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Wastewater from the wood and pulp industry is of environmental concern. It contains high concentrations of organic and inorganic matter. In this work a combined method of coagulation, adsorption and nanofiltration/reverse osmosis (NF/RO) was investigated in the purification of biologically treated wastewater from wood processing. Coagulation with 0.8 g dm^{-3} $AlCl_3{\cdot}6H_2O$ and adsorption on 2.5 g m^{-3} modified clinoptilolite tuff resulted in removal efficiencies of total carbon (TC), total organic carbon (TOC) and inorganic carbon (IC) up to 67.1%, 77.4% and 49.5%, respectively. Almost complete removal of solutes was achieved after NF/RO treatment. The TOC removal efficiency with RO membrane (CPA-3, LFC-1, XLE) and tight NF membrane (NF90) was 98% and with highly porous NF membrane (DK), 88%. After the proposed treatment the purified water stream can be recycled into the process or safely disposed to the river.

Keywords: wastewater; wood processing; organic contaminants; modified clinoptilolite tuff; nanofiltration; reverse osmosis

1. Introduction

A vast pulp and paper industry exists throughout the world to cater for an ever-increasing demand for a wide variety of paper products. This industry generates about 173 m^3 of wastewater per ton of paper produced and, in terms of fresh water use, ranks third after the primary metals and chemical industries [1,2]. About 300 chlorinated organic compounds in pulp mill effluents have been identified to date. About 200 of these include chlorinated resin acids, chlorinate phenolics and dioxins. These compounds, classified as acidic, phenolic and neutral compounds, are at least partly responsible for the wastewater biological oxygen demand (BOD), chemical oxygen demand (COD), effluent colour, toxicity, mutagenicity and carcinogenicity [3]. The problem of colour removal from pulp and paper mill wastewater has been a subject of great consideration and investigation in the last few decades. The colouring body present in this type of wastewater is organic in its nature and comprises wood extractives, tannins, resins, synthetic dyes, and lignin and its degradation products formed by the action of chlorine on lignin [4]. The discharge of coloured pulping effluents to the receiving waters inhibits photosynthetic activity of aquatic biota by reducing the penetration of sunlight, as well as having direct toxic effects on biota [5,6].

The imperative is to remove the pollutants and the colour that are present in pulp and paper mill effluents before they are discharged into receiving waters.

A number of techniques are being applied to treat wastewaters originating from the pulp and paper processing industry. Biological methods such as aerated lagoons and activated sludge systems do not cause sufficient decolorization mainly because of the high stability of lignin and its derivates [7,8].

Aerobic treatment systems are the most widely used method to treat effluents from pulp plants. The high toxicity of the effluents from chemical, semi-chemical and chemo–thermo–mechanical pulping has restricted the application of the anaerobic process for the treatment of these effluents [9].

Several physicochemical colour removal methods such as chemical precipitation and rapid sand filtration have also been developed [10]. Chemical precipitation using aluminium and ferric chloride, and lime, has been studied extensively. In spite of short detention times and low capital costs, there are some reported drawbacks, such as high cost of chemicals for precipitation as well as for pH adjustment, voluminous sludge production due to heavy dosages, problems associated with dewatering and disposing of generated sludge, high residual cation levels and colour, which remains in the supernatant [11–16].

The application of electrochemical methods is another way to treat the wastewaters from cellulose-paper production [17]. This method guarantees high treatment efficiency, but its effectiveness depends on the type of electrodes, the construction of electrocoagulators, and the conditions

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under which the process is run. Promising methods are, for example, electrochemical techniques, autotrophic denitrification, biofiltration and the combination of enzymatic and advanced oxidation process (AOP) treatments [18,19].

From the foregoing discussion, it is clear that all treatment methods in use have some drawbacks, and there is a need to look for other alternative methods. For processing of those previously mentioned effluents it is often necessary to link different methods of purification, and one of the alternative methods is adsorption in combination with membrane processes.

Natural zeolites are known to be effective adsorbents of cationic pollutants in water. To improve the efficiency of natural zeolite for the removal of non-polar and anionic pollutants, modification of the external surface of zeolite crystals is necessary. By replacement of inorganic cations with organic cations (usually of quaternary ammonium structure), it is possible to convert a naturally hydrophilic property of zeolite into a hydrophobic and organophilic property [20].

