Chemical Compounds Recovery in Carboxymethyl Cellulose Wastewater Treatment

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Abstract

Carboxymethyl cellulose (CMC) is a kind of cellulose ether widely used in industrial production. CMC wastewater usually have high chemical oxygen demand (COD) and salinity (>10 %), which result from organic and inorganic by-products during CMC production. It is significant that the wastewater is pretreated to decrease salinity and recover valuable organics before biochemical methods are employed. In this paper, distillation-extraction method was used to pretreat CMC wastewater and recover valuable chemical compounds from wastewater (Fig. 1). Initial pH of CMC wastewater was adjusted to different values (6.5, 8.5, 9.5, 10.5, 12.0) before distillation to study the effect of pH on by-products in wastewater. By-products obtained from CMC wastewater were extracted and characterized by NMR, XRD and TGA. Distillate obtained from distillation of wastewater was treated using biological method, *i.e.*, upflow anaerobic sludge blanket (UASB)-contact oxidation process. Domestic sewage and flushing water from manufacturing shop was added into distillate to decrease initial COD and increase nutrients such as N, P, K.

Experimental results showed that by-products extracted from CMC wastewater mainly include ethoxyacetic acid and NaCl, which were confirmed by NMR and XRD (Fig. 2). TGA results of by-products indicated that the content of NaCl in inorganic by-products reached 96 %. Increasing initial pH value of CMC wastewater might significantly raise the purity of ethoxyacetic acid in organic by-products. UASB-contact oxidation process showed a good resistance to shock loading. Results of 45-day continuous operation revealed that COD_{Cr} of final effluent might be controlled below 500 mg l^{-1} and meet Shanghai Industrial Wastewater Discharge Standard (COD_{Cr} < 500 mg l^{-1}), which indicated that the treatment process in this study was appropriate to treat distillate of wastewater from CMC production industry.

Keywords

Ethoxyacetic acid, carboxymethyl cellulose, wastewater treatment, recovery

Introduction

Cellulose ethers are widely used as gelation agents, thickeners, stabilizers, and emulsifiers in food industry as well as oil industry. These compounds include methyl cellulose (MC), hydroxypropyl cellulose (HPC), hydroxypropyl methyl cellulose (HPMC), and methyl ethyl cellulose (MEC). The most widely used cellulose compound is MC such as carboxymethyl cellulose (CMC) and its sodium salt (NaCMC).[1–3]

CMC is produced by etherification of the hydroxyl groups with sodium monochloroacetate (SMCA) in the presence of aqueous alkali. The method is based on Williamson's ether synthesis.[4] The first step in the carboxymethylation is an equilibrium reaction between NaOH and the hydroxyl groups of the cellulose. The second step is actual formation of the carboxymethyl group by the substitution of SMCA. The following steps are neutralization, purification and separation of CMC (Fig. 1).

Production of CMC is simpler than that of other cellulose ethers because all reactions are operated at atmospheric pressure using commercially available reagents. The etherifying reagent, sodium monochloroacetate, is easy to handle and very efficient. For these reasons, CMC has become the largest industrial cellulose ether. Large quantities of CMC are produced in crude commercial grades for use in detergents, oil drilling, and paper industry. High-purity grades are also employed as food additives.[5] However, in the process of CMC production, SMCA can also react by an undesired pathway with NaOH to form by-products that may further react by polycondensation or other pathways.

Since large quantities of by-products form in the process of CMC production, CMC wastewater have high salinity and chemical oxygen demand (COD). It is usually necessary that the wastewater is pretreated using physical

