

Removal of PAHs from leachate using a combination of chemical precipitation and Fenton and ozone oxidation

H. Ates and M. E. Argun

ABSTRACT

In this study, six emerging pollutants, belonging to the polycyclic aromatic hydrocarbons (PAHs) group, found in landfill leachate were investigated for their removal by sequential treatment processes including chemical precipitation (CP), Fenton oxidation (FO) and ozone oxidation (OO). Each treatment process was run under different conditions using an experimental design program. Optimization of both CP and FO processes was designed based on the measured values of the residual chemical oxygen demand (COD) of the samples analyzed. The analysis of variance test was applied to the obtained results for determination of statistical significance of the model. Removal efficiencies of micropollutants were determined in the optimal conditions both for CP and FO processes. Samples obtained after these processes were treated with different pH and ozonation times for observing the performances of ozonation on micropollutant removal under different operating conditions. In this study, the removal of acenaphthylene, acenaphthene, fluorene, phenanthrene, fluoranthene and pyrene micropollutants was investigated. The values obtained for PAHs in leachate were determined to be above 10 ppb. In the CP process, the removal efficiencies for PAHs were ranged between 6% and 40% except for pyrene. Removal efficiencies of all micropollutants with FO were over 70% except for fluorene (55%). The removal efficiencies of the investigated micropollutants were 80–100% as a result of consecutive treatment processes including CP, FO and OO respectively.

Key words | leachate treatment, micropollutants, polycyclic aromatic hydrocarbons (PAHs)

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INTRODUCTION

The presence of micropollutants in leachate

In the disposal of domestic solid waste, landfills are still the most widely used method worldwide.

However, leachate generated in the landfills is a significant problem due to the high content of organic contaminants. In many countries, separation of wastes is not common; therefore the characterization of leachate is highly variable (Robinson & Maris 1985). Leachate derived from both household waste and hazardous wastes found in landfills poses a major threat to surface and groundwater due to the variety of pollutants it contains (Christensen *et al.* 1994). Many micropollutant sources such as polycyclic aromatic hydrocarbons (PAHs), phenolic compounds, plasticizers, halogenated hydrocarbons, personal care products, drug residues and pesticides have been identified in landfill leachate (Kjeldsen *et al.* 2002). Several studies

have revealed that leachate can be treated with anaerobic and aerobic processes. Biological processes are suitable for the treatment of young leachate having a high 5-day biochemical oxygen demand to chemical oxygen demand (BOD₅/COD) ratio. However, these processes are not effective for the treatment of leachate having low BOD₅/COD ratio or high concentration of toxic compounds (Percheron *et al.* 1997; Ye *et al.* 2011; Lei *et al.* 2016). Some existing resistant organic contaminants in leachate can form complexes with metals which may increase solubility and toxicity of organic contaminants. For this reason, especially in recent years, advanced treatment technologies such as advanced oxidation have become more popular for treating these pollutants (Luo *et al.* 2014). By means of advanced oxidation methods it is possible to increase their biodegradability and/or remove such contaminants in higher removal rates (Li *et al.* 2017). In studies found in literature, removal of

doi: 10.2166/wst.2018.378

micropollutants from domestic and synthetic wastewater is generally carried out by various treatment methods such as activated carbon adsorption (Ocampo-Pérez *et al.* 2012), membrane filtration, chemical oxidation (Dempsey 1998) and catalytic ozonation (Li *et al.* 2017). However, studies on the monitoring of micropollutants in leachate are very limited.

One of the most important aims of this study is investigating the removal of six emerging micropollutants, belonging to the PAH group, found in landfill leachate by consecutive treatment processes including chemical precipitation (CP), Fenton oxidation (FO) and ozone oxidation (OO). Another important point is determining the optimum operating parameters for CP and FO (for the maximum COD removal rate). Besides these, investigating the effects of reaction time and pH on the removal of PAHs by the ozonation process with response surface methodology is the last but significant part of this study.

MATERIALS AND METHODS

Water samples

In this study, the leachate of Aslim landfill of Konya province, Turkey, was used. The landfill of Aslim has an area of approximately 28 hectares. Since 2016, rehabilitation work has been carried out on the site which has been closed for waste deposition. However, the landfill area has still been producing leachate. The daily amount of produced leachate in the field is nearly 150 m³/d, which is stored in concrete pools.

