Environment Protection Engineering

Vol. 14 1988 No. 3–4

STOYANKA G. CHRISTOSKOVA*, DOBRI L. LAZAROV**

ELECTROCHEMICAL METHOD FOR PURIFICATION AND DISCOLOURATION OF CELLULOSE-PAPER INDUSTRY WASTEWATERS

The possibility for purification and discolouration of wastewaters from cellulose-paper production by electrocoagulation has been studied and it is established that full discolouration is achieved after separation of the treated waters. Electrocoagulation with iron electrodes has a considerable purifying effect according to the main indices: for fibre flow COD – 98%, PV – 91%, ISC – 99%; for lye flow COD – 62%, PV – 63%, ISC – 80%; for "exit" COD – 80%, PV – 83%, ISC – 80%. The effect of current density on treatment efficiency has also been studied and it was found that the optimum density ensuring a maximum purifying effect is different for the different flows.

1. INTRODUCTION

The wastewaters coming from cellulose-paper industry are characterized by a high degree of pollution due to suspended, colloidal and original substances. Their dark brown colour is caused by the lignin which after alkaline boiling becomes water-soluble. Different technologies are employed depending on the required degree of wastewater treatment, determined by the receiver class. Mechanical removal of the suspended substances and their reuse in the production process are generally utilized [1]. At higher requirements, the wastewaters are subjected to mechanical and biological treatment. The latter does not cause discolouration mainly because of the high stability of lignin, which is only slightly decomposed at the biological stage [2]. Recently, there have been carried out studies concerning the discolouration of wastewaters coming from cellulose-paper industry in which coagulation with various coagulants and flocculants with subsequent sedimentation are applied [3]–[5]. Aluminium sulfate, ferrous sulfate, ferric chloride, aluminium hydroxy-nitrate, and

* University of Plovdiv "P. Hilendarski", Tsar Assen 24, 4000 Plovdiv, Bulgaria.

** University of Sofia "Kliment Ochridski", A. Ivanov-1, Sofia, Bulgaria.

aluminium hydroxyl chloride are used as coagulants, and WPK-101, PAA, WA-2, PPC, microfloc and fibrospan as flocculants.

The chemical treatment guarantees a high purification effect and a good discolouration of wastewaters. The main disadvantage of this method lies in the fact that reagents are introduced in considerable amounts and the sulfates and chlorides exceed the allowable limits. The application of electrochemical methods lacking the above mentioned disadvantages is a new trend in the treatment of wastewaters from the cellulose-paper production [7]–[8]. The analysis of research data shows that the treatment effect depends on the type of electrodes, the construction of electrocoagulators, and the conditions under which the process is run.

The aim of this work is to study the potentialities of the electrochemical method of treatment and discolouration of wastewaters from cellulose-paper industry. The effect of the current density i (A/m^2) and coagulation time t (s) upon the purification effect α (%) has been studied. The latter is expressed by the main indices of pollution, i.e., chemical oxygen demand (COD, mg O_2/dm^3), permanganate value (PV, mg O_2/dm^3), and insoluble substance content (ISC, g/dm^3). The values of these indices are determined according to the unified methods of water analyses [9].

2. EXPERIMENTAL PROCEDURE

The studies have been carried out in an experimental apparatus shown in fig. 1. The main part of it is the electrocoagulator, a tank of a capacity of 1.0×10^{-3} m^3, made of stainless steel. The apparatus is divided into sections and in each of them a cathode and anode made of low-carbon steel (St 3) of a total surface of 0.0468 m^2

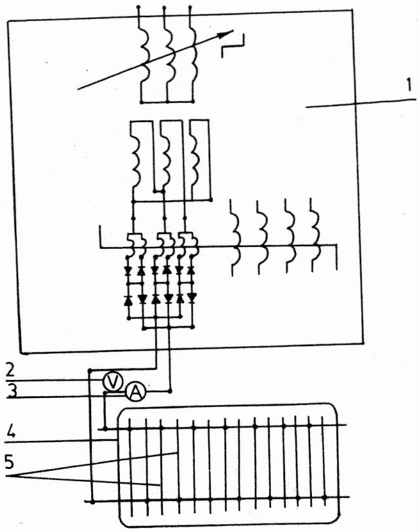

Fig. 1. Experimental apparatus

1 – rectifier, *2* – voltmeter, *3* – ammeter, *4* – electrocoagulator, *5* – electrodes are located. Every other electrode is connected through a common rim with the positive or negative pole of a TEC-88 rectifier, which maintains the required current density.