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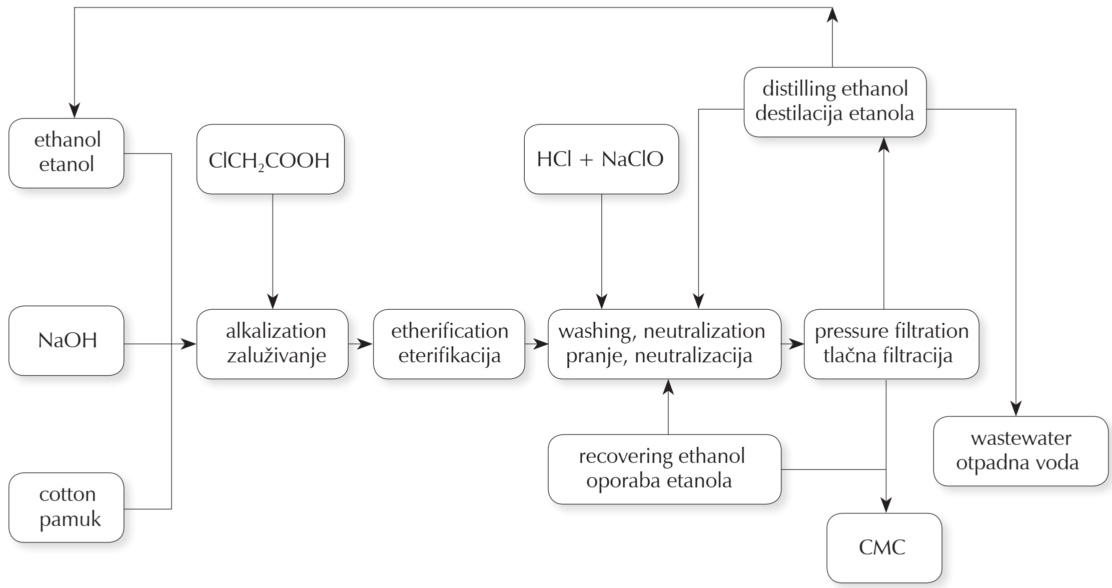

Fig. 1 – Carboxymethyl cellulose (CMC) production process
Slika 1 – Proizvodni proces karboksimetil-celuloze (CMC)

and/or chemical methods before biochemical methods are employed.[6] Common physical and/or chemical methods include distillation, coagulation, membrane filtration, redox, electrochemical treatment, etc.[7–11] A good pretreated method should not only decrease salinity of wastewater, but also recover valuable compounds from wastewater. However, to the best of our knowledge, the study on the compound recovery from CMC wastewater is rarely reported.

In this study, distillation-extraction method was used to pretreat CMC wastewater, and by-products in CMC wastewater were extracted and characterized by nuclear magnetic resonance (NMR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Effects of initial pH value of CMC wastewater on the purity of by-products were studied. The distillate obtained from distillation of wastewater was treated using upflow anaerobic sludge blanket (UASB)-contact oxidation process to meet drainage standard of effluent.

Experiments

Materials

CMC wastewater with ethanol was supplied by Shanghai Changguang Co. Ltd. Other chemicals including NaCl, HCl and ethyl acetate were all reagent grade, which were obtained from Aladdin Reagent, Ltd.

By-products recovery process

CMC wastewater with ethanol was distilled under vacuum (< 2 kPa) at different temperatures (45 – 70 °C). Initial pH of wastewater was adjusted to different values (6.5, 8.5, 9.5, 10.5, 12.0) before distillation to study the effect of pH on by-products in wastewater. The solid residue after distillation was washed using concentrated HCl (35 – 38 %) to dissolve out organic by-products adsorbed. The HCl-containing liquid phase was then separated from solid phase by centrifugation. The white solid obtained, *i.e.*, inorganic by-products, was dried at 110 °C for powder XRD analysis with Cu $K_{\alpha 1}$, graphite monochromator and Lynxeye detector (Bruker D2 Phaser, Germany) and TGA analysis with a 10 K min^{-1} heating rate under nitrogen (Linseis STA PT1000, Germany). The HCl-containing liquid phase was mixed with ethyl acetate and shaken 30 minutes in end-over-end manner at 26 rpm and 20 ± 1 °C to extract organic compounds. Volume ratio of liquid phase to ethyl acetate was 1 : 5. The same extraction process was conducted three times and then organic phase was separated, dehydrated and distilled under vacuum (< 2 kPa) at 40 – 70 °C (Fig. 2). The liquid residues in the distillation flask, *i.e.*, organic by-products, were taken for NMR (Bruker Avance III 400 MHz, Germany) and gas chromatography-mass spectrum (GC-MS, Shimadzu QP-2010Ultra, Japan) analysis. The capillary column used was Rtx-5MS (30.0 m × 0.25 mm × 0.25 μm). The initial oven temperature was 60 °C for 4 minutes, ramped to 140 °C for 2 minutes, then to 280 °C at 2 °C min^{-1} for 30 minutes. Helium was used as a carrier gas at 0.6 ml min^{-1}.

