*Desalination and Water Treatment*
www.deswater.com

doi: 10.5004/dwt.2018.22979

128 (2018) 351–357
October

# Modification of PES ultrafiltration membranes for removal of caffeine

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Received 5 April 2018; Accepted 13 August 2018

## ABSTRACT

This study describes the removal of caffeine by means of low-pressure filtration with thin-film composite (TFC)/thin-film nanocomposite (TFN) membranes prepared through the interfacial polymerization process. This type of membrane contains a thick dense polyethersulfone (PES) layer and a thin-film polyamide layer. The composite/nanocomposite membranes were prepared by a reaction between the aqueous solution of *meta*-phenylenediamine and a hexane solution of trimesoyl chloride on the surface of the PES support. TFC/TFN membranes were also modified with single-walled carbon nanotubes (SWCNTs) functionalized with carboxyl groups in the support and thin film layer. TFN/TFC membranes are mainly used for high-pressure techniques such as reverse osmosis or nanofiltration processes, but it has been found that they may be also applied in low-pressure filtration. The conducted research showed that fabricated TFN membranes had properties coherently linking with nanofiltration. This means that we achieved the similar retention performance with lower costs. The presence of the nanocomposite material greatly improved retention with the preservation of high flux during filtration. It was also found that the addition of SWCNTs changed the porosity and water contact angle of the membrane.

*Keywords:* Thin film; Interfacial polymerization; Carbon nanotubes; Caffeine; Ultrafiltration

## 1. Introduction

Caffeine is a substance, which is metabolized in 80% in human body mainly to derivatives like paraxanthine or theobromine, which may also be produced by microorganisms in wastewater plants [1]. A high consumption of tea, coffee, and energetic drinks by society has caused that caffeine occurs in high concentrations in the environment [2]. Studies conducted at sewage treatment plants in Beijing (China) demonstrated that caffeine was commonly detected in their effluents. It means that degradation of caffeine in conventional system of wastewater treatment is not complete [3]. Thus, major amount of caffeine escapes to surface waters and distributes in the environment and also affects adversely aquatic biota. For this reason, there is an increasing interest in developing methods to remove highly hydrophilic and well water soluble micropollutants, such as caffeine.

Thin-film composite (TFC) and thin-film nanocomposite (TFN) are new types of composite membranes prepared by means of a technique of interfacial polymerization (IP) process [4]. It is the main type of NF/RO (nanofiltration/reverse osmosis) membranes, widely used for desalination and removal of micropollutants such as pharmaceuticals, pesticides, and endocrine disrupting compounds [5]. They also find an application in a novel technique of the forward osmosis process. This method uses osmotic pressure differences to drive the permeation of water across a membrane to the concentrated solution from the diluted feed solution [6].

One of the major problem of membrane technologies is membrane-fouling, which leads to permeability loss of the membranes [7,8]. Many efforts have been devoted to improve the permeability, rejection, and antifouling

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*Presented at the XII Scientific Conference "Membranes and Membrane Processes in Environmental Protection" – MEMPEP 2018*
*13–16 June 2018, Zakopane, Poland.*

properties. One approach is to modify TFC membranes to TFN membranes by means of nanoparticles [9,10]. By adding nanoparticles to the thin-film layers membranes, better performance, higher permeability, mechanical strength, fouling resistance, and contaminant elimination are achieved. These features are obtainable due to the size, shape, and surface characteristics of nanomaterials [11]. Different types of nanoparticles such as nano-$TiO_2$, zeolite, silica, and graphene oxide have been used as modificators of TFC membranes [12]. Besides, special attention is focused on carbon nanotubes (CNTs) due to their high adsorption potential [13]. There are two main types of CNTs: single-walled and multiwalled. Both contain convoluted sheets of graphene enclosed by half-fullerenes and may be modified, for example, by strong acids, to obtain functional groups on their surfaces. The most frequently used nanotubes are ones functionalized with carboxyl groups [14]. In this study, single-walled CNTs were used.

As was mentioned RO and NF are highly effective in removal of micropollutants, however both processes are energy consuming. In this study TFC/TFN membranes were used for the first time for the removal of microcontaminants (caffeine) in low-pressure membrane filtration.