In the treatment system of a cellulose and paper plant near the town of Razlog, the following streams of water were examined: fibre stream, bark stream, lye stream, and the waters at the "exit" before outflowing.

The samples were taken before the biological treatment. After electrocoagulation, part of the sample was centrifugated at 500 rpm for 60 s, and the remaining part was subjected to settling for 72×10^2 s until the water was clarified.

The indices of the centrifugated and siphonated layer, i.e., COD, PV and ISC, were then determined. The results of the laboratory studies showed that electrocoagulation with a subsequent centrifugation resulted in a 100% removal of insoluble substances and complete discolouration of the wastewaters. The values of COD and PV for centrifugated and siphonated waters were almost the same. The data presented relate to the siphonated samples.

The presence of iron ions in the treated waters was controlled spectrophotometrically using sulfonsalicylic acid [9]. It has been established that their concentration is lower than 0.5 mg/dm^3, i.e., below the allowable limit for the second class receiver.

3. EXPERIMENTAL DATA

The laboratory studies comprised two steps:

1. Examination of the effect of current density and coagulation time on the treatment and discolouration efficiency.

2. Evaluation of the possibility for practical application of the process in the wastewater treatment technology.

Under laboratory conditions, current density varies from 10.46 to 42.43 A/m^2, and coagulation time from 3 to 12×10^2 s. On the basis of the results presented in tab. 1, it can be stated that due to electrocoagulation of industrial wastewaters it is possible to achieve a high treatment efficiency for all streams.

With the increase of anode density, the values of the examined indices decreased and got close to those typical of the third class receiver. The results of the study prove that the maximum treatment effect is attained at a definite anode density, which is different for the various streams. The anode densities in the case of the fibre stream, lye stream, and the "exit" are 15, 23, and 32 A/m^2, respectively. Further increase of anode density does not lead to an improvement of the indices and treatment effect. From the dependence of α on current density and coagulation time (fig. 2) it can be seen that under the same conditions (current density and coagulation time) treatment efficiency for the various streams has different values according to the following serie: fibre, "exit", lye.

Table 1

Industrial wastewater indices before and after electrocoagulation at different current densities

Stream	Current density, A/m^2		Indices			Treatment efficiency, %			Electric power consumption, kWh/m^3
			PV mg O_2/dm^3	COD mg O_2/dm^3	ISC g/dm^3	PV mg O_2/dm^3	COD mg O_2/dm^3	ISC g/dm^3	
Fibre	10.68	entrance	464.00	912.00	2.252	78.00	73.68	99.47	0.42
		exit	98.00	240.00	0.012				
	14.95	entrance	464.00	912.00	2.252	91.38	97.92	99.47	0.83
		exit	40.00	19.00	0.012				
	21.36	entrance	464.00	912.00	2.252	90.52	95.04	99.47	1.02
		exit	44.00	37.00	0.012				
	32.05	entrance	464.00	912.00	2.252	92.24	97.92	99.47	1.78
		exit	36.00	19.00	0.012				
Lye–bark	10.68	entrance	352.00	473.00	0.060	55.68	34.04	80.00	0.75
		exit	156.00	312.00	0.012				
	14.95	entrance	352.00	473.00	0.060	57.93	45.03	80.00	1.05
		exit	148.00	260.00	0.012				
	23.50	entrance	352.00	473.00	0.060	65.91	62.58	80.00	1.85
		exit	120.00	177.00	0.012				
	32.05	entrance	352.00	473.00	0.060	64.77	61.10	86.67	3.38
		exit	124.00	184.00	0.008				
"Exit"	10.68	entrance	240.00	295.50	0.236	45.83	56.01	94.07	0.42
		exit	130.00	130.00	0.014				
	14.95	entrance	240.00	295.50	0.236	66.67	73.33	94.07	0.48
		exit	80.00	78.80	0.014				
	21.36	entrance	240.00	295.50	0.236	75.00	80.00	91.52	0.85
		exit	60.00	59.10	0.020				
	32.05	entrance	240.00	295.50	0.236	83.33	80.00	93.67	2.04
		exit	40.00	59.10	0.015				