Biological treatment process

Since the distillate from distillation contained some dissolved organic compounds and still had high COD, it was important to treat the distillate by biological method. In this study, the distillate collected was imported into adjusting tank and mixed with domestic sewage and flushing water from manufacturing shop to form a combined wastewater (CW). The COD_{Cr}, BOD_5, volume fraction of three kinds of wastewater are listed in Table 1. The final pH of CW was adjusted to a range from 6.0 to 8.0. Then, CW was imported into UASB reactors where CW was allowed to stay 72 hrs for anaerobic reaction. UASB may promote sludge concentration in reactors and thus enhance treatment efficiency of wastewater. The anaerobic effluent was imported into the aerobic tank where biological contact oxidation process was adopted for aerobic degradation of CW. Hydraulic residence time (HRT) in aerobic tank was 28 hrs. Contact oxidation process has a high volume loading and good resistance to shock loading, which is appropriate to treat the wastewater in this study. The aerobic effluent was imported into the sedimentation tank for clarification and then discharged. All granular sludge was taken from Shanghai Songdong Purify Water Environment Co. Ltd., and inoculated to anaerobic and aerobic tanks at the beginning of operation. Experimental temperature was 25 ± 5 °C. CW treatment process is shown in Fig. 3.

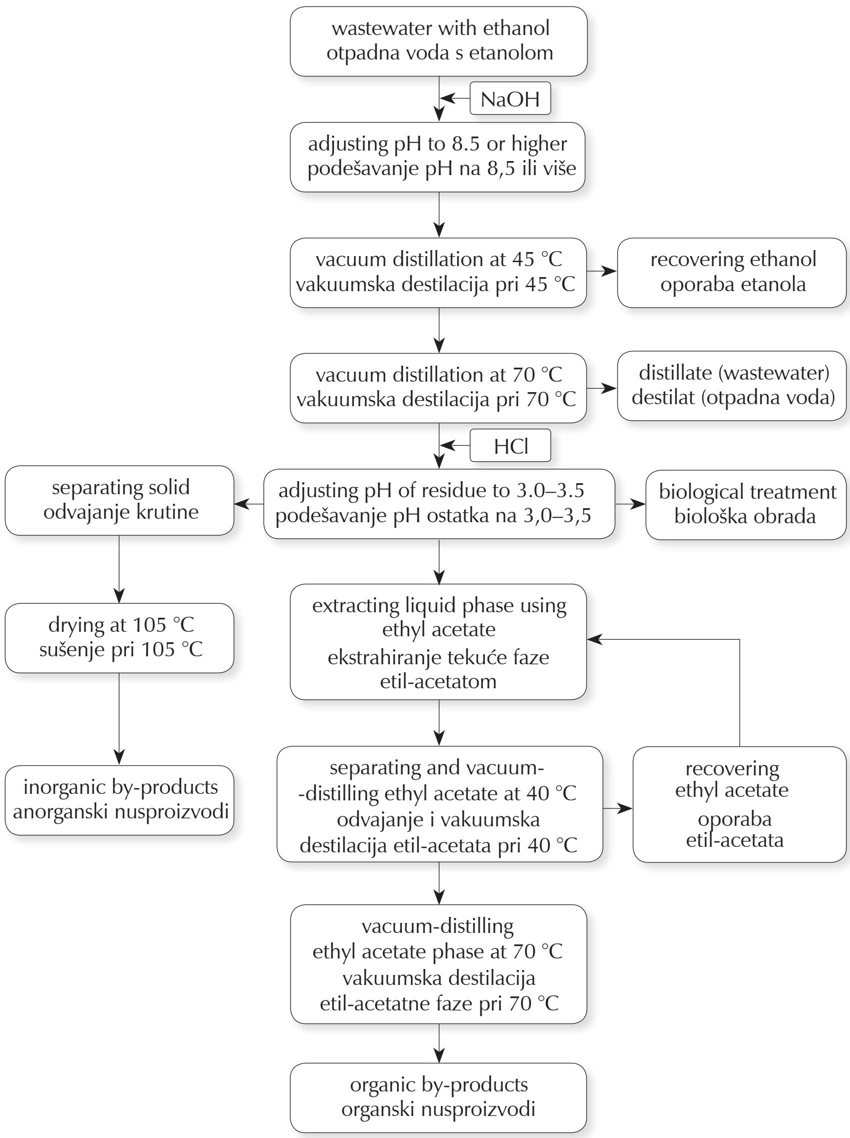

Fig. 2 – By-products recovery process
Slika 2 – Proces oporabe nusproizvoda

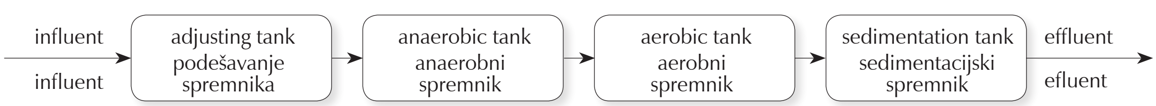

Fig. 3 – Treatment process of combined wastewater
Slika 3 – Proces obrade kombiniranih otpadnih voda

Table 1 – Composition and properties of combined wastewater for biological treatment
Tablica 1 – Sastav i svojstva kombiniranih otpadnih voda za biološku obradu

Wastewater type Vrsta otpadne vode	COD_{Cr} / mg l^{-1}	BOD_5 / mg l^{-1}	Volume fraction Obujamski udjel
distillate destilat	6336 – 16288	1810 – 3800	0.4
domestic sewage otpadna voda iz kućanstva	272 – 243.2	–	0.3
flushing water voda za ispiranje	406 – 606	121 – 158	0.3

