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Removal of effluent organic matter by purolite fluidised bed and submerged membrane hybrid system

Rana Tanveer Ahmad, Tien Vinh Nguyen, Saravanamuthu Vigneswaran*, Dang Phuong Ho

Faculty of Engineering and IT, University of Technology, Sydney (UTS), PO Box 123, Broadway, NSW 2007 Australia
Tel. +61 (2) 95142641; Fax +61 (2) 95142633; email: s.vigneswaran@uts.edu.au,

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ABSTRACT

In this study, Purolite®A500PS was used to remove effluent organic matter in a fluidised bed and submerged membrane hybrid system (SMHS). It was found that the fluidised bed purolite column can effectively remove 73% of dissolved organic compound (DOC) from synthetic biologically treated sewage effluent (BTSE). DOC removal can be reduced further, by up to 95% when the fluidised bed purolite column was combined with a treatment by granular activated carbon column. Purolite®A500PS was also used as an adsorbent in the SMHS. The results showed that critical flux of the SMHS depend on the purolite size. Critical fluxes of SMHS were 30 and 35 L/m^2.h where 0.1 g/L of purolite of sizes below 150 μm and 150–300 μm were used respectively. The removal efficiency of natural organic matter from synthetic BTSE by SMHS was a function of purolite dose. The removal efficiency increased from less than 60% to more than 70% when the purolite dose increased from 0.05g/L to 0.1g/L.

Keywords: Critical flux; Effluent organic matter, Purolite; Submerged membrane hybrid system

1. Introduction

Wastewater reuse has become the key strategy due to a problem of fresh water scarcity. One of the parameters of concern for human and environmental health is specific organic matter found in wastewater. The organic matter in wastewater may be toxic in varying degrees to plants, animals and humans. It can consume oxygen leaving oxygen-deprived state for many aquatic organisms including fish. During treatment process, organic matter can cause the problems such as membrane fouling, filter clogging and increase of chemical dose used etc [1,2]. Hence, wastewater needs to undergo several treatment processes for organics removal.

Conventional wastewater treatment methods can reduce the concentration of particulate matter such as suspended particles, parasites, bacteria, algae, fungi and a wide range of dissolved organic matter. However, the removal of persistent organic components is not high enough to meet the criteria and standards for reuse of treated water.

Membrane — an advanced wastewater treatment technique is now being successfully applied to obtain water of recyclable quality but the major challenge for membrane systems is membrane fouling. Several efforts have been made to minimise membrane fouling such as fouling control by operating the membranes at below critical flux, pre-treatment of feed water before it passes through membrane and modifying the hydrodynamic conditions of membrane surface properties. Physico-

* Corresponding author.

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chemical pretreatment such as coagulation, flocculation, adsorption or ion exchange, are the key processes to reduce the membrane fouling due to its simplicity and easy implementation [3].

Flocculation and adsorption can remove large and small molecular weight hydrophobic organic compounds. However, the biologically treated sewage effluent (BTSE) contains a significant portion of hydrophilic organic compounds [4,5]. These compounds can successfully be removed by ion exchange process.

The initial studies that demonstrated the strong potential of ion exchange resins for natural organic matter (NOM) removal appeared at the end of the 1970s [6]. The increase in ionic strength is helpful for the removal of NOM. Fettig [7] found that anion exchange resins and activated carbon could adsorb NOM effectively whereas activated alumina could only partially adsorb a fraction of NOM. Magnetic ion exchange (MIEX) resin, developed in Australia (Orica Watercare Ltd.) was found to remove natural organic matter faster than traditional ion exchange resins [8]. Other studies with MIEX showed that it can effectively remove hydrophilic compounds (70%) and hydrophobic components (55%) within a very short contact time of 20 min [9].

The purolite resins have been applied as ion exchanger in several water treatment plants. Different types of purolite resins can be used to remove toxic ions such as ammonia, nitrate, cyanide, lead, iron, cerium [10–12]. There is a limited study regarding the use of purolite exchange resins for organic matter removal from wastewaters.

In this study, fluidized bed column was used to determine the performance of Purolite®A500PS ion exchange resin in removing effluent organic matter from synthetic wastewater. The performances of purolite fluidized bed column in combination with coagulant and adsorption were also investigated. In addition, this study evaluated the improvement of submerged membrane hybrid system in terms of both effluent organic matter removal efficiency and critical flux.

