dosage of flocculant promotes the aggregation of these flocs into larger aggregates that are easily sedimented and removed. All this requires careful optimisation of the coagulant and flocculant dosages depending on the system conditions.

## Conclusions

The study investigated the composition of spent technological solutions after filling-greasing and dyeing processes at leather production enterprises. It was found that wastewater after the specified processes has high concentrations of pollutants and increased suspended solids content. The choice of reagents for the coagulation process was justified, and the process was modelled. According to the findings of experimental studies, aluminium-based coagulants and PGMG-HC flocculants have higher efficiency than other reagents studied (iron-based coagulants, PGMG-A, and F-PET flocculants). The findings showed a considerable improvement in treated water quality, according to the key indicators.

The principal reasons why aluminium sulphate showed better results included its ability to work effectively in neutral or slightly acidic conditions, to form more stable and larger flocs, and to provide better removal of organic pollutants. Due to lower sediment stability, ferric chloride may be less effective in such conditions. The efficiency of coagulation and flocculation with the addition of different doses of aluminium sulphate is non-linear because the coagulation process involves complex physicochemical interactions between the coagulant, pollutants, and colloidal particles. At the initial stage, the cleaning efficiency increases due to charge neutralisation, then it can decrease due to particle recharging, and, finally, it can improve due to floc stabilisation with a further increase in coagulant and interaction with the flocculant. The non-linear dependence of the degree of cleaning with the addition of a flocculant occurs due to complex interactions between pollutant particles, coagulant flocs, and the flocculant’s polymer chains. At the first stage, the flocculant increases the efficiency of coagulation, but at an excessive dose, it can prevent the formation of large flocs, which reduces the degree of purification. With a further increase in the flocculant dose, the process stabilises again, and large aggregates are formed, which leads to improved purification.

The balance between the doses of coagulant and flocculant is a delicate process that directly affects the efficiency of water purification. Incorrect dosages can insufficiently purify water and complicate the further processing or removal of sediments. Modelling and calculating the doses of coagulants and flocculants using mathematical models and algorithms enables effective control of the wastewater treatment process. This approach improves the quality of purification, reduces the consumption of



chemical reagents, and makes the system more stable and flexible. Using aluminium sulphate and flocculant PG-MG-A to purify a sample of real wastewater showed high efficiency and can be recommended for use. Further development of this study involves expanding the list of coagulants and flocculants.

## Acknowledgements

The research was conducted on initiative topics with State registration numbers: 0124U001966, 0124U002058.

## Conflict of Interest

None.