It was shown for clinoptilolite tuffs that, when the concentration of cationic surfactant hexadecyltrimethylammonium bromide (HDTMABr) ($C_{16}H_{33}(CH_3)_3N^+\ Br^-$) is changed, the configuration of HDTMA cations on the clinoptilolite surface changes from a monolayer to a bilayer. The compensating inorganic cations in the crystal structure of clinoptilolite are not available for exchange with HDTMA cations. Reactions in the system of clinoptilolite tuff and HDTMA cations involve only external cation exchange capacity, leaving the internal cation exchange capacity unchanged and still accessible for small ions [21]. These modified minerals are particularly attractive since they can sorb organic compounds, inorganic cations and inorganic anions. The positively charged head groups are balanced by anionic counterions making surfactant-modified zeolites potential adsorptive media for anionic contaminants. Oxyanions such as arsenate can be adsorbed from water on to the alternated mineral surface via an ion exchange mechanism. On the other hand, phenol, benzene, xylene, pyrene and naphthalene can be adsorbed on organozeolites owing to the increased hydrophobicity of the mineral surface after replacement of hydrated cations with various organocations. The sorption of hydrophobic organic contaminants seems to be due to partitioning of organics into the organic pseudo phase created by the surfactant tail groups [22].

Advantages in the usage of modified natural zeolites are a profitable price of natural zeolite and cationic surfactants, a large distribution of sediments and versatility in the preparation of selective organo-zeolite for the targeted pollutants [23–26]. Regarding the membrane processes, reverse osmosis (RO) and nanofiltration (NF) have been increasingly applied in process water and wastewater treatments, particularly where the high quality of a product is desired [27]. Additionally, the rejection of the uncharged organics by NF/RO membranes is affected by the physicochemical properties of the system, such as hydrophobic interactions between membrane and solutes, dipole moment of solutes and basicity/acidity of the solutes [28].

The aim of this study was to investigate the efficiency of removal of pollutants from the wastewater of the wood industry and to achieve a high quality permeate stream by using an adsorption-based technique of HDTMABr-modified clinoptilolite tuff and pressure-driven membrane processes – RO and NF.

2. Experimental

2.1. Materials and methods

2.1.1. Wastewater

The wastewater used in this work was collected from the mechanical pulp industry Fužine, Croatia. Conifer is used as the raw material in the plant. The plant produces 45,000 t of refined mechanical pulp annually. Biologically treated effluent has the following characteristics: total carbon (TC): 569.0 mg dm^{-3}; inorganic carbon (IC): 209.8 m dm^{-3}; total organic carbon (TOC): 359.2 mg dm^{-3}; chemical oxygen demand (COD): 422.0 mg dm^{-3}; total phosphorus: 5.1 mg P dm^{-3}; total nitrogen: 8.8 mg N dm^{-3}; pH 7.8; conductivity: 1427.7 μS cm^{-1}; turbidity (NTU): 862; and colour (spectral absorption coefficients (SAC) (m^{-1}) at wavelengths 435 nm, 525 nm and 620 nm: 39.1, 18.8 and 9.0 respectively. All tests were performed without adjusting pH.

2.1.2. Coagulant dosage control

The conventional process of pretreatment of the effluent was conducted using different mass concentrations of aluminium chloride hexahydrate ($AlCl_3{\cdot}6H_2O$, Kemika, Croatia). The mass concentrations of aluminium chloride hexahydrate used were 0.4, 0.6, 0.8, 1.2 and 1.8 g dm^{-3}. The above-mentioned dosages were added directly to the wastewater effluent. No pH adjustment was carried out during the experiments. The wastewater and aluminium chloride hexahydrate mixture was stirred with magnetic stirring (Rotamix 550 MM, Tehtnica, Slovenia) at a high speed (250 rpm) for 2 min and then at a low speed (50 rpm) for 10 min. Floccules, as a result of Al^{3+} ion hydrolysis, together with the suspended matter were allowed to settle for 30 min. After coagulation with $AlCl_3{\cdot}6H_2O$ the following parameters were measured: TOC, TC, zeta potential (ZP), COD and turbidity.