Results and discussion

By-products recovery

In the process of CMC production, large quantities of by-products including organic and inorganic compounds would form. In order to analyse the effect of pH on by-products, the initial pH of ethanol-containing CMC wastewater was adjusted to several different values (6.5, 8.5, 9.5, 10.5, 12.0) before distillation.

As shown in Table 2, the pH significantly affected components in organic by-products extracted from CMC wastewater. At pH 6.5, more than ten compounds were identified. 1,3-diethoxy-2-propanol (CAS 4043-59-8) was dominant with the content of 41.25 %, possibly resulting from polycondensation of multiple compounds. Howev-

Table 2 – Components in by-products detected by GC-MS
Tablica 2 – Komponente u nusproizvodima otkrivene pomoću GC-MS

pH	Time / min Vrijeme / min	Area / % Područje / %	CAS No. CAS-broj
6.5	8.53	41.25	4043-59-8
	14.717	7.32	84-66-2
	14.813	0.49	3782-85-2
	15.792	9.3	947-19-3
	15.855	1.02	42978-66-5
	15.949	2.23	42978-66-5
	16.05	2.19	541-1-5
	16.706	3.27	16397-66-3
	16.905	2.91	84-69-5
	17.148	2.4	541-1-5
	17.617	12.31	84-74-2
	18.143	3.43	541-1-5
	18.732	0.89	206-44-0
	19.038	3.32	541-1-5
	19.937	2.91	541-1-5
	20.944	2.11	541-1-5
	22.151	1.48	541-1-5
	23.658	1.17	541-1-5
8.5	3.495	4.92	64-19-7
	5.585	1.17	541-5-9
	6.055	8.37	629-14-1
	7.25	2.39	817-95-8
	8.095	0.31	556-67-2
	9.315	**82.84**	**627-3-2**
9.5	3.2	1.61	64-19-7
	7.565	2.37	817-95-8
	9.145	**89.12**	**627-3-2**
	11.835	0.61	0-0-0
	13.655	6.29	817-95-8
10.5	3.11	1.76	64-19-7
	7.31	6.61	817-95-8
	9.295	**91.63**	**627-3-2**
12.0	2.295	0.7	141-78-6
	6.965	0.22	817-95-8
	8.355	**99.08**	**627-3-2**

er, when pH of wastewater was elevated to 8.5, another chemical compound ethoxyacetic acid (CAS 627-3-2) was found to be dominant with the content of 82.84 %. Moreover, percentage of ethoxyacetic acid increased significantly with the increase of initial pH of CMC wastewater. When pH was adjusted to 12.0, percentage of ethoxyacetic acid reached 99.08 %, which indicated that recovery of by-products from CMC wastewater was feasible.