2. Material and methods

2.1. Material

2.1.1. Wastewater

In this study, synthetic wastewater was used. The synthetic wastewater used in this study represents the biologically treated sewage effluent. This synthetic wastewater was first recommended by Seo et al. [13]. The DOC concentration of synthetic wastewater is about 10 mg/L and pH is 7.3. The composition of synthetic wastewater is presented in Table 1.

Table 1
Constituents of the synthetic wastewater

Compounds	Weight (mg/L)
Beef extract	1.8
Peptone	2.7
Humic acid	4.2
Tannic acid	4.2
(Sodium) lignin sulfonate	2.4
Sodium lauryle sulphate	0.94
Acacia gum powder	4.7
Arabic acid (polysaccharide)	5.0
$(NH_4)_2SO_4$	7.1
KH_2PO_4	7.0
NH_4HCO_3	19.8
$MgSO_4.3H_2O$	0.71

2.1.2. Purolite resin

Purolite®A500PS was used in this study. This purolite is a premium quality macroporous type strong base anion exchange resin with an isoporous structure. The basic features of purolite are presented in Table 2.

Table 2
Characteristics of Purolite®A500PS

Parameters	Values
Polymer structure	Microporous polystyrene crosslinked with divinylbenzene
Functional group	$R\text{-}(Me)_3N^+$
Screen size range	16–49 mesh
Moisture retention	63–70%
Total capacity	0.8 eq/L min
Specific gravity	1.04 g/mL
pH limit	0–14 (stability)
Temp. limit	100°C

In the experiment, purolite was grinded by mortar and separated by sieve into sizes below 150 μm and 150–300 μm.

2.1.3. Granular activated carbon

The physical properties of granular activated carbon (GAC) used in this study are shown in Table 3. Due to its high porosity and large surface area (1112 m^2/g GAC), it is rated as highly adsorbent from wastewater. GAC is dipped in distilled water to separate the lighter (floated) particles and dried at 103°C and desiccated before use.

2.1.4. Membrane

The membrane module used in this study was a polyethylene hydrophilic membrane (Mitsubishi-Rayon, Tokyo, Japan). The detailed specifications of the membrane provided by the manufacturer are presented in Table 4.

Table 3
Physical properties of GAC

Specification of the GAC	Estimated value
Iodine number, mg/g.min	800
Maximum ash content, %	5
Maximum moisture content, %	5
Bulk density, kg/m^3	748
BET surface area, m^2/g	1112
Nominal size, m	3×10^{-4}
Average pore diameter, Å	26.14

Table 4
Characteristics of the hollow fiber membrane module

Specification	
Material	Hydrophilic polyethylene
Nominal pore size, µm	0.1
Outer diameter, mm	0.41
Inner diameter, mm	0.27
Number of fibers	320 (16×20)
Length of fiber, cm	12
Surface area, m^2	0.1
Membrane packing density, m^2/m^3	9858
Membrane manufacturer	Mitsubishi-Rayon, Tokyo, Japan

2.2. Experimental methods

2.2.1. Fluidized bed contactor

The effect of Purolite®A500PS ion exchange resin in fluidized bed contactor (a continuous flow system) in removing organic matter was studied. Particle size of 150–300 µm was used in fluidized bed column. A predetermined quantity of 28.0 g of Purolite®A500PS resin was added in the column having a diameter of 2.0 cm and a vertical length of 1.4 m. The wastewater was pumped through the resin at a rate of 30 mL/min from bottom using a pump (fluidized velocity = 6.0 m/h) and effluent was collected from the top. The fluidized bed height was measured on measuring tape fixed on column and samples were collected on an hourly basis.

Ion exchange can remove hydrophilic organic compounds. However, the biologically treated sewage effluent (BTSE) also contains hydrophilic organic compounds. These large and small hydrophilic organic compounds can successfully be removed by flocculation or adsorption. The effect of pre-adsorption by GAC on fluidized bed packed with Purolite®A500PS was also investigated. For this purpose, 28 g of GAC was packed in a column. The schematic diagram of Purolite®A500PS fluidized bed column with and without pretreatment of GAC column is shown in Fig. 1.