## References

- [1] Aboulhassan, M.A., Harif, S., Souabi, S., & Yaacoubi, A. (2021). Efficient and sustainable treatment of industrial wastewater using a tannin-based polymer. *International Journal of Sustainable Engineering*, 14(6), 1943-1949. doi: [10.1080/19397038.2021.1972181](https://doi.org/10.1080/19397038.2021.1972181).
- [2] Ang, W.L., & Mohammad, A.W. (2020). State of the art and sustainability of natural coagulants in water and wastewater treatment. *Journal of Cleaner Production*, 262, article number 121267. doi: [10.1016/j.jclepro.2020.121267](https://doi.org/10.1016/j.jclepro.2020.121267).
- [3] Bhardwaj, A., Kumar, S., & Singh, D. (2023). Tannery effluent treatment and its environmental impact: A review of current practices and emerging technologies. *Water Quality Research Journal*, 58(2), 128-152. doi: [10.2166/wqrj.2023.002](https://doi.org/10.2166/wqrj.2023.002).
- [4] Bingül, Z., Irdemez, Ş., & Demircioğlu, N. (2021). Effect of controlled and uncontrolled pH on tannery wastewater treatment by the electrocoagulation process. *International Journal of Environmental & Analytical Chemistry*, 103(16), 4269-4284. doi: [10.1080/03067319.2021.1925261](https://doi.org/10.1080/03067319.2021.1925261).
- [5] Bondarenko, S., Sanhinova, O., & Shakhnovsky, A. (2024). *Numerical methods in chemistry and chemical technology*. Kyiv: National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute".
- [6] Central Biochemical Laboratory "CBL". (n.d.). Retrieved from <https://environmentallab.com.ua/uk/>.
- [7] Chiampo, F., Shanthakumar, S., Ricky, R., & Ganapathy, G.P. (2023). Tannery: Environmental impacts and sustainable technologies. *Materials Today: Proceedings*. doi: [10.1016/j.MATPR.2023.02.025](https://doi.org/10.1016/j.MATPR.2023.02.025).
- [8] Gautam, S., & Saini, G. (2020). Use of natural coagulants for industrial wastewater treatment. *Global Journal of Environmental Science and Management*, 6(4), 553-578. doi: [10.22034/GJESM.2020.04.10](https://doi.org/10.22034/GJESM.2020.04.10).
- [9] Governing Normative Document (KND) No. 211.1.4.039-95 "The Method of Gravimetric Determination of Suspended Matter in Natural and Wastewater". (1995, April). Retrieved from [https://online.budstandart.com/ru/catalog/doc-page.html?id\\_doc=110594](https://online.budstandart.com/ru/catalog/doc-page.html?id_doc=110594).
- [10] Haydar, S., & Aziz, J.A. (2009). Coagulation-flocculation studies of tannery wastewater using combination of alum with cationic and anionic polymers. *Journal of Hazardous Materials*, 168(2-3), 1035-1040. doi: [10.1016/j.jhazmat.2009.02.140](https://doi.org/10.1016/j.jhazmat.2009.02.140).
- [11] Jiang, B., Niu, Q., Li, C., Oturan, N., & Oturan, M.A. (2020). Outstanding performance of electro-Fenton process for efficient decontamination of Cr(III) complexes via alkaline precipitation with no accumulation of Cr(VI): Important roles of iron species. *Applied Catalysis B: Environmental*, 272, article number 119002. doi: [10.1016/j.APCATB.2020.119002](https://doi.org/10.1016/j.APCATB.2020.119002).
- [12] Junaidi, Sudarno, & Santoso, R. (2023). Physical and chemical treatability study in wastewater treatment plant design (Case study: Leather tanning industry). *IOP Conference Series: Earth and Environmental Science*, 1268, article number 012025. doi: [10.1088/1755-1315/1268/1/012025](https://doi.org/10.1088/1755-1315/1268/1/012025).
- [13] Mim, S., Hashem, M.A., & Maoya, M. (2024). Adsorption-oxidation process for dyestuff removal from tannery wastewater. *Environmental Nanotechnology, Monitoring & Management*, 21, article number 100911. doi: [10.1016/j.enmm.2023.100911](https://doi.org/10.1016/j.enmm.2023.100911).
- [14] Mim, S., Hashem, M.A., & Payel, S. (2023). Coagulation-adsorption-oxidation for removing dyes from tannery wastewater. *Environmental Monitoring and Assessment*, 195(6), article number 695. doi: [10.1007/s10661-023-11309-3](https://doi.org/10.1007/s10661-023-11309-3).
- [15] Mouhri, G.E., Elmansouri, I., Amakdoug, H., Belhassan, H., Kachkoul, R., Oumari F.E.E., Merzouki, M., & Lahrichi, A. (2024). Evaluating the effectiveness of coagulation-flocculation treatment on a wastewater from the moroccan leather tanning industry: An ecological approach. *Heliyon*, 10(5), article number e27056. doi: [10.1016/j.heliyon.2024.e27056](https://doi.org/10.1016/j.heliyon.2024.e27056).
- [16] MVV No. 081/12-0004-01 "Surface and Purified Wastewater. Methodology for Measuring Mass Concentration of Chlorides Using the Argentometric Titration Method". (2002, September). Retrieved from [https://online.budstandart.com/ua/catalog/doc-page?id\\_doc=76335](https://online.budstandart.com/ua/catalog/doc-page?id_doc=76335).
- [17] MVV No. 081/12-0007-01 "Surface and Treated Wastewater. Procedure for Measuring Sulfate Mass Concentration by Gravimetric Method". (2002, September). Retrieved from [https://online.budstandart.com/ua/catalog/doc-page?id\\_doc=76337](https://online.budstandart.com/ua/catalog/doc-page?id_doc=76337).
- [18] MVV No. 081/12-0109-03 "Surface, Underground, and Return Waters. Method for Determining the Mass Concentration of Dry Residue (Dissolved Substances) by Gravimetric Method". (2004, June). Retrieved from [https://online.budstandart.com/ua/catalog/doc-page?id\\_doc=76431](https://online.budstandart.com/ua/catalog/doc-page?id_doc=76431).

