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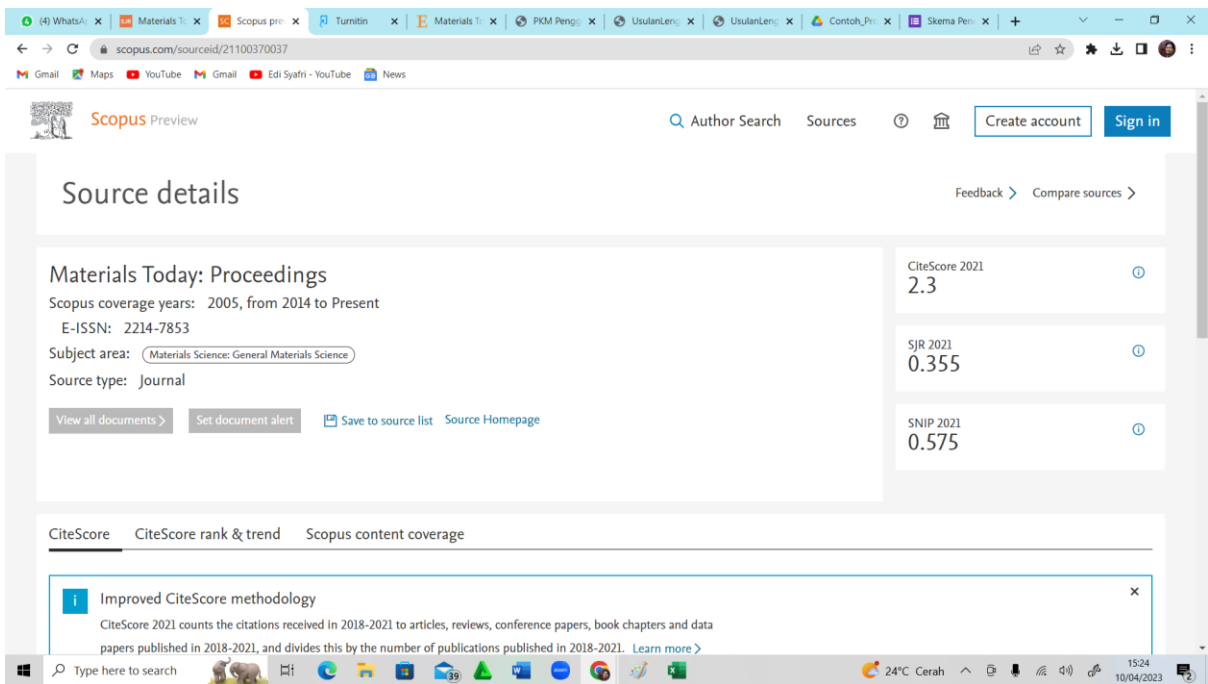
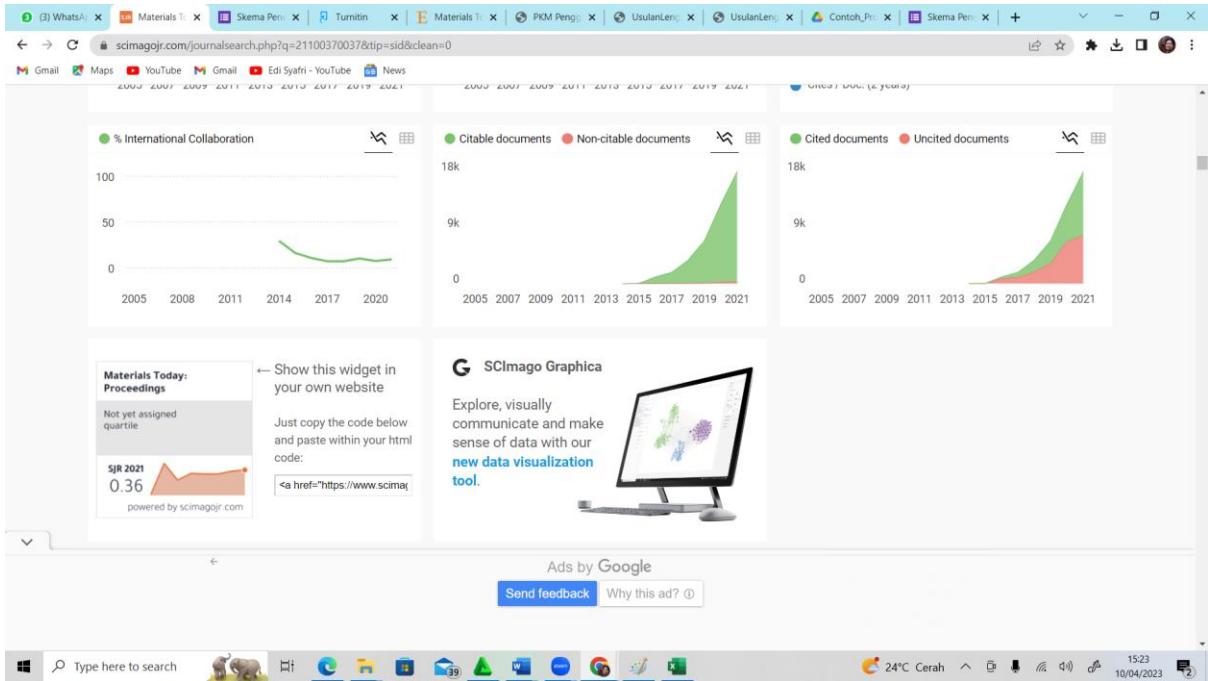


