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HYBRID PROCESSES COMBINING MICROFILTRATION AND ADSORPTION/ION EXCHANGE FOR DAIRY WASTEWATER TREATMENT

Key words: activated carbon, ion exchange resins, dairy wastewater, microfiltration.

Abstract: This study investigated the efficiency of synthetic dairy wastewater treatment using three commercial activated carbons (AC) originating from various raw materials and prepared with different granulations, such as powdered activated carbon and granular activated carbon from wood and granular activated carbon from coconut shell. The additional step after the treatment with AC was ion exchange using mixed-bed ion resins for the enhancement of impurities removal from dairy wastewater. This allowed selecting powdered activated carbon coupled with ion exchangers as the most effective system for the treatment of real dairy wastewater. Integrating these processes with microfiltration has allowed increasing the removal efficiency of both organic and inorganic impurities by 90%.

Wykorzystanie układu hybrydowego: mikrofiltracja – adsorpcja i wymiana jonowa do oczyszczania ścieków mleczarskich

Słowa kluczowe: węgiel aktywny, żywice jonowymienne, ścieki mleczarskie, mikrofiltracja.

Streszczenie: W pracy zbadano efektywność oczyszczania modelowych ścieków mleczarskich z wykorzystaniem trzech komercyjnych węgli aktywowanych (AC) o różnym uziarnieniu, wykonanych z surowców roślinnych. Były to: drzewny węgiel aktywny w postaci proszkowej i granulowanej oraz granulowany węgiel aktywny z łupin orzecha kokosowego. W celu zwiększenia efektywności oczyszczania usuwania zanieczyszczeń w kolejnym etapie zastosowano proces wymiany jonowej z wykorzystaniem mieszanki żywic jonowymiennych. Pozwoliło to wytypować najskuteczniejszy adsorbent w połączeniu z procesem wymiany jonowej do oczyszczania rzeczywistych ścieków mleczarskich. Do wstępnego oczyszczania rzeczywistych ścieków mleczarskich wykorzystano mikrofiltrację oraz membranę ceramiczną, a następnie układ – węgiel aktywny/złoża jonowymienne. W ten sposób zintegrowane procesy pozwoliły zwiększyć skuteczność usuwania zarówno zanieczyszczeń organicznych, jak i nieorganicznych po procesie mikrofiltracji ścieków mleczarskich.

Introduction

The rapid development of industry consuming large amounts of water results in an increase in the level of water pollution. Wastewaters from industry and urban agglomerations, increasing consumption of surfactants, artificial fertilizers, and the decomposition of organic matter contribute to the disposal of significant amounts of various pollutants into surface waters. A number of physical, biological, and chemical methods have been used in wastewater treatment processes, such as filtration, coagulation, advanced oxidation, and membrane processes [1-4]. As they are often insufficient in complete removal of pollutants, this stimulated the search of some alternatives as adsorbents originating from non-conventional agricultural bio-products such as wood, coconut shell, and vegetables processed into activated forms of charcoals. The activated charcoals are usually used as one of the last steps of the treatment cycles, where the variety of pollutants in water at very low concentrations, because the other methods do not bring the expected results. Adsorption using activated carbon is a technology with a wide spectrum of applications, i.e. in the processes of removing primarily organic, but also inorganic pollutants from both the air and water [5]. The efficiency of the treatment of the liquid phase using activated carbon in the reduction of pollutant parameters is greatly influenced by adsorbent porous structure, including pore volume and size distribution, specific surface area, the presence of functional groups, electrostatic interactions, hydrophobicity, ash content, molecular weight, structure, the chemical properties of the adsorbate, and the parameters of treated water (pH, ion concentration in solution, oxygen content) [6-13]. The determined properties of activated carbon are shaped during the processing stages, such as the carbonization of raw material in an inert atmosphere. During this process, most of the non-carbon elements (oxygen, hydrogen, nitrogen, and sulphur) are eliminated in the form of gaseous products, and the elemental carbon atoms form layers composed of irregularly connected aromatic rings, between which free spaces are formed, forming the porous structure of activated carbons [14].