Fig. 4 shows the ^{1}H NMR ($CDCl_3$) spectrum of organic by-products. Four main chemical shifts were found. The chemical shifts at about 1.2 ppm (CH_3) and 3.6 ppm (CH_2) were assigned to ethyl bonded to O. The chemical shift at about 4.1 was assigned to the other CH_2. The chemical shift at about 8.2 ppm could be assigned to the OH of carboxylic acid. The chemical shifts above confirmed that organic by-product extracted from CMC wastewater was mainly ethoxyacetic acid.

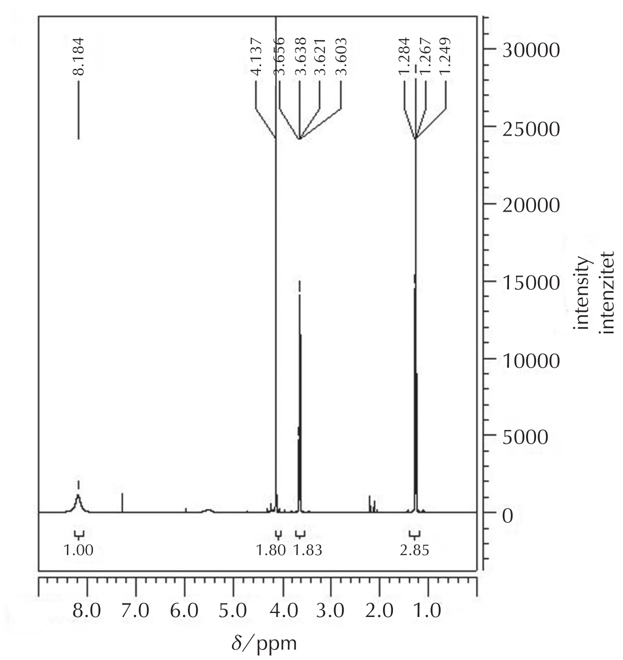

Fig. 4 – ^{1}H NMR spectrum of organic by-products
Slika 4 – ^{1}H NMR-spektar organskih nusproizvoda

According to organic components in by-products, possible main reaction equations were written as follows.

$$ClCH_2COOH + CH_3CH_2OH + NaOH \rightarrow \rightarrow CH_3CH_2OCH_2COOH + NaCl + H_2O \quad (1)$$

$$ClCH_2COOH + CH_3CH_2OH + 2NaOH \rightarrow \rightarrow CH_3CH_2OCH_2COONa + NaCl + 2H_2O \quad (2)$$

$$CH_3CH_2OCH_2COONa + HCl \rightarrow \rightarrow CH_3CH_2OCH_2COOH + NaCl \quad (3)$$

It is obvious that, under alkaline conditions, ethoxyacetic acid would be neutralized by NaOH, resulting in the formation of sodium ethoxyacetate. According to Fig. 2, CMC wastewater with ethanol was vacuum-distilled at 70 °C to remove ethanol and water. Sodium ethoxyacetate has better chemical stability than ethoxyacetic acid, which avoided further reaction of ethoxyacetic acid by polycondensation or other pathways under heating. Higher pH environment would result in the formation of more sodium ethoxyacetate, thus causing the higher percentage of ethoxyacetic acid according to Eq. (1), (2) and (3).

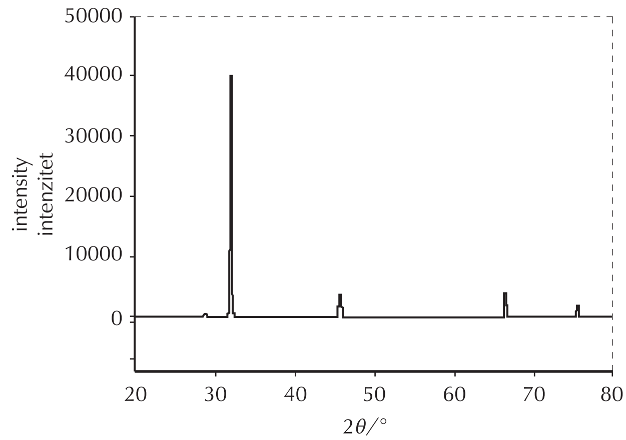

Fig. 5 – XRD pattern of solid by-products
Slika 5 – Rendgenski difraktogram čvrstih nusproizvoda