Effect of advanced oxidation process for chemical structure changes of polyethylene microplastics

Devita Amelia^a,^b, Eva Fathul Karamah^b, Melbi Mahardika^c, Edi Syafri^d, Sanjay Mavinkere Rangappa^e, Suchart Siengchin^c, Mochammad Asrofi^f

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Pages 2501-2504


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Saowapa T. Niyomthai, Pitt Supaphol, Prachaya Niyomthai

Pages 2505-2511


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Aumpava Kiatisereekul, Kittichai Fakpan

Pages 2523-2528


[Article preview](#) 

Research article [Abstract only](#)

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Natthaphon Ardhan, Pensiri Tongpadungrod, Chantaraporn Phalakornkule

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Pages 2539-2542

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Vasantha Kumar Shrvanabelagola Nagarajasetty, Govardhan Goud, Sanjay Mavinkere Rangappa, Suchart Siengchin
Pages 2543-2547

Article preview 



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ABSTRACT

Microplastic pollution in the aquatic systems is attracting continued concern globally. Microplastics can be needed a long degradation time due to the structural complexity and hydrophobicity. The advanced oxidation process (AOPs) can generate reactive oxygen such as hydroxyl (OH) radicals. These radicals initiate the plastic degradation process by changes in chemical structure with formed functional groups such as hydroxyl (O-H) and carbonyl (C=O) groups and modified C-H groups. The changes in chemical structure are the alternative to accelerate the degradation of microplastics. In this paper, polyethylene (PE) microplastics were modified the chemical structure by AOPs using the combination of ozonation and hydrogen peroxide (H₂O₂). The effect of the AOPs in samples of PE microplastics was characterized using Fourier Transform Infrared (FTIR) analysis. The results show increasing the intensity of the O-H and C=O bands and decreasing the intensity of C-H groups. The highest carbonyl index (CI) value was 1.33 at pH 12 with a flow rate of 3 L/min using the combination of ozonation and hydrogen peroxide method.

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1. Introduction

Microplastics pollution has become a global problem that causes the spread of micro-pollutants in aquatic systems. This pollution could harm ecosystems and human health. Microplastics smaller than 5 mm were sourced from primary and secondary microplastics. Primary microplastics were produced in microscopic sizes like microbeads in personal care products. Secondary microplastics were fragmentation from larger plastic of human activities [1].

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Due to structural complexity, high molecular weight, and hydrophobicity. Microplastics cannot be degraded directly by microorganisms and require a relatively long decomposition. Adding functional groups such as hydroxyl (O-H) and carbonyl (C=O) to the microplastics is the alternative to accelerate degradation. [2,3].