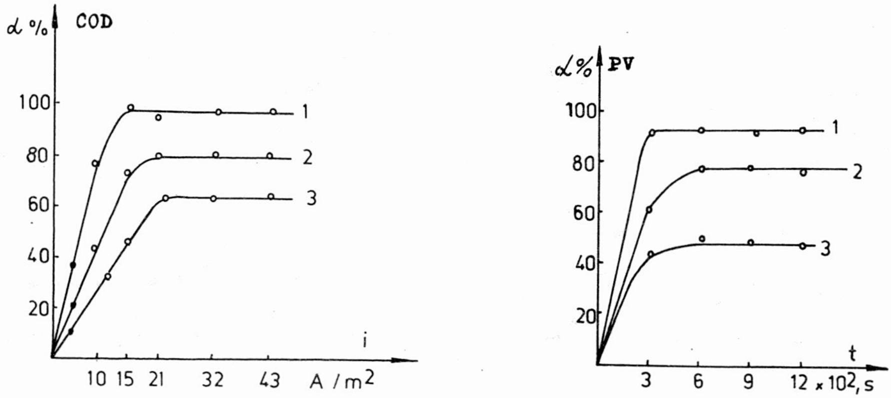

Fig. 2. A) treatment efficiency α_{COD} vs. current density at 6×10^2 s, B) treatment efficiency α_{PV}vs. electrocoagulation time at $i = 32.05$ A/m^2 = const

1 – fibre stream, *2* – "exit", *3* – lye stream

In highly efficient methods for wastewater treatment the following requirements should be fulfilled: a fast running of the process and attaining an appropriate treatment effect. The treatment time must correspond to the water flow rate and to the capacity of the treatment plant.

To define the optimum electrocoagulation time, some kinetic studies have been carried out. The kinetic curves (fig. 3) show that at the fifth minute from the beginning of electrocoagulation a significant reduction of the basic index values is achieved. Because of the power saving, the process should be put on motion for $6–9 \times 10^2$ s for all streams, whereupon a maximum treatment effect is achieved (figs. 3–5).

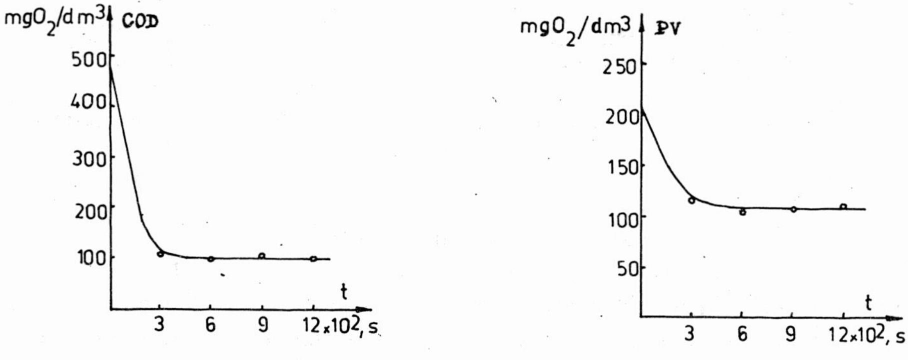

Fig. 3. Kinetic curves of COD and PV reduction for the lye stream at current density $i = 21.36$ A/m^2 = const

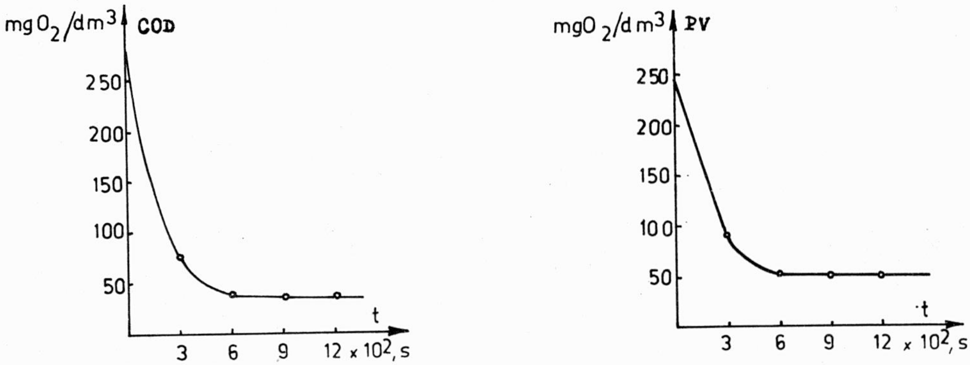

Fig. 4. Kinetic curves of COD and PV reduction for "exit" at $i = 32.05$ A/m^2 = const