Another alternative for conventional treatment methods are ion exchange resins in the form of beads. Ion exchange is a process of mobile exchange of ions from the medium over other ions of the same electric sign contained in the structure of resin beads. Among the ion exchangers, there are both cationic resins, which are able to exchange the ions containing positive charge, as well as anionic resins capable of exchanging the ions with negative charge [15]. A great solution to improve the quality of water is to use mixed beads that exchange both cations and anions creating a stronger driving force. Mixed-bed ion resin materials are commonly used in water purification for polishing process water which can be reused in the industry.

Nevertheless, the lack of effectiveness in overcoming the problem of variety of impurities in wastewaters makes the traditional treatment unprofitable. In order to enhance the performance of wastewater treatment plants, in recent years, integrated systems for water purification has become increasingly common [3,4,16]. Activated carbon is generally used both as a primary treatment, to facilitate other purification processes, and as the final tertiary stage in the purification of the wastewater. Both powdered and granular activated carbons can be used in water treatment, but the granular type has the advantage of the capability of regeneration [17].

The aim of this work was to study the possibility of using different sorbents for the treatment of dairy wastewater. In the first step, the performances of three types of activated charcoals were studied, such as powdered and granular made from plants and granular prepared from coconut shell activated carbons integrated with mixed ion resin beads in the treatment of dairy wastewater. As a result, the most efficient charcoal was selected to treat real dairy wastewater in the integrated system: microfiltration/activated carbon/mixed ion resins. The efficiency of the treatment methods and the quality of treated water was assessed based on the analysis of selected pollution parameters. Moreover, the obtained results allowed us to develop the conception and construction of a module using activated carbon and ion resins for post-treatment of industrial waste streams.

1. Experimental

Materials

The efficiency of dairy wastewater treatment was verified for three different types of commercially available activated carbons, such as powdered (AC 1) and granular (AC 2) made of wood and granular made of coconut (AC 3) activated carbon. AC 1 and AC 2 were provided by VWR and AC 3 was provided by Tropical Company. The characteristics of the activated carbons used for the treatment of dairy wastewater are presented in Table 1.

Table 1. Characteristics of activated carbons used in the treatment of dairy wastewater

Symbol	Type of activated carbon	Granulation	Specific surface area
AC 1	Powdered (wood)	50-75 μm	2500 m^2/g
AC 2	Granular (wood)	0.5-1.0 mm	1000 m^2/g
AC 3	Granular (coconut shell)	0.5-1.0 mm	1100 m^2/g

All of these carbons were used in a hybrid system with mixed-bed ion resins (cationic and anionic). The cationic ion resin was AMBERLITE IRN77 resin and anionic resin was AMBERLITE™ IRA410. Both were provided by VWR. The main characteristics are presented in Table 2.

Table 2. Characteristics of ion exchangers used after treatment with activated carbons

Ion resin	Mobile ion	Bead size	Exchange capacity
Cationic	H+	0.6-0.70 mm	≥ 1.90 mval/L
Anionic	Cl-	0.6-0.75 mm	≥ 1.25 mval/L

The construction of the prototype uses 'Star-sep TM' ceramic membrane from Mantec designed for use in a cross-flow regime (Table 3). The filtration module was equipped with six 19-channel membranes with a nominal pore diameter of 0.2 µm (max. 0.65 µm), a length of 1200 mm, and the filtration area of 0.33 m^2. The total filtration area of the installed membranes was approximately 2 m^2.

Table 3. Characteristics of ceramic membrane used to pretreat dairy wastewater

Parameter	Ceramic membrane 'Star-Sep™'
External diameter	32 mm
Number of channels	19
Channel shape	Star
Length	1200 mm
Filtration area	0.33 m^2
Pore size	0.2 µm

Methods

In order to check the performance of activated carbon-ion exchangers for wastewater treatment, in the first step, the synthetic dairy wastewater was based on powdered milk. The concentrations of the analysed pollution parameters are given in Table 4. The processes of the adsorption of pollutants in wastewater were conducted in the laboratory set-up, which allowed us to propose and design real industrial sorption module (Fig. 1). The volume of columns used in the experiments was 20 mL. The activated carbons were put in columns – 1 g. The cation and anion resins were mixed equally, and the total mass was 2 g, which was then put into a separate column. The model dairy wastewater with a volume of 50 mL was first filtered through the activated carbon and then filtered again through mixed-bed ion exchange resin. The effectiveness of the treatment of model wastewater was evaluated for Filtrate and Filtrate I (Fig. 1) based on the percentage efficiency removal of pollutions expressed as chemical oxygen demand (COD), total bound nitrogen (TNb), and sulphates. It was calculated with the formula $(1 - C_1/C_2) \cdot 100\%$, where C_1 – the concentration of the pollutant in the wastewater after the treatment, mg/L, and C_2 – the concentration of the pollutant in the wastewater before the treatment, mg/L. The analyses were conducted using cuvette tests with a spectrophotometer UV-VIS DR6000 from HACH Lange.