Advanced oxidation processes formed OH radicals, such as ozonation (O₃), UV radiation, hydrogen peroxide (H₂O₂), or combining these processes. These processes are recognized as a potential technology for degrading plastic waste [4]. According to Tian et al. (2017), ozonation of polystyrene (PS) microplastics could increase the C=O intensity [5]. As a result, ozonated samples had a higher percentage of biodegradation than non-ozonated. These results indicate that ozonation can change the chemical structure of microplastics by forming functional groups. Therefore, the hydrophobicity of microplastics can reduce and more them more susceptible to biodegradation [6].

Liu et al. (2018) found that the combination method of ozonation and H_2O_2 resulted in a higher percentage of Bisphenol-A (BPA) degradation than the single ozonation method [7]. The addition of H_2O_2 can cause more ozone to decompose into OH radicals. Uheida et al. (2021) stated that OH radicals could initiate degradation in polypropylene (PP) microplastics. Thus, the higher the concentration of OH radicals formed, the more microplastics oxidized to form functional groups. The flow rate of ozone gas influences the formation of OH radicals in the solution.

This study aims to modify the chemical structure by advanced oxidation process using ozonation and combination ozonation and hydrogen peroxide. The effect of the AOPs in samples of polyethylene (PE) microplastics characterized using Fourier Transform Infrared (FTIR) analysis. The sample used was PE microplastic with various ozone gas flow rates.

2. Experimental procedure

2.1. Materials

The materials used in this study from Merck Co., Indonesia, as H_2O_2 1 M, sulfuric acid (H_2SO_4) 10 M, sodium hydroxide (NaOH) 3 M. Aquadest, and PE microplastics with a size of 20 mesh purchased from the local market in Depok, Indonesia.

2.2. Tools

The experimental setup consists of a commercial Ozonator (H2K), flowmeter (VHS), and Erlenmeyer flask (PYREX). Other tools were needed filter paper (Whatman 41), oven (BIOBASE BOV-T50F), desiccator (DURAN), analytical balance (AND GR-200), and FTIR spectroscopy (Nicolet™ iSTM 5).

2.3. Procedure

Microplastics degradation was carried out by the ozonation method and combination of ozonation with H_2O_2 . The variations carried out were in the form of ozone gas flow rate (1, 3, and 5 L/min). 0.5 g of PE microplastics in 200 mL of pH adjusted aquadest and added 1 M H_2O_2 (for combination method). Inject ozone into the reactor for 180 min. Filter the ozonated sample using filter paper, oven for 4 h at a 115 °C, and weighed until constant.

2.4. Characterization

The FTIR spectroscopy using to quantify the O–H and C=O contents of PE microplastics from infrared spectra ranging from 4000 to 550 cm^{-1} . O–H groups were detected in wavenumber 3300–3600 cm^{-1} , C = O groups in wavenumber 1685–1760 cm^{-1} for oxidized PE microplastics, and the peak at 2721 cm^{-1} is associated with C–H bending and $-CH_3$ stretching, was used as a reference [8,9]. The carbonyl index (CI) was expressed by

$$CI = \frac{A_{C=O}}{A_{2721}} \quad (1)$$

where $A_{C=O}$ is the area of the carbonyl absorption bands (1685–1760 cm^{-1}), and A_{2721} is the area of the reference bands in the range of 2700–2750 cm^{-1} .

3. Results and discussion

The effect of ozonation and the combination of ozonation and H_2O_2 method can observe using FTIR spectroscopy to see the chemical structure changes in PE microplastics. Untreated PE microplastics (See Fig. 1) have vibrational peaks 717.00 cm^{-1}

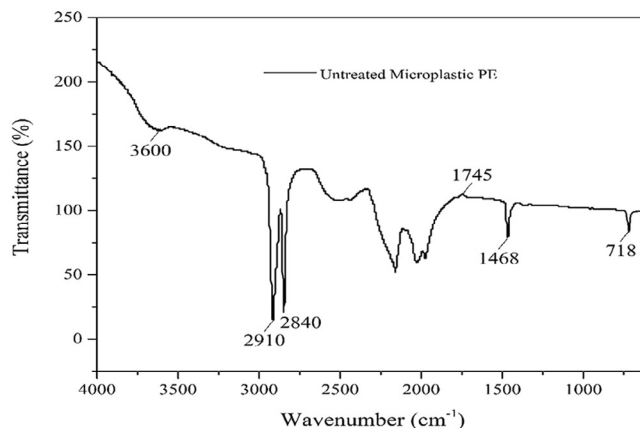


Fig. 1. Chemical structure for the untreated PE microplastics.