2.2.2. Flocculation

The effect of flocculation after Purolite®A500PS fluidized bed was also studied. 1% of ferric chloride ($FeCl_3.6H_2O$) solution was used as flocculent. Jar test [S.E.M. (SA) PTY. Ltd. Model No. 759] was used to find the optimum dose of flocculent. The effluent from fluidized bed reactor and predetermined amount of FeCl3 were mixed rapidly for 3 min at 110 rpm, followed a slow mixing at 30 rpm for 20 min. It was then allowed settling for 30 min. Samples filtered through 0.45 µm filter for DOC analysis.

2.2.3. Submerged membrane adsorption hybrid system

The hollow fiber membrane module was submerged in a 6 L tank. A pressure gauge was mounted on the top of the membrane to measure the transmembrane pressure

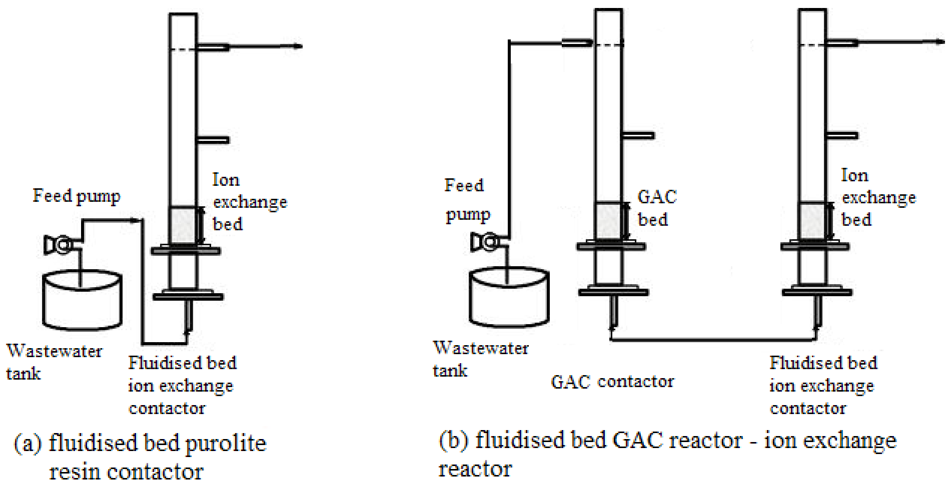


Fig. 1. Schematic diagram of Purolite®A500PS fluidized bed column.

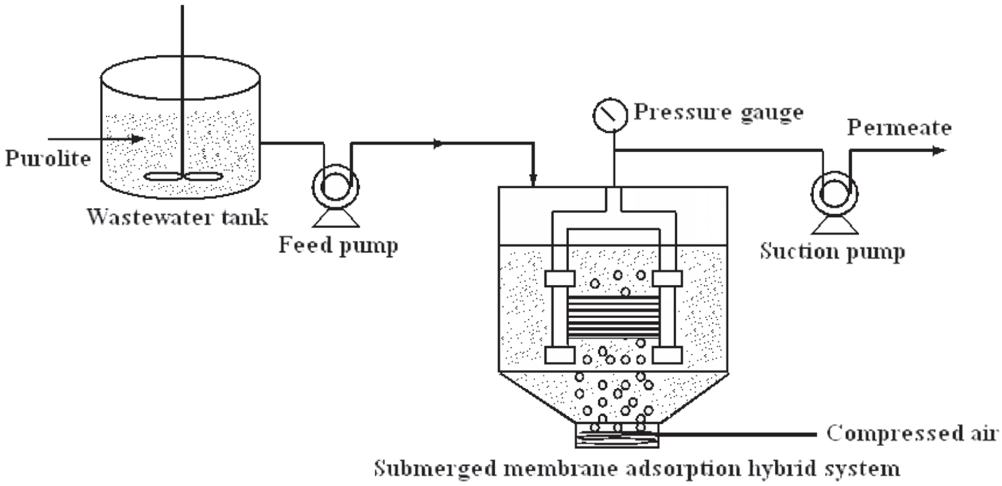


Fig. 2. Schematic of the submerged membrane reactor.

(TMP). At the bottom of the tank, a soaker hose air diffuser was connected to provide air bubbles for aeration.