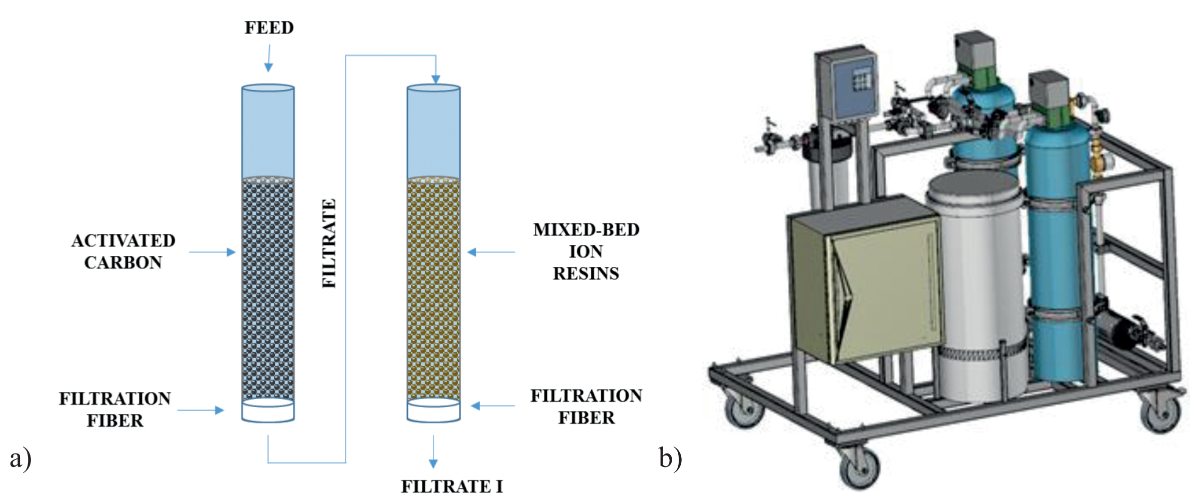

Fig 1. Scheme of two-stage wastewater treatment laboratory set-up using activated carbon and ion-exchange resins (a) and 3D visualization of designed industrial sorption module

Activated carbon-ion exchange integrated steps used for the treatment of synthetic dairy wastewater allowed selecting the most efficient adsorbent and ion exchange resin material for the post-treatment of real dairy wastewater after prior pressure driven process such as microfiltration. Dairy wastewater with a volume of 100 L was pumped from the feed tank through the membrane module at a pressure that was adequate for the membrane technique that was used (1.4–2.0 bar) and the 80 L of permeate was collected. After passing through the filtration module, the feed was separated into two different streams: a stream of purified filtrate (permeate), and a stream of concentrate (retentate). The Filtrate stream was collected in a separate tank and a retentate stream was recycled to the feed tank. As a result, the concentrations of compounds that were retained by the membrane were gradually increasing. Microfiltration (MF) was performed with a membrane installation using a ceramic membrane with a pore size of 0.2 μm. The microfiltration system was previously described in the work [18]. The retentate flow was set to the maximum level (1200–1250 L/h). The samples of permeate from the process was subjected to filtration through the selected sorbent and mixed-bed ion exchange resins. The values of parameters selected for testing in real wastewaters are given in Table 4.