- [19] Nath, A., Mishra, A., & Pande, P.P. (2021). A review natural polymeric coagulants in wastewater treatment. *Materials Today: Proceedings*, 46(14), 6113-6117. doi: 10.1016/j.matpr.2020.03.551.
- [20] Nigam, M., Mishra, P., Kumar, P., Rajoriya, S., Pathak, P., Singh, S.R., Kumar, S., & Singh, L. (2023). Comprehensive technological assessment for different treatment methods of leather tannery wastewater. *Environmental Science and Pollution Research*, 30(60), 124686-124703. doi: 10.1007/s11356-022-21259-x.
- [21] Nomanifar, N., Davoudi, M., Ghorbanian, A., Najafpoor, A.A., & Hosseinzadeh, A. (2024). Fe recovery from drinking water treatment sludge for reuse in tannery wastewater treatment: Machine learning and statistical modelling. *Journal of Water Process Engineering*, 60, article number 105224. doi: 10.1016/j.jwpe.2024.105224.
- [22] Order of the Executive Body of the Kyiv City Council (Kyiv City State Administration) No. 1879 “On Approval of the Rules for Acceptance of Wastewater from Subscribers into the Kyiv Sewerage System”. (2011, October). Retrieved from [http://vodokanal.kiev.ua/files/pravya\\_stichi\\_vody.pdf](http://vodokanal.kiev.ua/files/pravya_stichi_vody.pdf).
- [23] Othmani, B., Rasteiro, M.G., & Khadhraoui, M. (2020). Toward green technology: A review on some efficient model plant-based coagulants/flocculants for freshwater and wastewater remediation. *Clean Technologies and Environmental Policy*, 22(5), 1025-1040. doi: 10.1007/s10098-020-01858-3.
- [24] Sabliy, L., Kuzminskiy, Ye., Zhukova, V., Kozar, M., & Sobczuk, H. (2019). New approaches in biological wastewater treatment aimed at removal of organic matter and nutrients. *Ecological Chemistry and Engineering S*, 26(2), 331-343. doi: 10.1515/eces-2019-0023.
- [25] Sivaram, N.M., & Barik, D. (2019). Toxic waste from leather industries. In *Energy from toxic organic waste for heat and power generation* (pp. 55-67). Sawston: Woodhead Publishing. doi: 10.1016/B978-0-08-102528-4.00005-5.
- [26] State Standard of Ukraine (DSTU) EN ISO No. 11885:2019 “Water Quality. Determination of Selected Elements by Optical Emission Spectrometry with Inductively Coupled Plasma (ICP-OES)”. (2020, January). Retrieved from [https://online.budstandart.com/ua/catalog/doc-page.html?id\\_doc=88015](https://online.budstandart.com/ua/catalog/doc-page.html?id_doc=88015).
- [27] State Standard of Ukraine (DSTU) ISO No. 6060:2003 “Water Quality. Determination of Chemical Oxygen Demand”. (2004, July). Retrieved from [https://online.budstandart.com/ua/catalog/doc-page?id\\_doc=52804](https://online.budstandart.com/ua/catalog/doc-page?id_doc=52804).
- [28] State Standard of Ukraine (DSTU) No. 4077-2001 “Water Quality. pH Determination”. (2003, July). Retrieved from [https://online.budstandart.com/ua/catalog/doc-page?id\\_doc=52791](https://online.budstandart.com/ua/catalog/doc-page?id_doc=52791).
- [29] State Standard of Ukraine DSTU ISO No. 7150-1:2003 “Water Quality. Determination of Ammonia. Part 1. Manual Spectrometric Method”. (2004, July). Retrieved from [https://online.budstandart.com/ua/catalog/doc-page?id\\_doc=73305](https://online.budstandart.com/ua/catalog/doc-page?id_doc=73305).
- [30] Tolkou, A.K., & Zouboulis, A.I. (2020). Application of composite pre-polymerized coagulants for the treatment of high-strength industrial wastewaters. *Water*, 12(5), article number 1258. doi: 10.3390/w12051258.
- [31] Volokyta, A., & Selivanov, V. (2022). *Basics of the theory of experiment planning: Section of the discipline “Methodology and organisation of scientific research”*. Kyiv: National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute”.