Table 1

The functional groups for untreated PE microplastics

Characteristics peaks	Wavenumber (cm^{-1})	
	Tofa et al	In this study
–CH ₂ rocking	710.00	717.00
	719.00	
–CH ₂ scissoring	1462.00	1460.00
	1472.00	
Symmetric –CH ₂ stretching	2847.00	2840.00
Asymmetric –CH ₂ stretching	2915.00	2910.00
C=O stretching	-	1745.00
O–H stretching	-	3600.00

(–CH₂ rocking deformation), 1460.00 cm^{-1} (–CH₂ scissoring), 2840.00 cm^{-1} and 2910.00 cm^{-1} (symmetric and asymmetric –CH₂ stretching) and 3600.00 cm^{-1} (O–H stretching). At wavenumber 1900–2200 cm^{-1} , peaks appear due to samples analyzed in a solid phase. The functional group that appeared in this study was generally the same as the study results from Tofa et al (2019) for untreated PE (Table 1). Fig. 2

3.1. Effect of the ozonation method for chemical structure changes in the PE microplastics

Figure 2 shows the FTIR results for the PE microplastics after the ozonation method at pH 12 with ozone gas flow rates of 1, 3, and 5 L/min for 180 min. Degradation of PE microplastics is character-

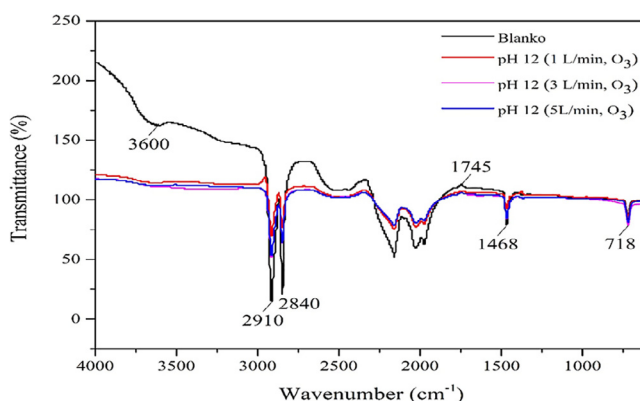
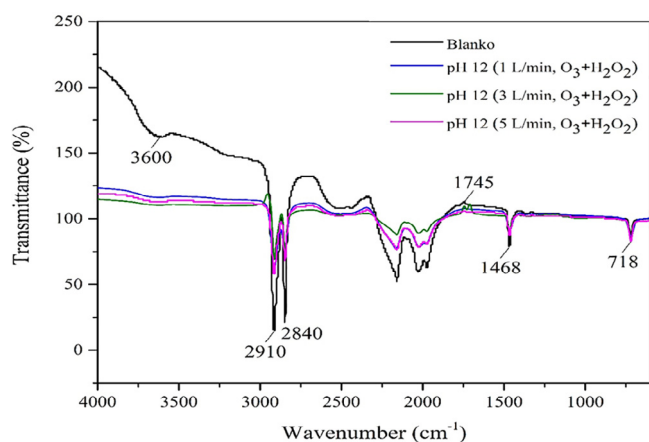


Fig. 2. Effect of the ozonation method for chemical structure changes in the PE microplastics (pH 12, 180 min).

Table 2

The CI values and changes in PE microplastics functional group absorption area on FTIR for variation of ozone gas flow rate after the ozonation method (pH = 12, 180 min).