Standards and chemicals

All standard chemicals are supplied from Accustandard and Supelco. In this study, six PAHs (mixed standard), acenaphthylene (Ac), acenaphthene (Ace), fluorene (Fl) phenanthrene (Ph), fluoranthene (Flu) and pyrene (Py), which are also characterized as priority pollutants by the EU Water Framework Directive, were investigated. Acenaphthene-d10 and phenanthrene-d10 were used as internal standard. Accuracy of the measured data has been determined by obtaining recovery values of the surrogate standard including 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d5, 2-fluobiphenyl, and p-terphenyl-d14. Obtained recovery values of surrogate standards were between 89% and 129%. Silica gel (Fisher Scientific, USA) and sodium sulfate (Merck) were both used in the clean-up procedure, and dichloromethane (Merck) was used for extractions. H₂SO₄

and NaOH were used to adjust the pH of samples in the range of 3–8. H₂O₂ (Merck) and FeSO₄·7H₂O (Sigma-Aldrich) were used in FO, and FeCl₃ (anhydrous form, Merck), used in CP. All chemicals were of analytical purity and the solutions were prepared with deionized water.

Instrumental analysis

The samples were extracted by liquid–liquid extraction method (EPA 3510C; US Environmental Protection Agency (1996)) and then obtained extracts were analyzed by a gas chromatography–mass spectrometry (GC-MS) instrument (Agilent 7890B GC & 5977A MSD). To measure the recovery values of the applied method, mixed surrogate standard was added to the samples before extraction. The extracts were concentrated on a rotary evaporator with operating conditions of 40 °C and 160 rpm. The concentrations of organic compounds were determined using standard calibration curves. For calibration, standard solutions were prepared (concentration ranges: Ac 7.5–2,368 ppb; Ace 3.7–1,184 ppb; Flu 0.7–237 ppb; Py, Fl and Ph 0.4–118 ppb) by adding different amounts of PAHs standard in 1,000 mL ultrapure water. Standard solutions were analyzed after extraction and calibration graphs were created. Although the concentration of some micropollutants in the treated samples was found to be below the limit of quantification (LOQ), the obtained values from the calibration equation are also given in Table 3. Measured concentrations even below LOQ were used to calculate removal efficiencies. Otherwise, accepting as zero the concentrations smaller than LOQ value may lead to an incorrect calculation of removal efficiencies.

The GC capillary column (HP-5MS 30 m × 0.25 mm × 0.25 μm, from 60 °C to 325 °C) was injected with 1 μL of sample volume via an auto-sampler. High purity (99.999%) He gas was used as a carrier gas and the flow rate was 1.2 mL/min. Temperatures of the port inlet and detector were set as 250 °C and 300 °C, respectively. After remaining stable for 2 minutes at starting temperature (40 °C), the temperature of the column was increased by 10 °C/min to final temperature (320 °C). After reaching 320 °C, the temperature of the column remained constant for 2 minutes. SIM/SCAN mode was selected for the analysis of the samples. The working temperature of the ion source (EI) in the MS part was 230 °C, quadrupole temperature was 150 °C and the EI voltage was 1,723 eV. Laboratory Fortified Blank sample was extracted and analyzed by GC for determination of the LOQ, which was determined by 10*S/N (signal:noise ratio).

Experimental treatment conditions

Design Expert Version 9.0 software program was used for experimental designs and statistical evaluations. Experiments were carried out in batch reactors using 1 L sample volume. Using the Design Expert (version 9.0) program, 13 and 20 experiments were planned for CP and FO respectively. The independent variables for CP were FeCl_3 dose and pH; for FO, Fe(II) , H_2O_2 dose and pH were used as independent variables.

Raw leachate was pretreated using optimum conditions which were determined considering the COD parameter for CP and FO. Then, 11 OO experiments were performed for different pH values and reaction times. The capacity of the ozone generator was 13 g/h and waste ozone which did not enter the oxidation was titrimetrically measured in a 10% potassium iodide (KI) solution. Because of a bubbling problem occurring in the ozonation process of the leachate, the foam formed during the ozonation phase was destroyed by the addition of chemicals in some other studies (Tizaoui *et al.* 2007). However, in this study, chemicals were not used due to the additional cost and the pollution that would be caused by the added chemical substances. For this reason, the circulation of formed foam was provided through a peristaltic pump by using two batch reactors which have 2 L volume. Because of the bubbling problem, 0.5 L sample was used for both reactors. In the first reactor more foam and waste ozone was produced compared to the second one and therefore foam and waste ozone were

transferred to the second reactor by a funnel placed inside the first reactor. There was also another pump to recirculate some ozone and foam from the second reactor to the first reactor. The schematic representation of the system is illustrated in Figure 1.

Elimination of micropollutants and removal of COD were observed for different treatment processes and changing ozonation conditions based on pH and time durations. Statistical significance of the model was assessed by subjecting the obtained results to the analysis of variance (ANOVA) test.