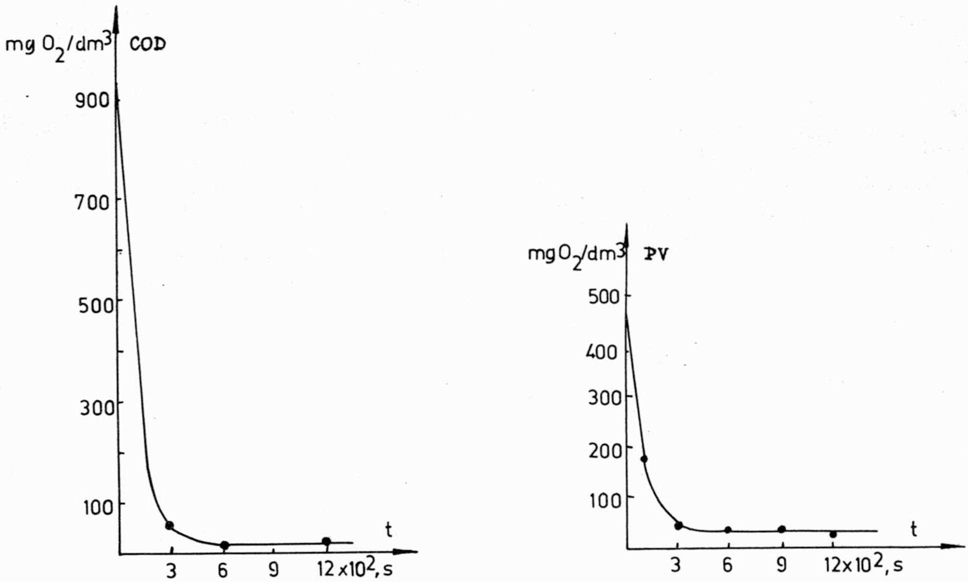

Fig. 5. Kinetic curves of COD and PV reduction for the fibre stream at current density $i = 32.05$ A/m^2 = const

Table 2 presents a comparison of the values of the indices investigated, depending on the method of treatment applied. It is evident that treatment efficiency is comparatively high in all the methods tested. Ozonization is efficient but the high consumption of ozone makes it difficult to introduce the method into treatment plants with a high flow rate of wastewaters. Treatment and discolouration of waters by means of coagulants requires 22 t of $Al_2(SO_4)_3$ and 28 t of $Al_2(OH)_5Cl$

Table 2

Indices of cellulose industry wastewaters treated in different techniques

Techniques for purification and discolouration of wastewater	Effect, %			References
	PV mg O_2/dm^3	COD mg O_2/dm^3	Colouration	
Ozonization	67.00	58.00	86.00	[10]
Coagulation by $Al_2(SO_4)_3$	68.70	68.50	72.40	[11]
Coagulation by $Al_2(OH)_5Cl$	71.10	72.20	78.40	[11]
Electrocoagulation	83.00	80.00	100.00 (after separation)	

daily for the waters at the "exit" at a flow rate of 2635 m^3/h [11]. The main disadvantage of the method lies in the introduction of a large amount of chemicals which would exceed the allowable norms, and we know that treatment plant performance depends on the chemical supply.

The electrochemical method suggested has none of the abovementioned disadvantages. Besides, it provides a possibility of attaining a high treatment efficiency for a short period of time, and no preliminary adjustment of the water pH is required. The electric power required for the treatment of 1 m^3 of water is 2 kWh on the average.

Comparing our results with those presented in [12], we can state that the method developed by us guarantees a higher treatment efficiency at a considerably lower consumption of electric power. These advantages are due to the different electrocoagulators employed and to the different optimum conditions.

4. CONCLUSIONS

1. Electrocoagulation of wastewater originating during cellulose-paper production guarantees high treatment efficiency. The values of the basic indices of wastewater are as follows: for fibre stream COD is 98%, PV 91%, ISC 99%; for lye and bark stream COD is 62%, PV 65%, ISC 80%; and for the "exit" stream COD is 80%, PV 83%, ISC 94%.

