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WAYS TO IMPROVE THE EFFICIENCY OF WASTEWATER TREATMENT OF A CARDBOARD AND PAPER MILL

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Abstract. The results of research on physical and chemical methods for the preliminary treatment of wastewater of a cardboard and paper factory in Khmelnytskyi region of Ukraine are presented. At the cardboard and paper factory, wastewater is treated at a sewage treatment plant, which includes sand traps, primary radial sedimentation tanks, aeration tanks with activated sludge regenerators, secondary radial sedimentation tanks, and bioponds. The use of coagulation and chlorination methods before biological treatment in aeration tanks was proposed. Alumoflock 18 % was used as a coagulant, polyacrylamide was used as a flocculant, and sodium hydroxide was used as an alkalizing reagent. The study was conducted on a mixture of industrial and domestic wastewater with COD and BOD_5 – 3200 and 1575 mg/dm^3, respectively, and on industrial wastewater with COD and BOD_5 – 4480 and 1960 mg/dm^3, respectively. The effects of reducing COD and BOD_5 indicators in the first case after coagulation were 30 and 40 %, after chlorination - 37.81 and 43.17 %, respectively, in the second after coagulation – 28.57 and 47.24 %, respectively. It was established that a significant proportion of organic substances according to the COD indicator is in a dissolved state – 60–70 %. It has been proven that as a result of chlorination, the maximum reduction of "pure" COD is achieved, therefore, the possibility and expediency of chlorination of water after the secondary settling tank with increased doses should be considered in the wastewater treatment technology of the cardboard and paper factory.

Keywords: industrial wastewater, cardboard and paper factory, coagulation, alumoflock, chlorination.

1. Introduction

Wastewater from paper and board mills is a significant contributor to environmental and water pollution. This water is a complex polydisperse system containing significant concentrations of mineral and organic contaminants. Organic substances present in wastewater cause complex changes in water bodies (Harif et al., 2021). They violate the established abiotic conditions and are involved in chemical and biochemical processes. As a result, irreversible changes in the composition of biocenoses occur, and the water quality of the river is significantly reduced.

Wastewater contains pulp and paper fibres, fillers, dyes, latexes, emulsions, adhesives, etc. Industrial wastewater is characterised by a high content of suspended solids (SS), organic pollutants in terms of COD and BOD, high temperature (over 30 °C), specific smell, grey colour, and high turbidity.

Sources of organic substances include cellulose degradation products generated during bleaching and processing. These are substances such as aliphatic (alcohols, amines, acids, aldehydes, etc.) and terpene hydrocarbons, aromatic hydrocarbons of the phenolic series, low molecular weight alcohols, fatty acids, etc. Due to the high content of organic matter, wastewater

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is characterised by high COD values ranging from 800 to 2000 mg/dm^3. BOD_5 values are in the range of 500–800 mg/dm^3. The BOD_5/COD ratio has average values, indicating the possibility of using a biological method of wastewater treatment. BOD_5/COD has a value in the range from 0.2 to 0.7. Suspended solids range from 900 to 3000 mg/dm^3. Therefore, factory wastewater requires preliminary mechanical treatment, which results in the removal of coarse, suspended solids and some colloidal particles (Ashrafi et al., 2015). The presence of low concentrations of phosphorus and nitrogen compounds in wastewater indicates that they should be added to the water for the biological process.

Today, the most common methods of wastewater treatment at paper and board mills are physical and chemical: reagent treatment – coagulation, flocculation, chemical and electrochemical oxidation (Eskelinen. et al., 2010; Birjandi et al., 2016), and biological, both aerobic and anaerobic. The use of reagent methods requires the purchase of chemical reagents: coagulants based on iron, aluminium, expensive flocculants or strong oxidants: ozone (Naoyuki et al., 2010; Ramosa et al., 2009), hydrogen peroxide (Fenton method) (Eskelinen . et al., 2010), and does not provide high treatment efficiency in the conditions of multicomponent pollution. Adsorption methods (Shaveta et al., 2018) can be used for wastewater treatment and require sophisticated equipment.

The most affordable and effective method in terms of high efficiency of the treatment process, low construction and operation costs, and environmental impact, in particular on natural water bodies, is the biological method (Ram, 2010; Singh, 2014; Cabrera, 2017; Schnell, 2011), namely aerobic (Curtis, 2010; Dubeski, 2001) and anaerobic (Tielbaard, 2002; Habets, 2007) processes.