Table 4. Initial values of pollution parameters in dairy wastewaters

Parameter	Synthetic dairy wastewater	Real dairy wastewater	
	Untreated	Untreated	Treated with MF
COD [mg O_2/L]	879	2090	629
TNb [mg/L]	249	47	38
Sulphates [mg/L]	475	176	49

2. Results and discussion

Performance of activated carbon-ion exchange resins in the treatment of synthetic dairy wastewater

The first stage of the study involved the analysis of the performance of activated carbons named AC 1, AC 2, and AC 3 along with mixed-bed ion resins (C/A) as an additional step for model dairy wastewater treatment. This was determined by the investigations of the removal efficiencies of pollution parameters such as COD, TNb, and sulphates. Comparative experiments using all of the activated carbons allowed observing that the highest removal efficiency of chemical oxygen demand in synthetic wastewater was obtained using powdered activated carbon (AC 1) (Fig. 1). The effectiveness of AC 1 was almost 50% higher than AC 2 and over 50% higher than AC 3 activated carbon. This was associated with the highest surface of powdered activated carbon. In this case, the additional step using mixed bed ion exchange resin allowed the enhancement of the removal efficiency of COD of about 10% for each of the tested activated charcoal (Fig. 2). The additional treatment after powdered activated carbon with a mix of cation and anion resin allowed reducing COD by almost 80% (Fig. 2).

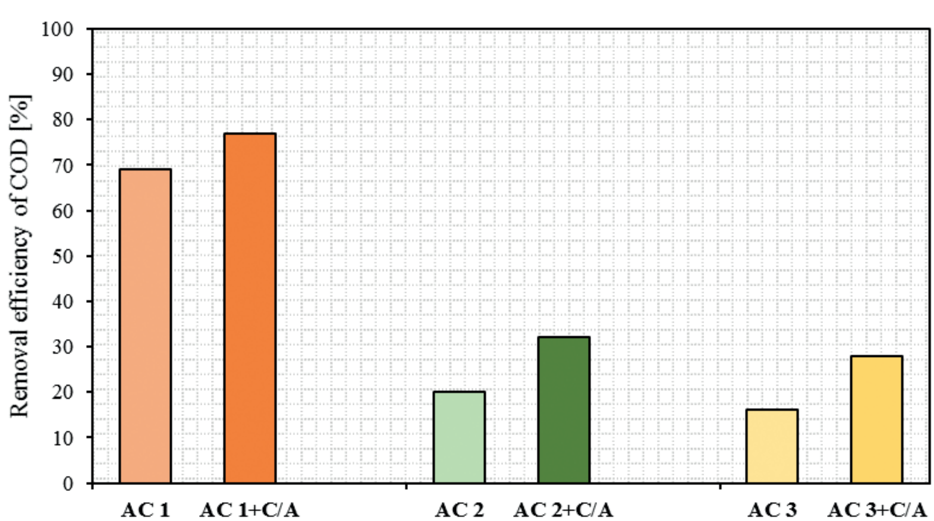

Fig. 2. Removal efficiency of chemical oxygen demand (COD) using activated carbons and coupled with mixed ion exchange resin

The performances of activated carbons were also investigated for the reduction of parameter of TNb (Fig. 3). It was found that the highest removal efficiency was again obtained by AC 1 and equal to 13%; however, the difference between particular activated carbon was not very significant. It was found that mixed-bed ion resins allow increasing the removal efficiency by about 45%. This might indicate that most of nitrogen was originated from the ion form. The smallest percentage reduction of TNb was observed for the AC 3 made from coconut shell (Fig. 3).

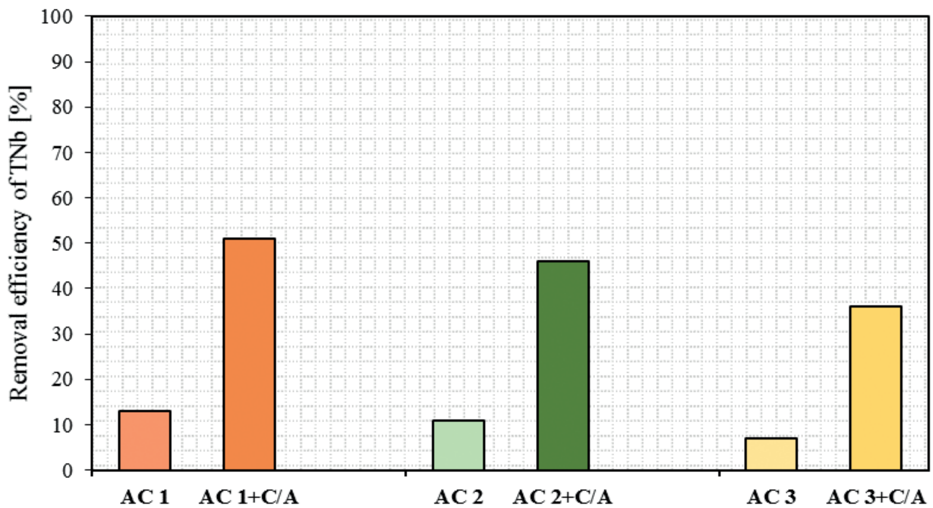

Fig. 3. Removal efficiency of total bound nitrogen (TNb) in model dairy wastewater using activated carbons and coupled with mixed ion exchange resin