## 2. Materials and methods

### 2.1. Materials

Single-walled carbon nanotubes functionalized with carboxyl groups (SWCNT-COOH) were obtained from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences and used for membrane modification. Polyethersulfone (PES) as the basic material for membrane preparation was supplied by BASF Company (Ludwigshafen, Germany). *N,N*-Dimethylformamide (DMF), hexane, acetonitrile and methanol (all analytically pure) were purchased from Avantor Performance Materials (Central Valley, Pennsylvania, USA). *m*-phenylenediamine (MPD) was obtained from Sigma-Aldrich Co. (St. Louis, USA). 1,3,5-benzenetricarbonyl chloride (TMC) was obtained from ThermoFisher (Kandel) GmbH (Germany). Deionized water was produced by the Milli-Q water purification system (Millipore LLC, Poland).

### 2.2. Micropollutants and feed water

The caffeine (CAF) was purchased from Sigma-Aldrich (Poland) in analytical purity grade. The physicochemical properties of the compound are presented in Table 1. The stock solutions of CAF were prepared with methanol (1 g $L^{-1}$). The feed solution for the retention tests was prepared by diluting the stock solution with deionized water.

The concentration of CAF in the feed and the permeate was determined by solid phase extraction and high-performance liquid chromatography (HPLC). For SPE, plastic columns filled with C18 phase (Supelco, Bellefonte, Pennsylvania, USA) were used. Firstly, the C18 cartridges were washed with 5 mL of methanol and 5 mL of deionized water. Next, 20 mL of sample was passed through the columns. Then, after the column was completely dried, the cartridges were flushed with 3 mL of methanol. The eluted portion was analyzed using HPLC at a wavelength of 272 nm. The chromatograph was equipped with a chromatographic column and UV-vis detector. The mobile phase contained 95% ACN and 5% deionized water. The retention of the tested compound was calculated according to the following equation:

Table 1
Properties of caffeine [15,16]

| Symbol | CAF |
|---|---|
| Molecular mass, g $mol^{-1}$ | 194.2 |
| pH | 6.9 |
| Solubility in water at 25°C, mg $L^{-1}$ | 21,600 |
| $\log K_{ow}$ | 0.07 |
| p*K*a | 6.1 |

$$R = \frac{C_f - C_p}{C_f} \times 100\% \quad (1)$$

where $R$ is removal degree (%), $C_f$ and $C_p$ are concentrations of caffeine in the feed and the permeate, respectively (mg $L^{-1}$).

### 2.3. Membrane preparation

#### 2.3.1. Pristine membranes

Two types of pristine membranes and for support to further TFC/TFN modification were prepared using the phase inversion method: PES 12 and PES 12 0.02. The casting solution consisted of 12 wt. % of PES and less than 88 wt. % of DMF. The content of SWCNT-COOH in solution for modified support was kept at 0.02 wt. %. The proper amounts of CNTs and PES were added to the DMF. The casting solution was shaken for 20 h to obtain a homogeneous solution. After that, membranes were cast using a doctor blade with 0.1 mm thickness on a glass plate and immediately immersed in deionized water at ±20°C. The precipitated membranes were stored in deionized water for 24 h in order to stabilize them. These membranes were also tested to compare the results with ones obtained for TFC/TFN membranes.

#### 2.3.2. TFC/TFN membranes

The support prepared during the previous stage was ready for interfacial polymerization. The PES support was removed from the deionized water. A piece of the membrane was placed in a container (active side facing down) and 30 mL of 2 wt. %. MPD solution was poured into container to cover the whole membrane. After 10 min, the membrane was placed on a flat surface and the excess MPD solution was removed by rolling the membrane with a rubber roller across the top surface. This activity ensured that no visible droplets remained on the membrane surface, because it could cause defects if left on the membrane. Afterwards, the membrane was placed into a container (top side up) and 20 mL of 0.02 wt. % of TMC/hexane solution was poured on it. After 2 min, the membrane was removed from the *n*-hexane solution and dried in an oven at 70°C in air at ambient pressure for 10 min. Such prepared TFC membranes were placed in deionized water for 24 h.

For TFN membrane preparation, 0.02 wt. % of SWCNT-COOH were dispersed in TMC/hexane solution right before they were poured onto the membrane surface. In this way, the top layer of the membrane was coated with nanotubes. The later stages of membrane preparation remained the same. The difference between the unmodified surface of the TFC membrane and the one modified with CNTs is demonstrated in Fig. 1. In Table 2, all types of membranes are described.