At a cardboard and paper mill in Khmelnytskyi region, Ukraine, wastewater is treated at a sewage treatment plant that includes sand traps, primary radial settling tanks, squeeze-out aeration tanks with activated sludge regenerators, secondary radial settling tanks, and biponds. The capacity of the treatment plant is 7000 m^3/day. The aeration tanks are designed for 14 hours of aeration and 12 hours of regeneration. To provide the activated sludge microorganisms with nutrients, nitrogen and phosphorus compounds are dosed into the wastewater before the biological stage. Air is supplied by blowers using a pneumatic aeration system through tubular aerators installed in the aeration tanks. The main disadvantage of the wastewater treatment plant is the insufficient efficiency of wastewater treatment from organic pollutants in terms of COD and BOD, which necessitated research to find and use methods of preliminary treatment of factory wastewater (up to the biological stage) by means of physical and chemical treatment using coagulation, flocculation and chemical oxidation with active chlorine.

The aim of the study is to investigate the processes of wastewater treatment of a cardboard and paper mill using physicochemical methods – coagulation and oxidation – to increase the efficiency of organic pollution removal in terms of COD and BOD.

2. Materials and Methods

A series of samples of the following types of wastewaters were collected for analysis:

– a mixture of industrial and domestic wastewater from the intake chamber of the sewage treatment plant of a cardboard and paper mill;

– industrial wastewater directly from the production site.

In the first case (for a mixture of wastewater), the following treatment was envisaged: coagulation and sedimentation followed by chlorination, and the following indicators were determined: pH; suspended solids; COD; BOD_5 for the initial wastewater (before treatment), water after coagulation and sedimentation, and chlorinated coagulated water (after all treatments).

In the second case (for industrial wastewater), coagulation and sedimentation methods were used and the same indicators were determined for the initial and coagulated water.

The COD value in wastewater was assessed on the basis of a standard method using the bichromate method, the BOD_5 value was determined by the difference in the concentration of dissolved oxygen before and after incubation of the wastewater sample for 5 days in a thermostat at a temperature of 20 °C. The concentration of dissolved oxygen was determined by the Winkler iodometric titration method. The pH value was determined by the potentiometric method, and the concentration of suspended solids was determined by the gravimetric method (by dry matter).

Reagents with the following doses were used for the study:

for coagulation:

– alumoflock 18 % – 0.6 cm^3/dm^3

– sodium hydroxide – 55 mg/dm^3;

– polyacrylamide flocculant – 2 mg/dm^3.

The volume of sludge after settling was 20 %.

The reagent used for chlorination was:
– active chlorine – 42 mg/dm^3.

3. Results and Discussion

The study of the process of wastewater treatment at a cardboard and paper mill using the coagulation method showed the following.

Coagulation was successful in both cases. The results of wastewater analyses are shown in Tables 1 and 2. In the clear water obtained after settling, in the first case, suspended solids decreased from 127 to 15 mg/dm^3, and in the second – from 162 to 20 mg/dm^3.

The following can be noted in terms of BOD_5 and COD. *In the case of a mixture of industrial and domestic wastewater*. In the mixture of wastewater from the receiving chamber of the sewage treatment plant, after coagulation, BOD_5 is reduced by 40 %, and COD – by 30 %.

Table 1

Changes in the characteristics of a mixture of industrial and domestic wastewater of a cardboard and paper mill in the processes of coagulation, sedimentation and chlorination

Number	Name of the indicator	Unit of measurement	Wastewater		
			Output	after coagulation and sedimentation	after coagulation, sedimentation and chlorination
1	pH	–	6.3	7.1	7.25
2	Suspended solids	mg/dm^3	127	15	15
3	COD	mgO_2/ dm^3	3200	2240	1990
4	BOD_5	mgO_2/ dm^3	1575	945	895
5	COD – BOD_5 (“pure” COD)	mgO_2/ dm^3	1625	1295	1095
6	Ratio COD / BOD_5	–	2.03	2.37	2.22
7	Ratio BOD_5/ COD	–	0.49	0.42	0.45
8	BOD_5 reduction	mgO_2/ dm^3	630 (40 %)		
			680 (43.17 %)*		
9	COD reduction	mgO_2/ dm^3	960 (30 %)		
			1210 (37.81 %)*		
10	“Pure” COD reduction	mgO_2/ dm^3	330 (20.3 %)		
			530 (32.62 %)*		

* Calculated differences between the values of the initial wastewater and water after coagulation, sedimentation and chlorination.