RESULTS AND DISCUSSION

Effects of chemical precipitation and Fenton oxidation

According to the obtained results from the ANOVA test, it was found that both independent variables (pH and FeCl_3) were important for COD removal in CP. However, it is understood from the p -values that the pH was more effective. In the FO process, from three independent variables, Fe and H_2O_2 doses have a significant relationship with COD removal ($p \leq 0.05$) (Table 1). To indicate accuracy of the data, standard deviation (SD), coefficient of variation (CV) and adequate precision were obtained as 0.69, 16.5% and 8.77 for CP and 0.52, 25.7%, and 10.94 for FO, respectively. AP measures the S/N ratio. A ratio greater than 4 indicates an adequate signal and shows that the model can be used to

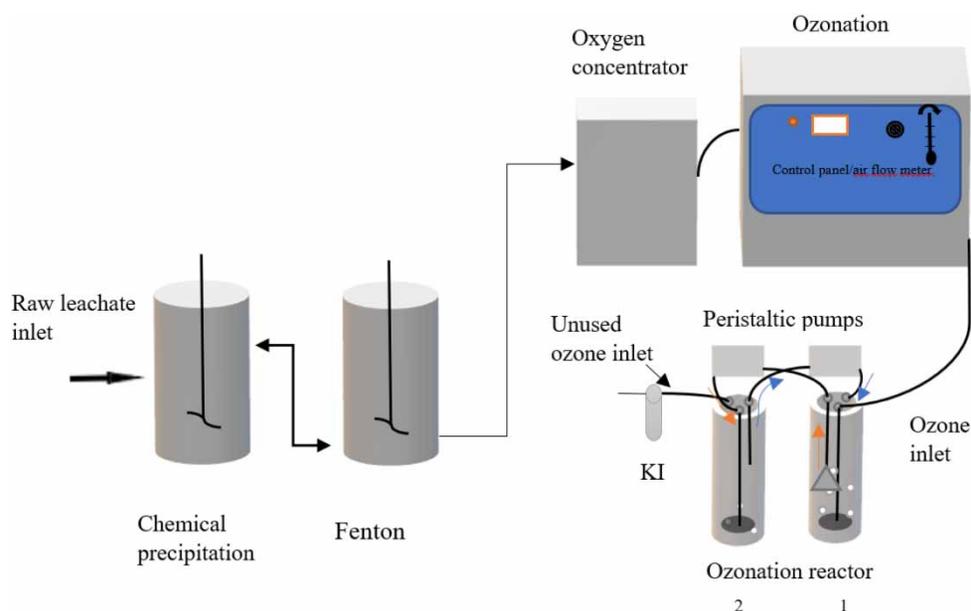


Figure 1 | The combined treatment process.

Table 1 | ANOVA results for the COD removal by chemical precipitation (CP) and Fenton oxidation (FO)

	CP			FO			
	F-value	p-value		F-value	p-value		
Model	7.07	0.0116	significant	Model	10.14	0.0006	significant
A – FeCl ₃	15.76	0.0054		A – FeSO ₄	4.37	0.0528	
B – pH	7.54	0.0287		B – pH	0.0992	0.7569	
				C – H ₂ O ₂	25.95	0.0001	
Lack of fit	5.89	0.0598	not significant	Lack of fit	1.71	0.2882	not significant

navigate the design space. According to the obtained results, the model for both treatment processes is statistically significant. However, the model is showing a quadratic distribution for CP and linear distribution for FO (Figure 2). The optimum operating conditions for the obtained models were determined for CP as pH: 5.5, dose of FeCl₃: 3.445 g/L; and pH: 3, H₂O₂: 7.84 g/L and FeSO₄·7H₂O: 1.579 g/L for FO.

Lower removal efficiencies were obtained for PAHs and COD by the CP process. Therefore, rather than being a main treatment process CP is generally preferred to reduce the organic load and to make the subsequent treatment processes more efficient (Poznyak *et al.* 2008; Wu *et al.* 2011). The log K_{ow} (octanol/water partition coefficient) value is an important factor for the adsorption of organic pollutants onto the precipitate (Zhou 2011). Compounds with log K_{ow} values between 2.5 and 4.0 tend to adsorb at a moderate level, but log K_{ow} higher than 4.0 means compounds tend to adsorb at a high level.

Log K_{ow} values for Ace and Ac were 2.4–4.0 but for Flu and Py compounds were higher than 4.0. The removal efficiencies of CP of these two compounds were found to be

higher than the others, which can be related to the higher log K_{ow} values (Table 2). The removal efficiency of all pollutants except Fl (55%) in FO was over 70%. While the COD removal efficiency was 30% for the CP, total removal efficiency after the FO process was 64%. Table 2 shows the treatment efficiencies obtained for different treatment stages.