Fig. 5 shows the XRD pattern of inorganic by-products. Four typical peaks (2θ = 31.8°, 45.5°, 66.3°, 75.4°) were observed, corresponding with the characteristic peaks of NaCl ((200), (220), (400), (420)), which indicated that the inorganic by-products obtained mainly contained NaCl.[12]

The thermal behaviour of inorganic by-products was examined by TGA. According to Fig. 6, the inorganics in the solid was about 96 %, which indicated that high purity NaCl was obtained. Besides, two stages of the thermal degradation of the solid were observed. The first stage, *i.e.*, the mass loss below 150 °C, should be attributed to evaporation of H_2O. The second stage, *i.e.*, the mass loss above 220 °C, was ascribed to degradation of the organics, indicating the existence of a small quantity of organics in inorganic by-products.

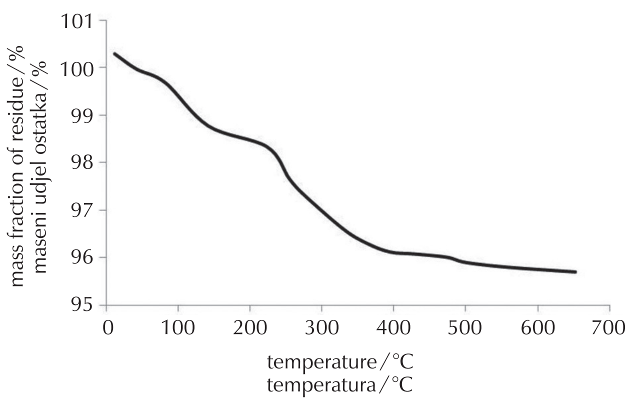

Fig. 6 – TGA curve of solid by-products
Slika 6 – Termogravimetrijska krivulja čvrstih nusproizvoda

Wastewater biological treatment

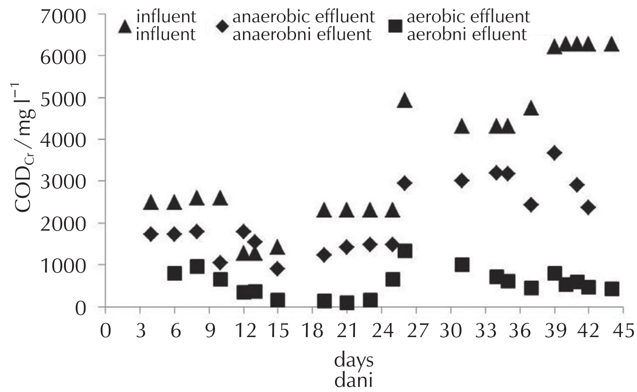

Fig. 7 – COD_{Cr} changes of combined wastewater (CW) in the treatment process
Slika 7 – Promjene u COD_{Cr} kombiniranih otpadnih voda (CW) u procesu obrade

As shown in Fig. 7, the COD_{Cr} of influent CW changed from 2100 to 6500 mg l^{-1}, indicating the relatively great COD_{Cr} fluctuation. The results of 45-day continuous operation show that the treatment process used had a good resistance to shock loading. The COD_{Cr} of anaerobic effluent was between 1000 and 4000 mg l^{-1}. The COD_{Cr} of aerobic effluent after 45-day operation was below 500 mg l^{-1} which met Shanghai Industrial Wastewater Discharge Standard (COD < 500 mg l^{-1}) and indicated the treatment process in this study was feasible.

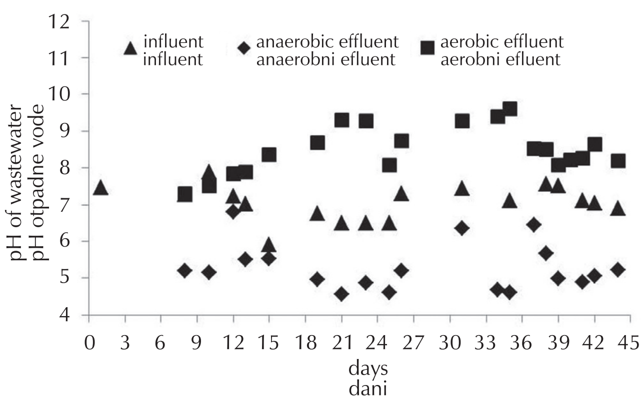

Fig. 8 – pH changes of CW in the treatment process
Slika 8 – Promjene pH otpadnih voda u procesu obrade