### 2.4. Measurement of contact angle

Measurements of the contact angle (CA) were performed using a goniometer (Pocket Goniometer PG-1) and the sessile drop method, in which 10 strips of dried tested membrane were inserted into the device, was also applied. By syringe on top, drop of distilled water was applied onto the membrane surface. Through an enlarged projection of the water drop on gauge, the value of the CA was measured. For every type of membrane, 10 samples were measured and the average value was calculated.

### 2.5. Transport-retention characteristic of membrane

In order to classify the prepared membranes to the given type (UF (ultrafiltration)/NF/RO), water flux at different transmembrane pressure was evaluated. Then membrane permeability was calculated and compared with literature data. Water flux and permeability were calculated according to the following equations:

Fig. 1. Unmodified membrane (L) and membrane modified with CNTs (R).

Table 2
Types of prepared membranes

| Symbol | PES (wt. %) | Thin-film application | CNTs application (0.02 wt.%) |
|---|---|---|---|
| PES 12 | 12 | – | – |
| PES 12 0.02 | 12 | – | In support |
| PES12 TFC | 12 | Yes | – |
| PES 12 TFN 0.02 | 12 | Yes | In thin-film |
| PES 12 0.02 TFN | 12 | Yes | In support |
| PES 12 0.02 TFN 0.02 | 12 | Yes | In thin-film and support |

$$J_w = \frac{V}{A \times t} \tag{2}$$

$$L_p = \frac{J_w}{\Delta P} \tag{3}$$

where $J_w$ is water flux (L m$^{-2}$ h$^{-1}$), $A$ is membrane area (m$^2$), $t$ is time (h), $V$ is permeate volume (L), $L_p$ is water permeability (L m$^{-2}$ h$^{-1}$ bar$^{-1}$), $\Delta P$ is transmembrane pressure (bar). Retention of divalent ion of magnesium was also tested using 2 g L$^{-1}$ solution of $MgSO_4$. Magnesium content was determined by ethylenediaminetetraacetic acid titration in the pH 10 against Eriochrome Black.

### 2.6. Measurement of membrane porosity

A sheet of a membrane with a calculated surface was dried using paper towel, then weighed in the wet state. After this, the same membrane was dried in an oven at 60°C for 24 h and then weighed in the dry state. Five sheets of each membrane were used for this measurement. The equation for the calculation of the membrane porosity is as follows:

$$\varepsilon = \frac{m_w - m_d}{A \times L \times \rho} \times 100\% \tag{4}$$

where $\varepsilon$ is porosity (%), $m_w$ is the weight of the wet membrane (g), $m_d$ is the weight of the dry membrane (g), $A$ is the area of the membrane (cm$^2$), $L$ is the membrane thickness (cm), and $\rho$ is pure water density (about 0.998 g mL$^{-1}$).

### 2.7. Setup and filtration run

Retention tests were carried out with an ultrafiltration setup consisting of a nitrogen gas supply, a pressure reducer, a filtration cell, and a volume measuring system. The mounted membranes had an area of 38.5 cm$^2$.

Ultrafiltration was carried out for all membranes at 0.1 MPa. The experiment included two stages: (1) membrane conditioning with deionized water and (2) retention tests with feed water. All stages were conducted at the same conditions, that is, transmembrane pressure, temperature, and velocity. For each stage, permeate flux was measured and calculated from Eq. (2).

## 3. Results

### 3.1. Membrane characterization

As seen in Fig. 2, the CA for the prepared membranes had different values. More specifically, the highest value was attributed to an unmodified PES 12 membrane, which was not undergone an IP. The value of the CA of this membrane was 73° indicating on hydrophobic properties. The nanotubes in the PES 12 0.02 membrane caused the 10° drop in CA. A similar observation was found in most studies on membranes with nanotubes, for example, Celik et al. [17]