2. It has been established that the optimum current densities needed for attaining a maximum treatment efficiency are different for the various streams. For the fibre stream, lye and bark streams, and the "exit" they are 15, 23 and 32 A/m^2, respectively. The treatment time of the wastewaters ranged within $6–9 \times 10^2$ s, at electric power consumption of 2 kWh per 1 m^3 of water. The electrocoagulation method is applicable for clarification and treatment of wastewaters containing suspended and dissolved substances.

REFERENCES

[1] VALCHEV V., IVANOVA N., VENCHEVA S., ROSALINOV D., ATANASOVA R., Pulp and paper, 3 (1983).
[2] SVITELSKIJ V. P., Tselljulosa, bumaga, karton, 16 (1971), p. 5.
[3] MENEROV N., Industr. Water Pollution. Reading Mass Addition, Wesley, (1977).
[4] BAJCHEVA D., BOGOEV S., Tr. vodosnab. kanalis. san. techn., 14 (1979), (2), p. 92.
[5] US Patent No. 32052, 1980.
[6] Japan Patent No. 47–1804, 1978.
[7] BELOV L. P., ELKIN A. V., HOLLKIN Yu. I., Khim. technol. tselljul., 3 (1979), p. 85.
[8] SERDOVOLSKIJ E. N., ANISIMOVA M. I., BABAKIN V. A., Khim. dreves., 3 (1979), p. 30.
[9] *Unified methods for water analysis,* M., Khimia, (1973).
[10] BARDARSKA G., *III symposium of effective methods and equipments for purification of civil and industrial waste waters,* Varna 1982.
[11] IVANOV M., DIMITROVA Iv., KOSTURKOV I., ibidem.
[12] TABAKOV D., GRIVENOV A., Pulp and paper, 3 (1983), p. 28.

METODA ELEKTROCHEMICZNEGO OCZYSZCZANIA I ODBARWIANIA ŚCIEKÓW Z PRZEMYSŁU CELULOZOWO-PAPIERNICZEGO

Zbadano możliwość oczyszczania i odbarwiania ścieków celulozowo-papierniczych w procesie elektrokoagulacji. Stwierdzono, że całkowite odbarwianie ścieków następuje po zastosowaniu procesów mechanicznego rozdziału. W procesie elektrokoagulacji z użyciem elektrod żelazowych uzyskano następujące obniżenie wskaźników zanieczyszczenia: dla ścieków celulozowych – ChZT o 98%, utlenialność (PV) o 91%, sucha pozostałość (ISC) o 99%; dla ługów powarzelnych – ChZT o 62%, PV o 63%, ISC o 80%; dla ścieków ogólnych – ChZT o 80%, PV o 83%, ISC o 80%. Zbadano również wpływ gęstość prądu na efektywność oczyszczania. Stwierdzono, że optymalna wartość gęstości prądu, dla której uzyskuje się maksymalny efekt oczyszczania, zmienia się w zależności od rodzaju ścieków.

МЕТОД ЭЛЕКТРОХИМИЧЕСКОЙ ОЧИСТКИ И ОБЕСЦВЕЧИВАНИЯ СТОЧНЫХ ВОД, ПРОИСХОДЯЩИХ ИЗ ЦЕЛЛЮЛОЗНО-БУМАЖНОЙ ПРОМЫШЛЕННОСТИ

Исследована возможность очистки и обесцвечивания в процессе электрокоагуляции сточных вод, происходящих из целлюлозно-бумажной промышленности. Было установлено, что полное обесцвечивание наступает после применения процессов механического разделения. В процессе электрокоагуляции с употреблением электродов из железа получили следующее понижение показателей загрязнения: для целлюлозных сточных вод – ХПК на 98%, окисляемость (PV) на 91%, сухой остаток (ISC) на 99%; для отработанных варочных щелков – ХПК на 62%, PV на 63%, ISC на 80%; для общих сточных вод – ХПК на 80%, PV на 83%, ISC на 80%. Исследовано также влияние плотности тока на эффективность очистки. Установили, что оптимальное значение плотности тока, для которого получается максимальный эффект очистки, меняется в зависимости от вида сточных вод.