2.1.3. Clinoptilolite tuff

Adsorption processes were studied on clinoptilolite tuff from Croatia (Donje Jesenje, Krapina) containing approximately 60% of clinoptilolite. Plagioclase feldspars and quartz were present in concentrations of 10–15% each, while K-feldspars and celadonite were present as traces (<5% of each). The mineralogical composition of clinoptilolite tuff was determined by X-ray powder diffraction (Philips X.pert instrument) [21]. The diameter of clinoptilolite tuff particles in all experiments was less than 0.125 mm.

2.1.4. Clinoptilolite tuff sample preparation

In this study the quaternary ammonium salt HDTMABr (Merck), of molar mass 364.46 g mol^{-1} and minimum 99% of active substance, was used. A mixture of 10.0 g of the clinoptilolite sample and 0.5 dm^3 of 5.0 mmol dm^{-3} surfactant solution was stirred at 30°C (above the Krafft point, which is 25°C) for 48 h on a mechanical shaker (GFL 3031) at 150 rpm [21]. The HDTMABr solution was prepared with deionized water. The surfactant-modified sample was filtered through a Büchner funnel and filter paper (Blue band, Munktell 90 mm/391, Filtrak, Germany). The sample was washed with distilled water until the reaction with 1% $AgNO_3$ solution was negative. The modified sample was dried in a laboratory oven (Memmert UNB 400) at a temperature of 30°C.

2.1.5. Treatment of effluent with the modified clinoptilolite tuff

In the first test, wastewater was treated directly with the modified clinoptilolite tuff (MCT) of the following mass concentrations: 2.5, 5.0, 10.0 and 20.0 g dm^{-3}. In the second step, two concentrations of $AlCl_3{\cdot}6H_2O$ were used: 0.8 and 1.2 g dm^{-3}. After the wastewater was coagulated with either of these concentrations of $AlCl_3{\cdot}6H_2O$, it was then mixed with MCT. Given mass concentrations of MCT were stirred with 1.0 dm^3 of effluent for 15 min on a magnetic stirrer at a speed of 250 rpm. The suspensions were spinning in a centrifugal device for 10 min and the solution above the sediment was then analysed.

2.1.6. Analytical methods

The wastewater colour is defined by specifying the value of SAC in accordance with ISO 7887 [29]. Measurements were conducted at three wavelengths in the yellow spectral region (435 nm), red (525 nm) and blue (620 nm), using a UV–Vis spectrophotometer, Lambda EZ 201, Perkin Elmer. Based on the measured absorbance the spectral absorption coefficient is determined:

$$SAC(\lambda) = \frac{A}{d} f \ (\mathrm{m}^{-1})$$

where SAC is the spectral absorption coefficient at a particular wavelength (m^{-1}), A is the absorbance of the sample at a specific wavelength (λ), d is the optical path (mm) and f is a factor for the conversion of units ($f = 1000$).

The concentration of pollutants in wastewater was determined as TOC/mg dm^{-3}, TC/mg dm^{-3} and IC/mg dm^{-3} by a Total Organic Carbon Analyser (Shimadzu TOC-V$_{WS}$).

Zeta potential was measured by a Zetasizer 3000 (Malvern).

Chemical oxygen demand was determined using the colourimetric determination method and the samples were analysed with a spectrophotometer, Hach DR/2000.

2.1.7. Treatment of the effluent by NF/RO membranes

The membranes used in this work were commercially available composite polyamide RO membranes: CPA-3 and LFC-3 supplied by Hydranautics/Nitto Denko (Oceanside, CA, USA) and XLE membrane supplied by Dow/FilmTec (Midland, MI, USA); and NF membranes: NF90 supplied by Dow/FilmTec (Midland, MI, USA) and DK from Desal/Osmonics, GE Infrastructure Water Process & Technol., Vista, CA, USA. The membranes were tested in a laboratory set-up illustrated schematically and described in details previously [30].

The membranes were pressurized at 18 bar for 8 h in order to stabilize the membrane porous structure in its upper selective layer (skin). Details of the membranes and their properties given by the manufacturers are listed in Table 1. Nominal membrane characteristics (manufacturer's data) were verified by measuring pure water flux and rejection to 300 g dm^{-3} NaCl solution at the working pressure of 1 bar. Seven organic reference solutes (markers) of concentrations of 70 mg dm^{-3} were used for determination of membrane pore size and pore size distribution (PSD). The NF/RO experiments with the sodium chloride and the organic markers were of the short-run type, each lasting for about three hours.