Different particle sizes and predetermined doses of purolite were added to the synthetic wastewater. The solutions underwent physical adsorption for 1 h before they were filtered through the submerged microfilter. Schematic diagram of a submerged membrane reactor is presented in Fig. 2.

In this experiment, critical flux was measured quantitatively by a "flux stepping" method. The membrane reactor was operated at a fixed flux starting from 20 L/m^2.h for around 40 min and the TMP was monitored simultaneously. The flux was then increased and operated at a constant flux for another 40 min and so on. As the flux was increased gradually, the critical condition was detected where TMP no longer remained steady but increased with time. The maximum flux which showed no increase in TMP was taken as the critical flux.

2.3. Analytical methods

Dissolved organic carbon (DOC) was measured after filtering samples through 0.45 micron filter and using Multi N/C2000 TOC analyser.

3. Results and discussion

3.1. Fluidized bed experiments

3.3.1. Fluidized bed experiment with synthetic wastewater

The performance of Purolite®A500PS on removing DOC is shown in Fig. 3. The depth of Purolite®A500PS during fluidization was 35 cm. This corresponds to a detention time of 3 min through the fluidized column. The result showed that Purolite®A500PS could remove 77% DOC in a consistent manner during 7 h of experiment.

This result was comparable with the DOC removal by fluidized bed MIEX® contactor. Zhang et al. showed that MIEX® contactor could remove 75–85% DOC from synthetic wastewater when fluidization velocity was kept at 8.6 m/h [14].

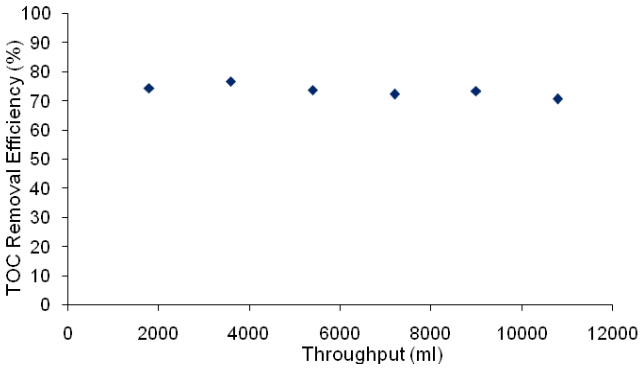


Fig. 3. Performance of Purolite®A500PS on DOC removal efficiency (synthetic wastewater, fluidization velocity = 6 m/h, initial DOC = 10 mg/L).

3.3.2. Effect of pretreatment of GAC on performance of Purolite®A500PS

The effect of GAC pre-treatment on performance of Purolite®A500PS is presented in Fig. 4. As expected, the combination of GAC column - Purolite®A500PS fluidised bed reactor could remove both hydrophilic and hydrophobic organic compounds. As a result, a higher DOC removal was achieved with 95% of DOC removal was observed (Fig. 4).

3.3.3. FeCl3 flocculation as post-treatment to Purolite® A500PS fluidized bed

Optimum dose of ferric chloride (determined by Jar-

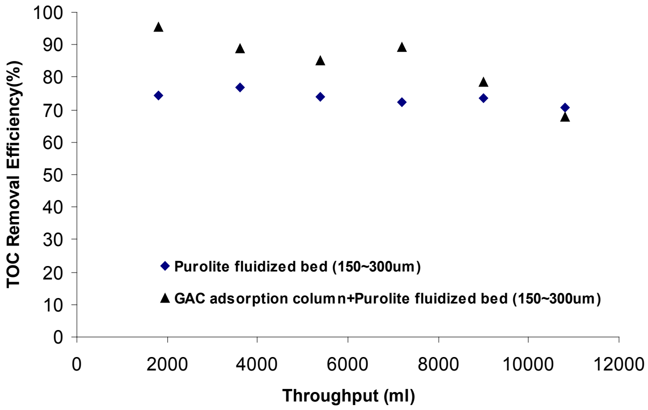
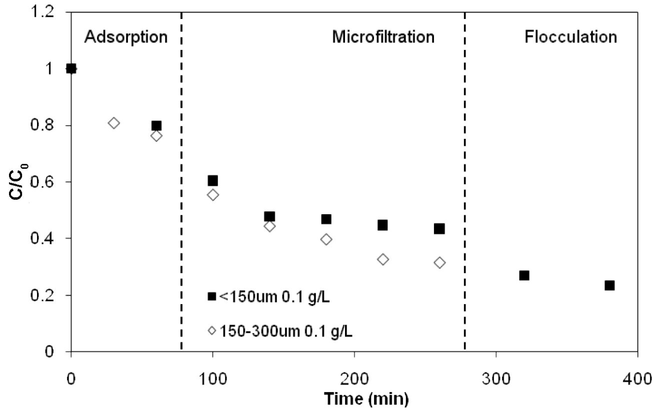