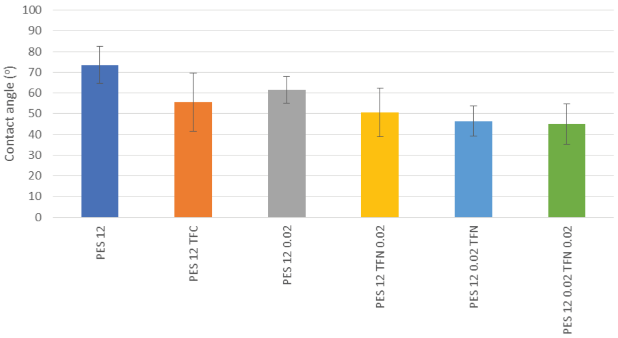

Fig. 2. Water contact angle of tested membranes.

reported that membrane made of pure PES had a CA of 70°, while the introduction of functionalized CNTs caused a 5° decrease in this value. Similarly, in Vanatpour's studies [18], hydrophilicity (measured with the same method as in our study), the addition of a similar amount of modified nanotubes (0.04 wt. %) resulted in a drop in hydrophobicity from 66.3° to 59.6°.

Conducting the IP process on membranes results in the formation of a new polymer according to the reaction proposed by Low et al. [19]. This polymer is a polyamide, that has slightly different properties than PES used as a support. Its properties were well confirmed by in this work, because the PES 12 TFC membrane was a composite membrane without the addition of a nanocomposite in the skin layer and support. The CA of this membrane was 20° lower that meant that this polymer was more hydrophilic than PES. According to the previously mentioned study, the PES membrane had a CA in the range of 65°–75° [17,18], while membranes with a skin layer formed in the reaction of MPD and TMC had a slightly lower CA. In the study of Yin et al. [20] the CA of the membrane with an unmodified (by nanocomposite) skin layer was around 60°, which closely corresponded to our results.

TFN membranes, that are "PES 12 TFN 0.02", "PES 12 0.02 TFN" and "PES 12 0.02 TFN 0.02" had similar values of CA, that is, between 50.6° and 45°. That major decrease in values was induced by the presence of polyamide on the membrane surface as well as nanotubes in the membrane structure. Nanotubes are often functionalized with carboxylic groups in order to decrease their hydrophobicity, therefore their presence in the membrane structure decreases the value of the CA of the whole surface (apart from the patchy distribution of the nanotubes in the casting solution) [21]. The lowest CA had a membrane with nanotubes embedded in the skin layer and in the support. In that case, the formation of possible defects in the skin layer did not cause a significant increase in the CA. Moreover, a similar value was observed for the PES 12 0.02 TFN membrane, suggesting that the skin layer was so thin that nanotubes embedded in the support could affect it. It is likely that the higher value of CA in the 12 TFN 0.02 membrane could be caused by defects in the structure of the skin layer and the direct impact of pure polymer in those places. That contingency is suggested by Lau et al. [22].

The mean deionized water flux is shown in Fig. 3 as a function of transmembrane pressure (data presented only for membrane PES 12 TFN 0.02). The water permeation of prepared membranes seems to be typical for ultrafiltration membrane.

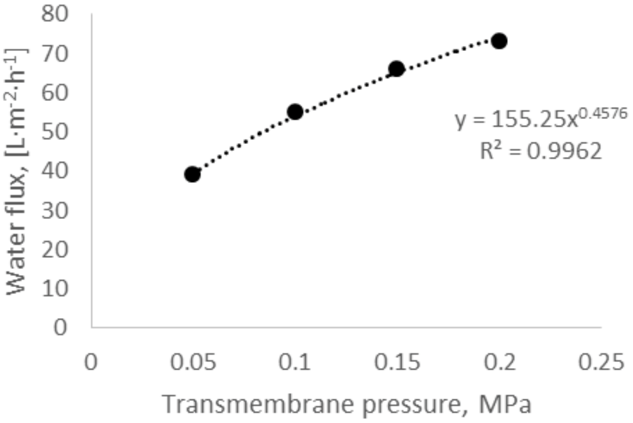

Fig. 3. Deionized water flux of PES 12 TFN 0.02 membrane as function of transmembrane pressure.