Two types of pretreated wastewater effluent were treated with NF/RO membranes. The first type of effluent was wastewater previously treated with 0.8 g dm^{-3} of $AlCl_3{\cdot}6H_2O$ and additionally treated with 2.5 g dm^{-3} of MCT, and the second type of effluent was wastewater treated with 1.2 g dm^{-3} of $AlCl_3{\cdot}6H_2O$ and additionally treated with 2.5 g dm^{-3} of MCT.

The experiments with pretreated effluent were done in a different way, compared with the experiments with organic 'markers'. Before the samples were taken from the permeate side, the feed solution had circulated for 24 h and permeate was being constantly returned to the feed tank. The aim was to reach adsorption equilibrium. Each time before a different effluent circulated through, the lab set-up was washed with deionized water and the permeate flux of pure water was measured. At the end of all measurements the membranes were chemically treated with NALCO PC-99 alkaline solution, purchased from NALCO Italiana s.r., Rome, in order to restore the initial membrane flux.

The reported permeate flow rates, J_w (L m^{-2} h^{-1}), referring to the membrane permeated solution are the values measured at the laboratory temperature and corrected to 25°C using the relative viscosity and density data for pure water. The retention factor, R, is defined as:

$$R = 1 - \frac{c_p}{c_f}$$

Table 1. Nominal characteristics of the membranes.

Membrane	Type of membrane	Manufacturer	Membrane polymer	MWCO (Da)	R_{NaCl}	Max. operating temperature (°C)	Max. applied pressure (bar)	pH range
DK	NF	Desal/Osmonics, GE Infrastructure Water Process Technol.,Vista, CA, USA GE	Composite polyamide Negatively charged	150–300	0.98*	50	41	2–11
LFC3	RO	Hydranautics/Nitto Denko, Oceanside, CA, USA	Composite polyamide Neutrally charged	100–200	0.997	45	41	2–10
CPA3	RO	Hydranautics/Nitto Denko, Oceanside, CA, USA	Composite polyamide	100–200	0.997	45	41	2–10.8
NF90	NF	Dow/FilmTec, Midland MI, USA	Composite polyamide	200	0.85	45	41	2–11
XLE	RO	Dow/FilmTec, Midland MI, USA	Composite polyamide	100–200	0.99	45	41	2–11

Note: MWCO – molecular weight cut-off, R:
$^{*}R_{MgSO4}$

with c_p and c_f as permeate and feed concentrations ($mg\,dm^{-3}$), respectively. The concentrations of sodium chloride were determined by conductivity measurements, and those of the markers and wastewater treated samples were determined by the Total Organic Carbon Analyser (Shimadzu TOC-VWS).

3. Results and discussion

3.1. Coagulation with aluminium chloride and adsorption on modified clinoptilolite tuff

Coagulation of wastewater (biologically treated effluents from the pulp and wood industry) was carried out with aluminium chloride hexahydrate. Values of the measured parameters of the wastewater (TOC, TC, COD, turbidity and ZP) decreased with the increase in the mass concentration of the coagulant, $AlCl_3{\cdot}6H_2O$, Figure 1.

The optimal mass concentration of $AlCl_3{\cdot}6H_2O$ is the one when ZP ranges from $-5\,mV$ to $0\,mV$ [31]. Consequently, the optimum concentration of $AlCl_3{\cdot}6H_2O$ was found to be greater than $0.4\,g\,dm^{-3}$. The values of TC, TOC and COD remained more or less constant with dosages of $AlCl_3{\cdot}6H_2O$ greater than $0.8\,g\,dm^{-3}$. The ZP of the solution measured after coagulation with $0.8\,g\,dm^{-3}$ of $AlCl_3{\cdot}6H_2O$ was $-3.92\,mV$. The removal efficiencies for turbidity (measured through NTU), COD, TC, TOC and IC with $0.8\,g\,dm^{-3}$ of $AlCl_3$ were 97%, 60.0%, 58.8%, 64.2% and 49.6% respectively. The removal efficiencies for turbidity, COD, TC, TOC and IC with $1.2\,g\,dm^{-3}$ of $AlCl_3{\cdot}6H_2O$ were 99.0%, 42%, 80.0%, 77.5% and 85.0%, respectively. The COD removal of about 60%, with aluminium chloride as a coagulant, is in accordance with the published data from Chaudhari *et al.* [32]. They used three types of coagulant but they kept the dosage of the coagulant constant so they could evaluate the effect of pH of the wastewater on the removal of COD. Maximum removal of COD with aluminium chloride was found to be at pH = 4. They found that increase in dosage of coagulant decreased the pH of the effluent, which is correlated with reduced removal of COD. Considering COD removal, our data are in accordance with theirs. But we found that even though higher dosage of coagulant resulted in lower removal of COD, the removal of TOC increased from 64% to 78%. This is illogical because COD should be directly proportional to TOC and it may be