The pH changes in the wastewater treatment process can provide significant information with regard to biological states. Fig. 8 shows the changes of pH of influent and effluent CW in the treatment process. The pH of influent CW was at a range from 6.0 to 8.0. In comparison, the pH of anaerobic effluent decreased, which could result from hydrolysis and acidification of organic pollutants in the wastewater under the action of anaerobic bacteria.[13] However, pH of aerobic effluent significantly ascended and maintained a range from 7 to 9.5, possibly due to degradation of organic acid and nitrification of ammonium nitrogen in wastewater.[14]

Conclusion

In this paper, distillation-extraction method was used to pretreat CMC wastewater. By-products including ethoxyacetic acid and NaCl in wastewater were recovered and identified by NMR and XRD. Initial pH of CMC wastewater was found to affect significantly the purity of ethoxyacetic acid in organic by-products. A relatively high purity (96 %) of NaCl was recovered from CMC wastewater. UASB-contact oxidation process was employed to treat distillate from CMC wastewater distillation and showed good resistance to shock loading. Results of 45-day continuous operation show that COD_{Cr} of final effluent might be controlled below 500 mg l^{-1}, which indicates that the treatment process in this study was appropriate to treat wastewater from CMC production industry.

ACKNOWLEDGEMENTS

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List of symbols and abbreviations
Popis simbola i kratica

δ – chemical shift, ppm
– kemijski pomak, ppm

θ – Bragg angle, °
– Braggov kut, °

BOD_5 – biochemical oxygen demand, mg l^{-1}
– biokemijska potreba za kisikom, mg l^{-1}

CMC – carboxymethyl cellulose
– karboksimetil-celuloza

COD – chemical oxygen demand, mg l^{-1}
– kemijska potreba za kisikom, mg l^{-1}

COD_{Cr} – chromate determined chemical oxygen demand, mg l^{-1}
– kemijska potreba za kisikom određena kromatom, mg l^{-1}

CW – combined wastewater
– kombinirana otpadna voda

HPC – hydroxypropyl cellulose
– hidroksipropil-celuloza

HPMC – hydroxypropyl methyl cellulose
– hidroksipropil-metil-celuloza

HRT – hydraulic residence time
– hidrauličko vrijeme zadržavanja

MC – methyl cellulose
– metil-celuloza

MEC – ethyl methyl cellulose
– etil-metil-celuloza

SMCA – sodium monochloroacetate
– natrijev monokloracetat

TGA – thermogravimetric analysis
– termogravimetrijska analiza

UASB – upflow anaerobic sludge blanket
– reaktor s lebdećim muljem

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SAŽETAK

Oporaba kemijskih spojeva pri pročišćavanju otpadnih voda s karboksimetil-celulozom

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Otpadne vode s karboksimetil-celulozom (CMC) obično imaju visoku kemijsku potrebu za kisikom (COD) i salinitet (> 10 %). Prije primjene biokemijskih metoda važno je otpadne vode pročistiti radi smanjenja saliniteta i oporabe vrijednih spojeva. U ovom je radu otpadna voda s CMC-om predobrađena destilacijom i ekstrakcijom. Iz otpadne vode izvučeni su vrijedni kemijski spojevi uključujući etoksioctenu kiselinu i NaCl. Analize metodama GC-MS i NMR pokazuju da čistoća etoksioctene kiseline raste s povećanjem početnog pH otpadne vode. Primijenjen je anaerobno-aerobni postupak za pročišćavanje destilata (reaktor s lebdećim muljem i kontaktna oksidacija), koji je pokazao dobru otpornost na udarna opterećenja.
Nakon 45-dnevnog kontinuiranog rada COD_{Cr} se može održati ispod 500 mg l^{-1} što je u skladu sa šangajskim standardima za ispuštanje industrijskih otpadnih voda.

Ključne riječi
Etoksioctena kiselina, karboksimetil-celuloza, pročišćavanje otpadnih voda, oporaba

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