As shown in Table 3, prepared membranes exhibited much higher permeability than comparable nanocomposite membranes (data from literature). For example, membrane support in Zhang et al. [23], with no addition of nanoparticles had permeability around 1,200 (L m$^{-2}$ h$^{-1}$). In comparison, permeability of membrane PES 12 was almost four times higher (4,263.16 L m$^{-2}$ h$^{-1}$) and for PES 12 0.02 it was three times higher (3,552.63 L m$^{-2}$ h$^{-1}$). This was caused by low membrane thickness (0.1 mm) and very loose density (only 12% of polymer in membrane solution). Additionally, retention of magnesium was very low (20%) which univocally classified prepared within this study membranes as ultrafiltration membranes.

The values of porosity varied similarly to the values of the CA (Fig. 4). Unmodified by the IP process membranes, that is, PES12 and PES 12 0.02 had the highest percentage value of porosity, which in turn, affected other membrane properties. The highest porosity of membrane with low polymer concentration in the casting solution was confirmed by Hołda et al. [25], while according to a study conducted by Wang et al. [26], membranes with a very low polymer concentration in the range of 10–12 wt. % had a porosity of 87%–69%. In contrast, the membrane with a polymer

Table 3
Permeability of prepared membranes in comparison with selected literature values

| Type of membrane | Pressure (MPa) | Membrane permeability (L m$^{-2}$ h$^{-1}$ bar$^{-1}$) |
|---|---|---|
| PES 12 | 0.1 | 4,263.16 |
| PES 12 0.02 | | 3,552.63 |
| PES12 TFC | | 117.89 |
| PES 12 TFN 0.02 | | 557.89 |
| PES 12 0.02 TFN | | 507.89 |
| PES 12 0.02 TFN 0.02 | | 473.68 |
| UF membrane [23] | | 1,200 |
| NF membrane [24] | | 461 |

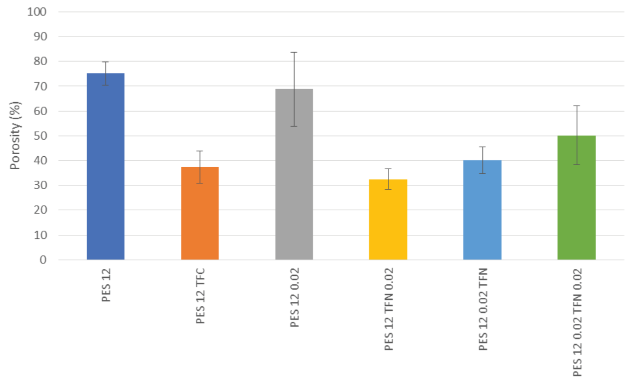

Fig. 4. Porosity of tested membranes.

concentration of 17 wt. %. had a porosity at the level of 60%. Moreover, the presence of nanotubes marginally affected membrane porosity [27].

In this work, membranes with a deposited active layer (thin-film) had significantly lower values of porosity than PES12 and PES 12 0.02 membranes. TFC/TFN membranes had relatively comparable values in the range from 32% to 50%. The decrease in porosity is linked with the skin layer that smooth the membrane surface and decreases the number and size of the pores. On the other hand, fluctuations in these values were connected with lower or higher amounts of nanotubes and also with the fact that they were located on the membrane surface or in the support.

### 3.2. Caffeine removal

In this part of the work, the removal of caffeine was studied. Caffeine belongs to the category of hydrophilic compounds, it has a low coefficient log $K_{ow}$ – thus, it does not have the affinity to adsorb on the membrane, in contrast to compounds with a high log $K_{ow}$ coefficient, for example, nonylphenol or bisphenol [3,28]. According to the membrane type, the removal degree of caffeine was different (Fig. 5). The lowest retention level was observed for membranes with the highest porosity. These were membranes (PES12 and PES 12 0.02) that were not undergone the IP process. High porosity and loose structure of these membranes affected a high flow rate through the membrane, thus a significant part of the contaminants was transported to the permeate – for both membranes, the retention level did not exceed 9%. Similarly, in many studies, composite membranes with the highest flux have the lowest retention potential [29–31].

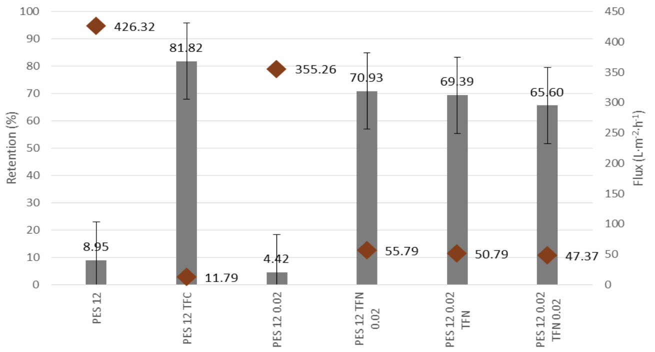

Fig. 5. Flux (diamonds) and retention (bars) of caffeine on tested membranes.