Fig. 4. Effect of GAC preadsorption on Purolite®A500PS fluidized bed (synthetic wastewater, initial DOC = 10 mg/L, fluidized velocity = 6 m/h).



test experiment) before and after the Purolite®A500PS fluidized bed are presented in Table 5. The results show that the optimum flocculent dose of $FeCl_3$ reduced dramatically from 40 mg/L to 18 mg/L when Purolite®A500PS fluidized bed was used as pre-treatment. The DOC in the effluent also reduced from 3.4 mg/L with flocculation only to 1.6 mg/L after Purolite®A500PS pre-treatment in combination with flocculation. This improvement was much better than the previous observation by Hugues et al. [15] in which the combination of coagulation prior to or after resin treatment (MIEX® resin from Orica or IRA958® resin from Rohm and Hass) only slightly improved the removal of DOC (0.2–0.3 mg/L) from surface water (about 6 mg DOC/L).

3.2. Submerged membrane adsorption hybrid system

3.2.1. Effect of particle sizes

Different particle sizes and doses of purolite were added to the synthetic wastewater. The solutions underwent ion exchange/adsorption for 1 h before they were filtered through the submerged microfilter.

In the 1st set of experiment with the submerged membrane reactor, only a small amount of Purolite®A500PS of 0.1 g/L was used. The DOC removal efficiency of system is presented in Fig. 5. Adsorption on purolite particles helped to remove about 20% of organic pollutants. The removal efficiencies were then improved significantly by microfiltration. Also, the results show that the DOC removal efficiency of size 150–300 μm was higher than that of size below 150 μm but the difference was very small. Upon filtration, the effluent was collected and treated further with ferric chloride and the improvement of 20% in the DOC removal was observed.

The adding of Purolite®A500PS in synthetic wastewater before they were filtered through the submerged membrane reactor led to increase of critical flux. The critical flux for synthetic wastewater without purolite adding was only 20 L/m^2.h whereas this value increased to 30 L/m^2.h and 35 L/m^2.h when 0.1 g/L of purolite of sizes below 150 μm and 150–300 μm were added in respectively (Fig. 6).

As can be seen from Fig. 6, the adding of purolite also helped reduce the TMP of submerged membrane system. At filtration flux 20 L/m^2.h, the TMP of submerged membrane system without adding purolite was 10.5 kPa whereas this value was only 2.5 kPa when 0.1 g/L of purolite was added in synthetic wastewater.

3.2.2. Effect of purolite doses

The purolite doses (size 150–300 μm) were varied from 0.01 to 0.25 g/L. After 1 h adsorption, the organic removal was about 10–20%. As expected, the removal efficiency was a function of purolite doses. The adsorption efficiency

Table 5
Optimum flocculent dose for wastewater with and without purolite®A500PS column as pre-treatment (28.0 g Purolite®A500PS fluidized bed operated at 6 m/h for 7 h)

Treatment condition	Optimum dose (mg/L)	Turbidity (NTU)	pH	Average effluent DOC (mg/L)
Flocculation only	40	0.97	5.61	3.4 (66%)
Purolite®A500PS + flocculation	18	0.57	5.97	1.6 (84%)

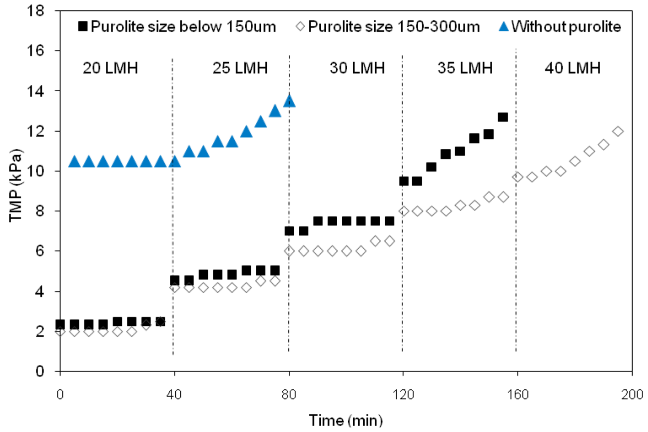


Fig. 6. The effect of purolite sizes on the filtration flux (initial TOC = 10 mg/L, purolite dose = 0.1 g/L).