The ratio of BOD_5/COD for subsequent biological treatment in the aeration tanks of the sewage treatment plant should be greater than 0.5. In this case, the results showed that coagulation worsened the ratio from 0.49 to 0.42. The second, lower, half of Table 1 (lines 5–10) shows the results of some recalculations of BOD_5 and COD, which characterise the efficiency of wastewater treatment from organic pollutants using the applied methods of coagulation, sedimentation and chlorination.

The “pure” COD is defined as the difference between COD and BOD_5 and allows to estimate the content of hardly oxidisable organic pollutants. It is determined, for example, for a mixture of industrial and domestic wastewater at the inlet (in untreated wastewater) and after coagulation and sedimentation: 3200 – 1575 = 1625 mgO_2/dm^3 (lines 3, 4, column 4 of Table 1).

The decrease in COD concentration, which is the sum of BOD_5 and “pure” COD (in Fig. 1, the COD value is displayed as the height of the whole column), confirms the effectiveness of using both coagulation alone and a combination of coagulation and subsequent chlorination (Fig. 1). A higher percentage of removal, namely “pure COD” – 32.62 %, is observed after coagulation and chlorination (Fig. 2).

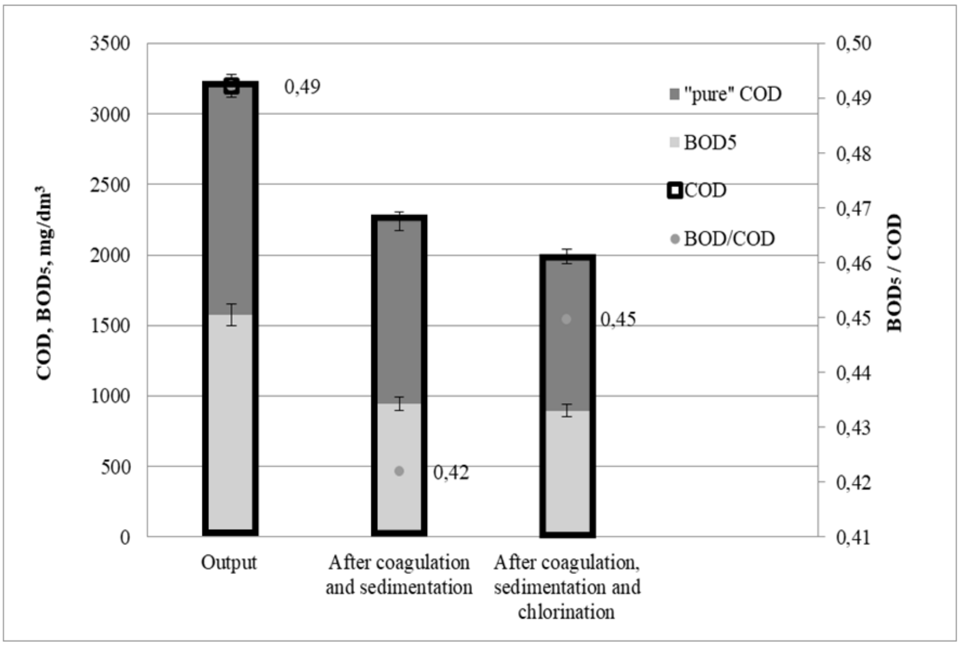

Fig. 1. Dynamics of organic matter concentration by COD, BOD_5 and the value of the BOD_5/COD ratio

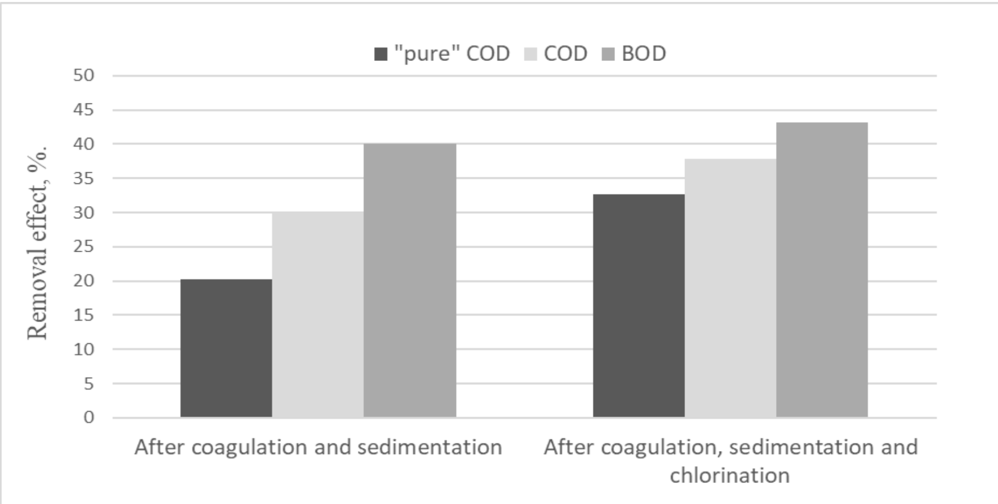

Fig. 2. Comparison of the effect of organic matter removal in terms of "pure" COD, BOD_5 and COD after coagulation and after coagulation and chlorination