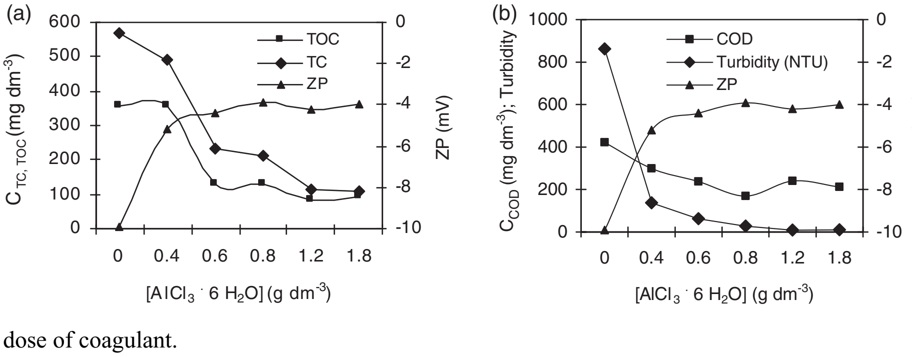

Figure 1. Optimal dose of coagulant.

Table 2. Parameters of wastewater after adsorption on modified clinoptilolite tuff (MCT).

	MCT (g dm^{-3})				
Parameter (mg dm^{-3})	0	2.5	5.0	10.0	20.0
TC	569.0	482.1	332.2	308.4	277.6
IC	209.0	182.6	205.0	185.5	182.6
TOC	359.2	299.5	127.2	122.9	95.04

Table 3. Parameters of wastewater after coagulation with 0.8 g dm^{-3} $AlCl_3 \cdot 6H_2O$ and adsorption on modified clinoptilolite tuff (MCT).

	MCT (g dm^{-3})				
Parameter (mg dm^{-3})	0	2.5	5.0	10.0	20.0
TC	234.3	186.9	151.3	145.4	140.1
IC	105.7	106.0	94.51	95.58	93.18
TOC	128.6	80.97	56.78	49.82	46.95

assumed that COD is not a good criterion for the estimation of the optimal dosage of coagulant.

It can be noticed from Tables 2 and 3 that the increase in the mass concentration of the MCT does not contribute significantly to overall IC reduction. Haggerty and Bowman [23] stated that the sorption of different inorganic anions by the MCT can be described by the Langmuir isotherm. Tables 2 and 3 do show that overall sorption of IC on the MCT can be described by the Langmuir isotherm. The value of IC in raw wastewater (without $AlCl_3 \cdot 6H_2O$ as pretreatment) was 209.8 mg dm^{-3}, and after treatment with the highest dosage (2.5 g dm^{-3}) of MCT, it was 182.6 mg dm^{-3} (Table 2). The removal of TOC with 2.5 g dm^{-3} of MCT was found to be 74%, which is very high compared with removal of IC (13%) at the same concentration of MCT. The above data clearly indicate that MCT is mostly suitable for the removal of organic contaminants in this type of wastewater. This statement is logical because MCT is in its nature more hydrophobic than non-modified tuff, which facilitates the adsorption of organics on it.

The largest part of IC is removed with $AlCl_3 \cdot 6H_2O$ and very little is removed with the MCT. The value of IC after coagulation with 1.2 g dm^{-3} $AlCl_3 \cdot 6H_2O$ was 32.0 mg dm^{-3}, and after additional treatment with 2.5 g of modified clinoptilolite tuff it was reduced to 22.4 mg dm^{-3} (Table 4).