In the case of the removal efficiency of sulphates from synthetic dairy wastewater, none of the activated carbons were highly efficient (Fig. 4). As sulphates were mainly present in the ionic form, their concentration was greatly reduced with the filtration through columns containing mixed cationic and anionic Amberlite-resins.

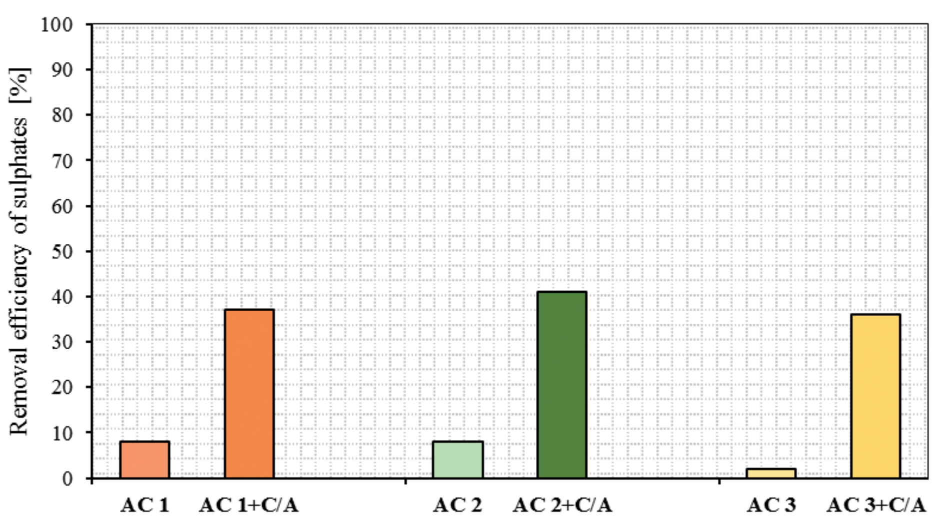

Fig. 4. Removal efficiency of sulphates in model dairy wastewater treatment with activated carbons and coupled mixed-bed ion exchange resin

Based on the obtained results, the powdered activated carbon was selected as the most efficient for the treatment of dairy wastewater. It was particularly noted for reducing the COD parameter quantifying the amount of mainly organic but also inorganic matter. However, the mixed bed ion exchangers were much more efficient for the reduction of ion concentrations. Differences in the amount of adsorbed pollutions using a particular sorbent have been attributed to surface area and the presence of surface functional groups and electrostatic interactions [19].

Real dairy wastewater treatment with integrated system

Treatment of real dairy wastewater was started with microfiltration (MF) conducted with a ceramic membrane in order to remove suspended solids. Then, based on the highest efficiency of synthetic wastewater treatment with activated carbon, the AC 1 was selected for further treatment of the wastewater along with mixed-bed ion resins. It was noted that microfiltration itself is not sufficient to highly reduce concentrations of pollutants in dairy wastewater (Fig. 5). Powdered activated carbon used with cation-ion exchangers reduced the organic impurities content expressed as COD by over 90%, which was 20% more than MF. The TNb level decreased only 19% when using MF. This means that impurities containing nitrogen compounds could freely pass through the pores of the ceramic membrane resulting in low removal efficiency. However, the integrated system of powdered activated carbon and ion exchange resins after MF yielded a 80% reduction of TNb. For the removal efficiency of sulphates from wastewater, only C/A as an additional post-treatment step allowed the reduction of the content of sulphates by nearly 90% (Fig. 5).