Flow Rate (L/min)	CI	Transmittance (%)			
		–CH ₂ rocking (718 cm ⁻¹)	–CH ₂ scissoring (1468 cm ⁻¹)	–CH ₂ stretching	
				Symmetric (2840 cm ⁻¹)	Asymmetric (2910 cm ⁻¹)
Untreated	0.33	83.600	78.948	24.800	18.200
1	0.60	85.400	92.800	77.500	69.800
3	0.67	78.838	84.294	63.584	52.059
5	0.67	80.910	84.702	64.010	53.364

**Fig. 3.** Effect of the combination ozonation and H₂O₂ method for chemical structure changes in the PE microplastics (pH 12, 180 min).

ized by increasing intensity in the O–H and C=O bands with wavenumber at 3600 cm⁻¹ and 1715 cm⁻¹ (See Figure 2). The results showed that the ozone gas flow rates increase causes the intensity of the O–H and C=O bands to increase during ozonation, characterized by a decrease in the percentage of transmittance [9,10,11].

The CI values were used to characterize the degree of oxidation of PE microplastics that defined the ratio between C=O with C–H bending and –CH₃ stretching bands [8]. The results for the ozonation method (See Table 2) showed an increase in carbonyl adsorption for PE microplastics with increasing ozone gas flow rates. The highest CI values were shown when the ozone gas flow rates were 3 and 5 L/min. These results indicate that the degree of oxidation increase when the ozone gas flow rates increase, thus increasing the intensity of the carbonyl index value. The degradation of PE microplastics also affects the intensity of the –CH₂ rocking, –CH₂ scissoring, and –CH₂ stretching bands for each variation of the ozone gas flow rate (See Fig. 1). Table 2 also shows the intensity of –CH₂ rocking, –CH₂ scissoring, and –CH₂ stretching bands decrease because increasing ozone gas flow rate will be increased ozone production. The more ozone production in the solution so that the more ozone was decomposed to form OH radicals to oxidize the carbon chains present in the polymer [12,13].

Table 3The CI values and changes in PE microplastics functional group absorption area on FTIR for variation of ozone gas flow rate after the combination method of ozonation and H₂O₂ (pH = 12, 180 min)

Flow Rate (L/min)	CI	Transmittance (%)			
		–CH ₂ rocking (718 cm ⁻¹)	–CH ₂ scissoring (1468 cm ⁻¹)	–CH ₂ stretching	
				Symmetric (2840 cm ⁻¹)	Asymmetric (2910 cm ⁻¹)
Untreated	0.33	83.600	78.948	24.800	18.200
1	0.60	86.742	91.456	77.708	62.702
3	1.33	83.736	89.870	73.776	68.967
5	0.60	83.760	92.600	81.490	70.530

3.2. Effect of the combination of ozonation and H₂O₂ method for chemical structure changes in the PE microplastics

Fig. 3 shows the FTIR results for the microplastics polyethylene after combining of ozonation and H₂O₂ method at pH 12 with ozone gas flow rates of 1, 3, and 5 L/min for 180 min. The addition of H₂O₂ can accelerate the rate of decomposition of ozone into OH radicals. The more concentration of OH radicals in the solution, the more PE will be oxidized by the OH radicals [12,14].

The chemical structure changes are same as the ozonation method results. The CI values in the combination of ozonation and H₂O₂ methods (Table 3) showed an increase in carbonyl absorption for PE microplastics through the flow rate of ozone gas increase. However, the highest CI value was shown when the ozone gas flow rate was 3 L/min. At a flow rate of 5 L/min, the CI value should be higher than the 3 L/min flow rate because an increases ozone production. The more ozone production in solution so that the more ozone decomposed to form OH radicals to oxidize the carbon chains present in the polymer (See Fig. 4) [12]. At the flow rate of 5 L/min, the OH radicals that play a role are more important in breaking the carbon chains than producing new functional groups. The intensity of the C–H absorption area was smaller than untreated PE microplastics (See Table 3).