Removal of the solution colour was measured as well. Much better colour removal was obtained by coagulation as a pretreatment process to the adsorption (Figure 2). Coagulation followed by adsorption on MCT gave very good results for the colour removal from the wastewater. Even though coagulation has its drawbacks in terms of sludge production, and treatment with MCT produces solid waste, these processes are still more favourable compared with some money- and energy-consuming processes such as AOP combined with UV [18].

Coagulation with 0.8 g dm^{-3} $AlCl_3 \cdot 6H_2O$ and adsorption on 2.5 g dm^{-3} MCT resulted in removal efficiencies for TC, TOC and IC up to 67.1%, 77.4% and 49.5%, respectively. It can be noticed from Table 4 that part of the organic (40 mg TOC dm^{-3}) and inorganic (22 mg IC dm^{-3}) contaminants remained present after the coagulation and adsorption on MCT. The remaining contamination in wastewater was removed with NF and RO membranes.

3.2. Reverse osmosis and nanofiltration treatment

The final, tertiary step with NF and RO membranes was done with wastewater pretreated with: 0.8 g dm^{-3} of $AlCl_3 \cdot 6H_2O$ and 2.5 g dm^{-3} of clinoptilolite tuff, and 1.2 g dm^{-3} of $AlCl_3 \cdot 6H_2O$ and 2.5 g dm^{-3} of clinoptilolite tuff. Pretreatment of the wastewater is highly recommended to reduce membrane fouling and thereby membrane flux decrease.

Nanofiltration membranes are often more favourable because of their high flux, but low-flux RO membranes are recommended because of their high rejection of solutes from water. In the study conducted by Mänttäri *et al.* [33], high-flux NF membranes didn't give a satisfactory permeate quality, and considering this fact in this work we chose only one high-porous NF membrane, DK. In other to compare membranes used in this study results are supplemented with experimental determination of the membrane porosity. Each membrane has a different pore size distribution. The rejection of solutes [28], governed by size exclusion, strongly depends on the membrane pore size, and hence pore size distribution (PSD) of each membrane is an important parameter which has to be determined in order to predict the performance of each membrane. The membranes were characterized and the PSDs in the membranes' skin were determined by an indirect, modified examination

Table 4. Parameters of wastewater after coagulation with 1.2 g dm^{-3} $AlCl_3 \cdot 6H_2O$ and adsorption on modified clinoptilolite tuff (MCT) and natural clinoptilolite tuff (NCT).

	MCT (g dm^{-3})					NCT (g dm^{-3})
Parameter (mg dm^{-3})	0	2.5	5.0	10.0	20.0	20.0
TC	113	61.40	60.67	62.79	62.69	75.43
IC	32	22.42	22.11	22.49	22.53	22.45
TOC	81	38.98	38.57	40.30	40.16	52.98

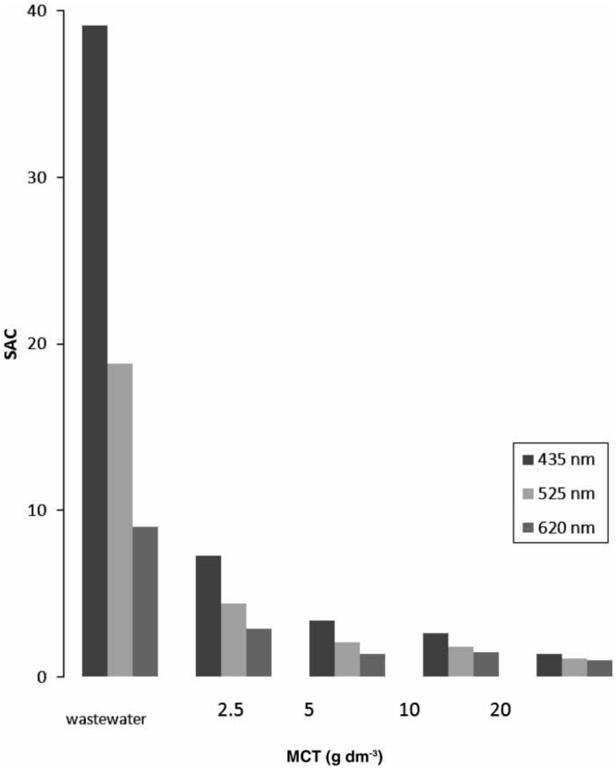

Figure 2. SAC values of wastewater after coagulation with $AlCl_3{\cdot}6H_2O$, mass concentration 0.8 g dm^{-3}, treated with different mass concentrations of the modified clinoptilolite tuff.