## Коагуляційно-флокуляційні ефекти при очищенні відпрацьованих розчинів шкіряного виробництва

### Анатолій Данилкович

Доктор технічних наук, професор  
Київський національний університет технологій та дизайну  
01011, вул. Мала Шияновська, 2, м. Київ, Україна  
<https://orcid.org/0000-0002-5707-0419>

### Ольга Сангінова

Кандидат технічних наук, доцент  
Національний технічний університет України  
«Київський політехнічний інститут імені Ігоря Сікорського»  
03056, просп. Берестейський, 37, м. Київ, Україна  
<https://orcid.org/0000-0001-6378-7718>

### Наталія Толстопалова

Кандидат технічних наук, доцент  
Національний технічний університет України  
«Київський політехнічний інститут імені Ігоря Сікорського»  
03056, просп. Берестейський, 37, м. Київ, Україна  
<https://orcid.org/0000-0002-7240-5344>

### Тетяна Обушенко

Старший викладач  
Національний технічний університет України  
«Київський політехнічний інститут імені Ігоря Сікорського»  
03056, просп. Берестейський, 37, м. Київ, Україна  
<https://orcid.org/0000-0003-0731-0370>

### Дмитро Яворський

Аспірант  
Національний технічний університет України  
«Київський політехнічний інститут імені Ігоря Сікорського»  
03056, просп. Берестейський, 37, м. Київ, Україна  
<https://orcid.org/0009-0003-3216-9740>

**Анотація.** Існуючі методи очищення стічних вод підприємств шкіряної промисловості потребують удосконалення для забезпечення необхідної ефективності очищення та регенерації цінних компонентів, які містяться у відпрацьованих технологічних розчинах. Дане дослідження направлено на комплексне коагуляційно-флокуляційне очищення рідких відходів шкіряних заводів із застосуванням методів математичного моделювання. Проведені експериментальні дослідження ефективності коагулянтів – сульфату алюмінію та хлориду заліза (III) – та флокулянтів: полігексаметиленгуанідину гідроксихлориду та його ацетату, а також реагенту П228. Досліджено вплив рН на процес коагуляції. Ефективність процесу коагуляції оцінювалась за інтегральним показником – ступенем очищення, який визначався з урахуванням каламутності та оптичної густини очищених зразків води. У роботі наводились результати дослідження коагуляційно-флокуляційних ефектів, які виникають у процесі очищення зразків відпрацьованих технологічних розчинів шкіряного заводу після процесів наповнювання-жирування та фарбування. Досліджувані зразки характеризувались високими концентраціями сульфатів (більше 9000 мг/дм<sup>3</sup>) та хлоридів (більше 1500 мг/дм<sup>3</sup>), підвищеним вмістом завислих твердих речовин (більше 843 мг/дм<sup>3</sup>) та іонів металів: хрому (III), заліза та алюмінію. За результатами досліджень встановлено, що коагулянт на основі алюмінію мав вищу ефективність, ніж коагулянт на основі заліза. Серед флокулянтів найбільш ефективним був полігексаметиленгуанідину гідроксихлорид, а значення рН має дорівнювати 10. Результати експериментальних досліджень використані для отримання математичної моделі, яка описує процес коагуляції з достатнім ступенем точності. Результати математичного моделювання можуть бути використані для розрахунку оптимальних параметрів процесу коагуляції

**Ключові слова:** стічні води шкіряних заводів; хімічне осадження; ступінь очищення; оптимізація процесу коагуляції