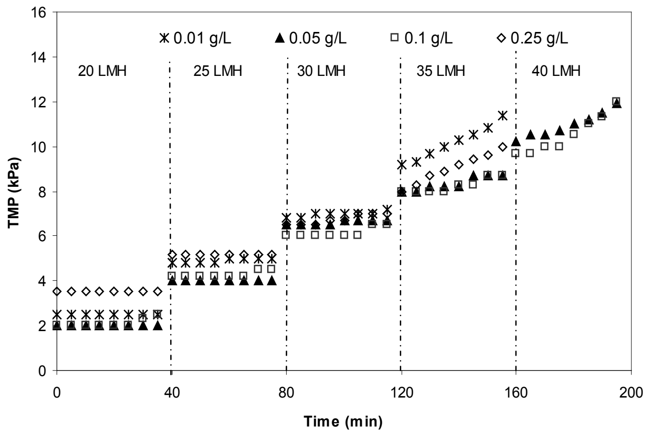


Fig. 8. The effect of doses on the filtration flux (initial TOC = 10 mg/L, purolite dose = 0.1 g/L).

at higher doses of 0.1 and 0.25 g/L were relatively similar. During the filtration, the performance of the reactor with 0.25 g/L addition of purolite remained fairly stable. On the other hand, as the dose was reduced to 0.1 g/L, the removal of organics was comparatively low at the beginning but kept increasing and reached 70% after 3 h at the flux of 30 L/m^2.h (Fig. 7).

The smaller dose on the other hand had a higher critical flux (35 L/m^2.h) (Fig. 8). Therefore, the optimal dose for the submerged reactor was selected at 0.1 g/L at the flux of 35 L/m^2.h.

4. Conclusions

Fluidized bed purolite reactor can effectively remove the organic matter from the wastewater effluent in a consistent manner and thus can help reduce membrane fouling. The combination of fluidised bed GAC reactor — ion exchange reactor could reduce more organic matter in wastewater by removing both hydrophilic and hydrophobic organic compounds. In addition, when purolite process was combined with flocculation, it was found that a greater amount of DOC was removed and there was an extensive reduction in the amount of flocculant used. The experimental results showed that the critical flux increased from 20 L/m^2.h to 35 L/m^2.h when only a small amount of 0.1 g/L purolite of size 150–300 µm was added into the synthetic wastewater. The increase of purolite dose from 0.05 g/L to 0.1 g/L led to the improvement of DOC removal efficiency from less than 60% to more than 70%.

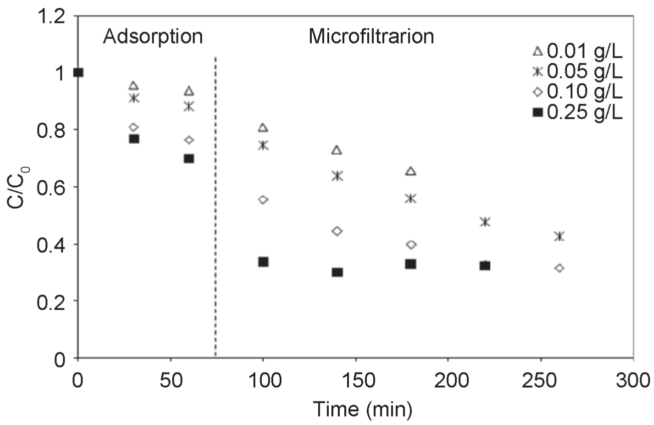


Fig. 7. TOC removal efficiency compared between different purolite doses (initial TOC = 10 mg/L, purolite dose = 0.1 g/L, purolite size 150–300 µm).

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