In the case of TFC membrane, very high caffeine retention was obtained at a very low flux. This may be explained by the very low porosity and relatively high hydrophobicity of this membrane. The low porosity of the TFC was attributed to the presence of the deposited thin skin layer.

TFN membranes seem to be the most favorable in the sense of retention of caffeine and permeate flux. The presence of nanocomposite in the support and in the skin layer caused a significant decrease in the hydrophobicity of the membrane and in the maintenance of optimal porosity. Both factors were responsible for a relatively high flux, at a level of 47–55 L $m^{-2}$ $h^{-1}$.

Retention level of caffeine varied from 65% to 71% for different types of TFN membranes. This is a significant improvement in the properties of membranes and it is caused by the selective skin layer and nanocomposite [4]. It was found that the place (skin layer/support) where nanotubes were located in studied types of TFN membranes did not have a significant importance for the performance of the filtration and caffeine retention. In a study presented by Pendergast et al. [32], a membrane with nanocomposite in the support definitely indicated on better properties than a TFC membrane without this addition.

## 4. Conclusions

TFN membranes were prepared by means of the introduction of CNTs (SWCNT-COOH) onto the membrane surface in the TMC solution in hexane or by introduction to the support. The study was carried out using a concentration of nanotubes of 0.02 wt. %. Their presence had a significant influence on the surface properties of the membranes and their permeability and also on the retention of selected chemical. Conducting the IP process also caused a change in the membrane properties and caffeine retention. The combination of these two factors caused the formation of a more favorable membrane with a flow rate higher than it was in the case of TFC membrane and also with the retention at a higher level than for the membrane modified only with nanotubes.

In comparison with another study, similar effectiveness was obtained only for RO membranes. In this work, tests were performed using very low pressure: 0.1 MPa. For the RO membrane, the operating pressure is much higher – it reaches values from 2 to 5 MPa. Hence, similar retention was obtained in a more economical way using safe and low-pressure conditions.

Nevertheless, the removal of caffeine was not complete, therefore the formation of a membrane with a retention potential at the level of 90% is required. That membrane should also be tested for other chemicals with different properties and for different feed solutions. For this purpose, it may be necessary to change the concentration of the polymer constituting the support layer, the amount of applied nanotubes, or the modification of the polymerization interphase process. However, the obtained membranes point to a good direction in the low energy consuming removal of micropollutants by means of membrane filtration.

## Symbols

$A$ — Membrane area, $m^2$
ACN — Acetonitrile
$R$ — Removal degree, %
CAF — Caffeine
$C_f$ — Concentration of caffeine in the feed, mg $L^{-1}$
$C_p$ — Concentration of caffeine in the permeate water, mg $L^{-1}$
DMF — *N,N*-Dimethylformamide
$\varepsilon$ — Porosity, %
$J_w$ — Water flux, $L \cdot m^{-2} \cdot h^{-1}$
$L$ — Membrane thickness, cm
$L_p$ — Water permeability, $L \cdot m^{-2} \cdot h^{-1} \cdot bar^{-1}$
$m_d$ — Weight of the dry membrane, g
$m_w$ — Weight of the wet membrane, g
MPD — *m*-phenylenediamine
NF — Nanofiltration
$\Delta P$ — Transmembrane pressure, bar
$\rho$ — Pure water density (about 0.998 g $mL^{-1}$)
PES — Polyethersulfone
RO — Reverse osmosis
SWCNT-COOH — Single-walled carbon nanotubes modified with carboxyl groups
TFC — Thin-film composite
TFN — Thin-film nanocomposite
TMC — 1,3,5-benzenetricarbonyl chloride
$t$ — Time, h
UF — Ultrafiltration
$V$ — Permeate volume, L

## Acknowledgments

This work was performed with financial support from the National Science Centre, Poland under grant no. UMO-2016/21/B/ST8/03128.

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