The following indicators were obtained as a result of chlorination. In the wastewater from the intake chamber of the CWS, after coagulation, sedimentation and chlorination, BOD_5 decreased by 43.17 % and COD by 37.81 %. Chlorination (separately, after coagulation and sedimentation) resulted in a 3.18 % reduction in BOD_5 and a 7.82 % reduction in COD.

Chlorination compared to coagulation further reduced BOD_5 by 5.3 % and COD by 11.17 %. The ratio of BOD_5/COD in the case of coagulation and chlorination decreased from 0.49 to 0.45.

The "pure" COD of the wastewater (excluding its BOD_5) after coagulation and chlorination decreased by only 530 mgO_2/dm^3 or 32.62 % compared to the "pure" COD of the wastewater (excluding its BOD_5) after coagulation – 330 mgO_2/dm^3 or 20.3 %.

The "pure" COD of wastewater (excluding its BOD_5) between coagulated and chlorinated wastewater decreased by only 200 mgO_2/dm^3 or 12.4 %. In the case of production wastewater from a cardboard and paper mill, the COD value decreased from 4480 to 3200 mgO_2/dm^3 (Table 2, Fig. 3), which is 28.57 %.

After coagulation, BOD_5 decreased by 47.24 %, and "pure" COD (excluding BOD_5) decreased by only 354 mgO_2/dm^3 or 14.05 % (Fig. 4).

Table 2

Changes in the parameters of industrial wastewater from a cardboard and paper mill in the process of coagulation and sedimentation

Number	Name of the indicator	Unit of measurement	Wastewater	
			Output	After coagulation and settling
1	pH	–	6.5	7.2
2	Suspended solids	mg/dm^3	162	20
3	COD	mgO_2/ dm^3	4480	3200
4	BOD_5	mgO_2/ dm^3	1960	1034
5	COD – BOD_5 (“pure” COD)	mgO_2/ dm^3	2520	2166
6	Ratio COD / BOD_5	–	2.28	3.09
7	Ratio $BOD_{5/}$ COD	–	0.43	0.32
8	BOD_5 reduction	mgO_2/ dm^3	926 (47.24 %)	
9	COD reduction	mgO_2/ dm^3	1280 (28.57 %)	
10	“Pure” COD reduction	mgO_2/ dm^3	354 (14.05 %)	

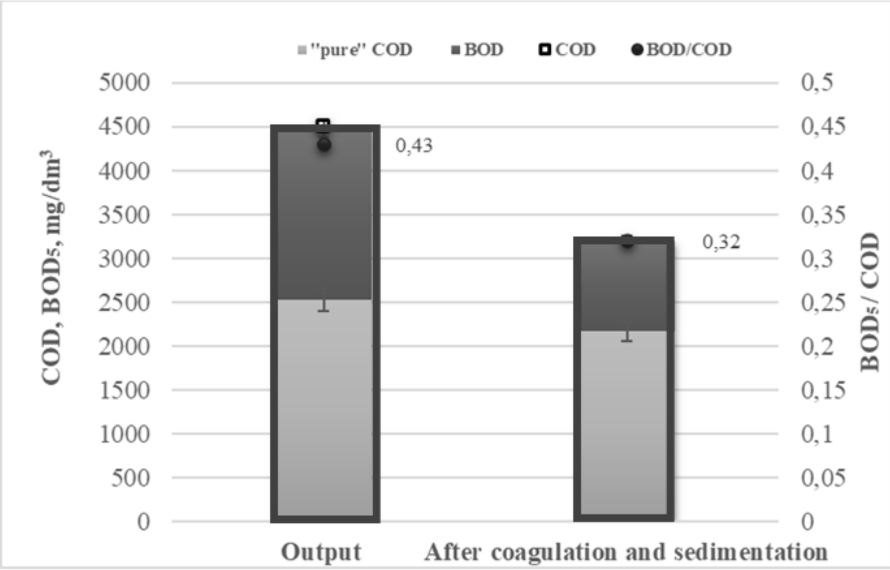

Fig. 3. Dynamics of organic matter concentration in terms of “pure” COD and BOD_5 for the initial industrial wastewater and after its coagulation