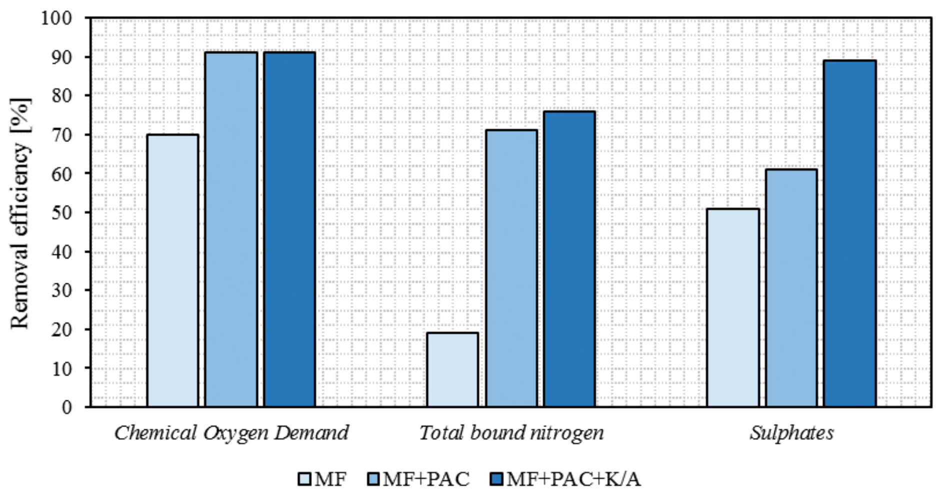

Fig. 5. Removal efficiency of chemical oxygen demand (COD), total bound nitrogen (TNb) and sulphates with MF used as a single process, coupled with powdered activated carbon and both activated carbon and mixed-bed ion resins

The low efficiency of MF used as a single process for dairy wastewater treatment can found in Levine's work [20], which shows that particles of organic compounds such as polysaccharides or fatty acids in filtered water are smaller than the pore diameters of microfiltration membranes and can freely pass contaminating the water.

Using powdered activated carbon is an alternative to the water purification process in granular activated carbon filters [21]. The main advantage of the powdered activated carbon compared to granular one is the low investment cost and the flexibility of application. It can be dosed periodically when the quality of the collected water requires an additional treatment process. Activated carbon in the form of powder is useful to treat organic impurities, especially those contributing to odorous smell in dairy wastewater, which also results from inorganic compounds [22]. Using the integrated ion-exchange resins for the removal of charged particles and activated carbon for organic molecules might be an effective solution for the treatment or post-treatment of industrial wastewater. Employing membrane processes such as microfiltration as a pre-treatment integrated with adsorption and ion exchange can result in the enhancement of reducing impurities, which, in consequence, might contribute to the system development and optimization of high quality water production that can be reused in the particular industry. Thus, it is necessary to continue the work toward selecting appropriate process conditions for adsorption of pollutants on various types of sorbents. For this purpose, it was necessary to design and build a research post-treatment plant involving columns for sorbents such as activated carbon and ion exchange resins, which can work in a technological line with microfiltration module as a pre-treatment step (Fig. 6). This module consists of two columns working both individually or in parallel which can be used depending on the required quality of treated water. During the laboratory study, it was confirmed that, at the outlet of the columns, a non-woven filter with a pore size of 5 µm should be employed at the outlet of the columns, which allows the retention of solid particles released from activated carbon. The additional element of the module is the brine tank used for the regeneration of ion exchange resins. The whole system is planned to be used for post-treatment of wastewaters regenerated with membrane processes.

a)

b)

Fig. 6. Technological line involving microfiltration plant (a) and sorption module (b) consisting of columns for both activated carbon and ion exchange resins.

Conclusions

The results obtained in the study have shown that the most efficient tested activated carbon for the removal of most impurities in synthetic dairy wastewater was powdered activated carbon, which then was integrated with mixed-bed ion resins in order to enhance the removal efficiencies. This integrated system was used to treat real dairy wastewater after prior microfiltration through ceramic membrane. It turned out that powdered activated carbon coupled with Ambulate ion resins employed after microfiltration greatly affected the performance of dairy wastewater treatment. This resulted in the removal of unwanted pollution originating from both organic matter and ions expressed as chemical oxygen demand, total bound nitrogen, and sulphates. Thus, in further work, the designed module will be used to post-treat the technological liquids in order to obtain water that can be reused in industrial plants.

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