method based on the transport of specific solutes (markers) [30,34–36]. The PSDs in the membranes' selective layers are presented in Figure 3 and Y(R) stands for probability density function which corresponds to a relative number of pores. The PSDs of the examined membranes' active layer display one similar feature and remarkable differences for two proposed membrane groups – NF and RO membranes. The similarity can be seen on the left-hand side of all distributions, which have evidently higher peaks in comparison with the low right-hand side of the curves. This shows the presence of a noticeable amount of very small pores, smaller than those shown by the main peak of all the curves. The PSDs of the RO membranes are practically unimodal. The XLE membrane, which is an RO membrane, has the majority of pores of size range 0.55–0.85 nm. The PSDs of the LFC-1 and CPA-3 membranes are shifted towards wider pores with the main peak at 0.9 nm for CPA-3 and 0.85 nm for LFC-1, indicating that these membranes are approaching the NF-type membranes.

In contrast to the RO membranes, the PSD of the NF membranes, as shown in Figure 3, are bimodal with two clearly separated peaks. The higher peak for the DK-type membranes is at 1.25 nm followed by a significant amount of pores between 1.2 and 1.4 nm. The pores with the highest incidence in the case of NF90-type membranes are those of 0.73 nm, followed by a significant frequency of pore sizes between 0.55 and 0.9 nm. Nevertheless, the NF90 membrane has smaller pores compared with the DK membrane and it is in the class of 'tight' NF membranes; hence, by its porosity, it is very similar to low pressure RO membranes. The presented PSD curves confirmed the reflection that the mechanism of size exclusion is decisive in the treatment of the examined pretreated wastewater.

Measured parameters of the permeate stream (pretreated wastewater that passed through the membranes) are shown in Tables 5 and 6. These data are in accordance with those of Mänttäri *et al.* [34]. The porous DK membrane removed only 66% of IC because, according to [34], IC mostly consists of monovalent cations, which are known to be poorly rejected by this type of membrane. Also, according to [34] biologically treated effluent from the pulp industry consists of organic molecules with high molecular masses. The DK membrane removed 88% of TOC, whereas the tight NF90 and RO membranes removed 98% of TOC. Thus these results verify the fact that the membrane pore size was the decisive parameter (Figure 3) in the removal of TOC and IC.

If a membrane highly rejects the pollutants, which is our case, a gel layer can be formed as a result of concentration polarization. This layer results in an increase in osmotic pressure near the surface of the membrane, causing flux decline by the reduction of the driving force (pressure) [37]. Concentration polarization facilitates adsorption of substances on all membranes, causing irreversible fouling and a decrease in permeate flux (Figure 4) through the membranes but at the same time an increase in the membrane separation factor, which was the case with all membranes except the DK membrane. The reduced retention factor of DK may be explained by the different physicochemical nature of the membrane, which eventually became more porous to pollutants. Considering the fact that in most cases polyamide membranes have a hydrophobic character and that the wastewater is a mixture of various organic and inorganic compounds, it can be assumed that, with time,

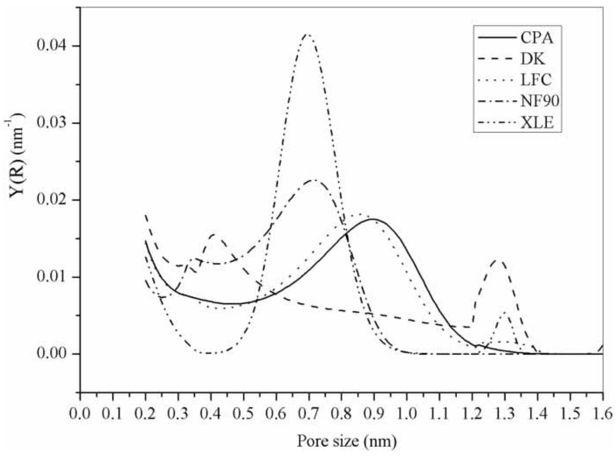

Figure 3. Membrane pore size distributions.