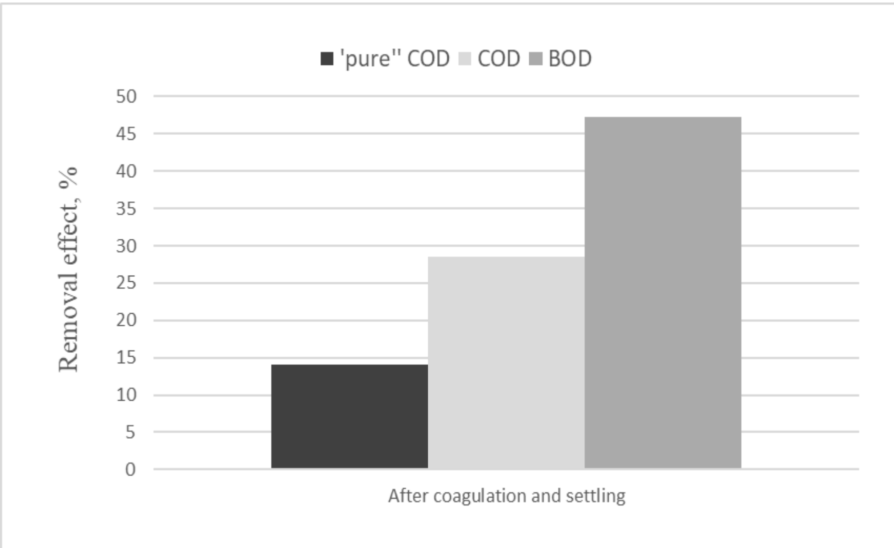

Fig. 4. Effect of organic matter removal in terms of “pure” COD, BOD_5 and COD after coagulation and settling of industrial wastewater

To assess the effectiveness of biological wastewater treatment at a paper and board mill, the COD/BOD_5 ratio and the inverse of BOD_5/COD are determined (lines 5, 6 of Tables 1 and 2). The acceptable ratio should be greater than 0.5. In other words, BOD_5 should be at least half of COD, otherwise the reduction of COD in the process of wastewater treatment using activated sludge will not ensure the achievement of acceptable values of indicators (COD less than 70–80 mgO_2/dm^3), since microorganisms are not always able to decompose highly oxidised compounds during the aerobic process, which will be too much at a BOD_5/COD ratio > 0.5.

As can be seen from Tables 1 and 2 (lines 7, 8), the use of coagulation and sedimentation can reduce BOD_5 in the first and second cases by 40 % and 47.17 %, COD – by 30 % and 28.57 %, respectively. These indicators indirectly indicate the percentage of organic contaminants (according to BOD_5) and the total organic content (according to COD) in the wastewater in suspended and colloidal forms. At the same time, it should be noted that coagulation is more effective in reducing BOD_5 than COD, which indicates that most of the hard to oxidise compounds are in the dissolved state.

In order to evaluate these values in non-relative terms and eliminate the influence of BOD_5, the COD reduction minus the corresponding BOD_5 (line 7 of Tables 1 and 2) is recalculated as a percentage before and after coagulation and sedimentation (for 1 case of coagulation, sedimentation and chlorination) – line 10 of Tables 1 and 2.

The use of oxidation (high-dose chlorination) of coagulated wastewater in the first case reduced BOD_5 and COD by 3.18 % and 7.82 %, respectively, which in terms of “pure” COD was already 12.4 % (lines 8–10 of Table 1).

4. Conclusions

As a result of the study of the coagulation process for the treatment of wastewater from a cardboard and paper mill, a decrease in suspended solids, BOD and COD was obtained.

The ratio of BOD_5/COD was less than 0.5, and this should be taken into account when adjusting the composition of wastewater (by changing the ratio of easily and hardly oxidisable substances due to the identification and reduction of chemical components coming from production).

It has been established that a significant proportion of organic substances in terms of COD is in a dissolved state – 60–70 %.

During the coagulation of wastewater, the treatment efficiency in terms of BOD_5 was found to be 40–47 %.

It has been established that chlorination results in the maximum reduction of “pure” COD, therefore, in the technology of wastewater treatment of a cardboard and paper mill, the possibility and feasibility of chlorination of water after the secondary settling tank with increased doses should be considered.

It should be noted that the use of reagents in the doses used in the studies is unlikely to be economically feasible, but it would be advisable to arrange an oxidant-biocoagulator before the primary settling tank, where activated sludge is used instead of reagents.

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