Table 3 shows the transmittance of –CH₂ rocking, –CH₂ scissoring, and –CH₂ stretching bands of PE microplastics overall increased from the untreated PE microplastics. The highest transmittance value was at a flow rate of 5 L/min compared to variations in other flow rates. The transmittance in the C–H absorption area increased because the absorption intensity was decreasing [15]. At the combination of ozonation and H₂O₂, the lowest C–H absorption intensity produced the flow rate of 5 L/min, and the highest CI values produced the flow rate of 3 L/min. Reviewing the lowest C–H absorption intensity and the highest CI values in the combination method at pH 12 with an ozone gas flow rate of 3 L/min showed effective results in degrading PE microplastics. It is known that in the single ozonation method, the best results are obtained at pH 12 with an ozone gas flow rate of 5 L/min and in the combination method of ozonation and H₂O₂ at pH 12 with an ozone gas flow rate of 3 L/min. The comparison of the absorption intensity of the C–H group in the two methods can be seen in Table 4 to find out the effective results between the two methods used.

Table 4 shows the highest CI values and the lowest C–H absorption intensity using ozonation and the combination. The combina-

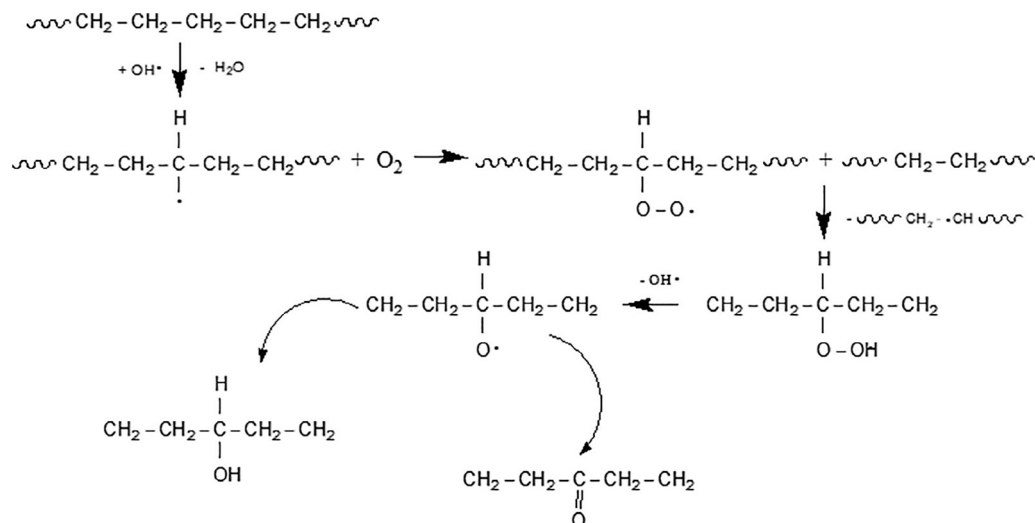


Fig. 4. PE microplastics degradation mechanisms.

Table 4

The Comparison of CI values and functional groups of PE microplastics absorption area in FTIR for best results in all method configurations (pH = 12; 180 min).

Method	Flow Rate (L/min)	CI	Transmittance (%)			
			-CH ₂ rocking (718 cm ⁻¹)		-CH ₂ scissoring (1468 cm ⁻¹)	
			-CH ₂ stretching			
				Symmetric (2840 cm ⁻¹)	Asymmetric (2910 cm ⁻¹)	
Untreated		0.33	83.600	78.948	24.800	18.200
Ozonation	5	0.67	80.910	84.702	64.010	53.364
Ozonation + H ₂ O ₂	3	1.33	83.736	89.870	73.776	68.967

tion method (3 L/min; pH 12) was more effective than the ozonation method in degrading PE microplastics because more OH radicals formed. The OH radicals initiated the degradation of PE microplastics into simpler and more hydrophilic intermediates, which were indicated by the formation of O–H and C=O bands or by increasing the value of CI [2,3]. The simple structure and hydrophilic character are expected to increase the activity of microorganisms to degrade the polymer later [16,17,18].

4. Conclusions

In this work, the combination method of ozonation and H₂O₂ had a synergistic effect in degrading PE microplastics. It shows structural changes in microplastics, namely increasing the intensity of the O–H and C=O bands where the carbonyl index value was 1.33 at pH 12 with a flow rate of 3 L/min and followed by a decrease in the intensity of the C–H groups. The simple structure and hydrophilic character are expected to increase the activity of microorganisms to degrade the polymer later. This method is recommended as a pretreatment before the biodegradation process.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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