Table 5. Membrane permeate parameters of wastewater after coagulation with 0.8 g dm^{-3} $AlCl_3 \cdot 6H_2O$ and adsorption on 2.5 g dm^{-3} of modified clinoptilolite tuff.

		Membrane				
Parameter	Feed	DK	LFC-1	CPA-3	XLE	NF90
TC (mg dm^{-3})	94.44	19.53	2.531	2.794	2.729	2.727
IC (mg dm^{-3})^3	60.21	16.26	1.877	2.058	2.094	1.276
TOC (mg dm^{-3})	34.23	3.267	0.654	0.737	0.635	1.452
Conductivity (μS cm^{-1})	1552	874	28.0	37.7	23.3	11.9
pH	6.95	7.03	6.83	6.90	6.70	6.80
COD (mg dm^{-3})	80	16	6	7	6	11

Table 6. Membrane permeate parameters of wastewater after coagulation with 1.2 g dm^{-3} $AlCl_3 \cdot 6H_2O$ and adsorption on 2.5 g dm^{-3} of modified clinoptilolite tuff.

		Membrane				
Parameter	Feed	DK	LFC-1	CPA-3	XLE	NF90
TC (mg dm^{-3})	63.17	13.11	1.787	1.432	1.164	1.588
IC (mg dm^{-3})^3	24.03	8.420	0.788	0.186	0.584	0.765
TOC (mg dm^{-3})	39.13	4.693	0.999	0.615	0.581	0.823
Conductivity (μS cm^{-1})	2000	1432	35.3	34.1	38.8	32.8
pH	7.82	7.25	6.52	6.93	7.03	6.86
COD (mg dm^{-3})	109	22	8	6	4	4

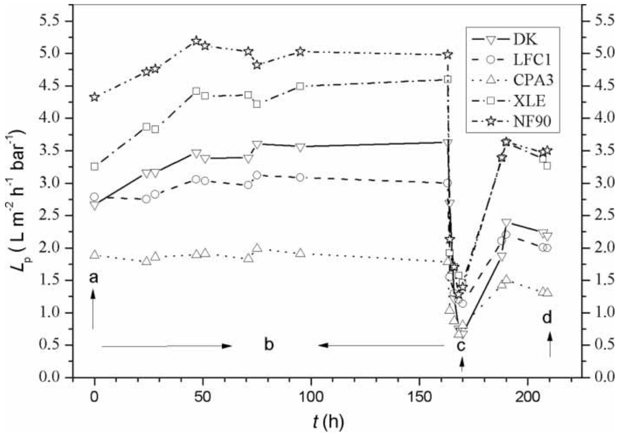

Figure 4. Membrane permeate flux, L_p, vs time, t: a – initial pure water flux; b – permeate flux during membrane characterization; c – permeate flux after wastewater treatment; d – water flux after cleaning.

adsorption of organic contaminants within the membrane has increased and has changed the membrane's properties. After cleaning the membranes with a 1% NALCO 99 solution, the permeate flux of the membranes was restored to 80% of the initial flux value.

4. Conclusions

Clinoptilolite tuff modified with HDTMA can be used for decolorization and purification of the biologically treated effluent from mechanical-pulping industry wastewater, and it will sufficiently remove organic carbon. Coagulation with 0.8 g dm^{-3} $AlCl_3 \cdot 6H_2O$ and adsorption on 2.5 g m^{-3} MCT resulted in removal efficiencies for TC, TOC and IC up to 67.1%, 77.4% and 49.5%, respectively.

Removal efficiencies for TOC with RO membranes (CPA-3, LFC-1 and XLE) and a tight NF membrane (NF90) were around 98%, and 88% with a highly porous NF membrane (DK). Removal efficiencies for IC with RO membranes (CPA-3, LFC-1 and XLE) and a tight NF membrane (NF90) were around 97%, and 66% with a highly porous NF membrane (DK). The observed TOC and IC removal efficiencies led to the conclusion that the performances of the examined composite membranes are mainly caused by the different porosities of the membranes' skin, and the dominant rejection mechanism by all the membranes was the size exclusion effect. The use of coagulation and adsorption on MCT as pretreatment methods to the NF/RO process resulted in almost complete removal of organic and inorganic content in the wastewater from the wood and pulp industry.

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