Effects of ozone oxidation

OO increased the removal efficiencies of micropollutants up to 32% after FO. As a result of this, in order to better observe the effectiveness of ozonation, we recommended that ozonation should be applied after CP. It was also observed that concentration of some micropollutants such as Ace and Pyr increased after OO. The reason for this situation can be the conversion of more complex organic compounds to the simpler structured components by oxidation, which is compatible with some studies found in literature such as Silva *et al.* (2013).

Removal efficiency of COD was 64% by the pretreatment process including CP and FO. After OO, this ratio increased

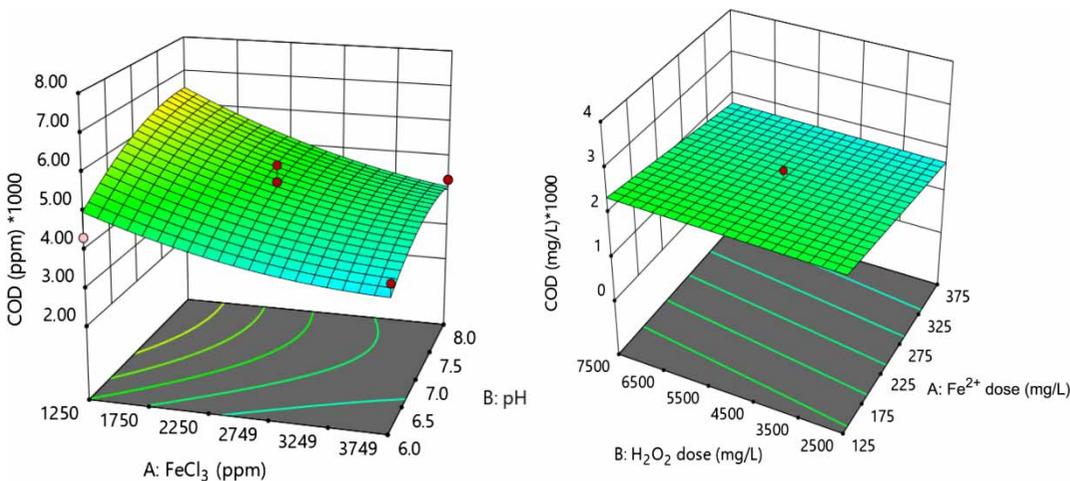
**Figure 2** | The effects of independent variables on the remaining COD for CP and FO.

Table 2 | Concentrations of organic micropollutants detected in the leachate in various treatment effluents

Micropollutants	Raw leachate	CP		FO		Total removal %
		Residual	Removal %	Residual	Removal ^a %	
Acenaphthylene, ppb	58.47	47.60	19	12.62	73.4	78
Acenaphthene, ppb	25.40	16.56	35	4.96	70.0	80
Fluorene, ppb	16.93	11.49	32	7.67	33	55
Phenanthrene, ppb	12.52	11.71	6	1.16	90	91
Fluoranthene, ppb	10.09	6.12	39	0.97	84	90
Pyrene, ppb	13.54	4.40	68	0.13 ^b	99	99
COD, ppm	6,384	4,480	30	228	50	64
BOD, ppm	450	200	55	40	72	91

^aThese values calculated between chemical precipitation and Fenton oxidation.

^bThis value determined as below calibration (<0.4 ppb).

up to 98%. After the sequential treatment process in terms of COD concentration remaining in the samples, effluent COD of the treated sample was decreased to below 1,000 ppm, which met the regulatory legislation of Turkey for treated leachate discharge to sewage systems. In literature there are some studies which achieved 71–89% removal efficiencies only using ozonation for compounds belonging to the PAH group (Ning *et al.* 2015). However, as the leachate has a higher organic content compared to other wastewater types (domestic, industrial wastewater, etc.), pretreatment and reduction of organic load is important for decreasing the organic content below the discharge standards. Due to the old age of the leachate taken from the studied area, the BOD₅/COD ratio was

found as 0.07. In some studies, the BOD₅/COD ratio ranges from 0.02 to 0.24 (Robinson 1995; Kruempelbeck & Ehrig 1999). It is known that when the leachate is in the acidogenic phase, all the existing contaminants are at high concentrations but in the methanogenic phase it is more stable and less biodegradable (Kjeldsen *et al.* 2002). In addition to higher COD treatment efficiency, biodegradability has been enhanced through advanced oxidation processes. The BOD₅/COD ratio increased from 0.17 (after FO) to 0.32 after OO. It was found that biodegradability increased at high reaction times of the ozonation process and pH values (Table 3).

The results of ANOVA for the effects of pH and ozone time on COD and PAHs removal is shown in Table 4.

Table 3 | PAHs removal efficiencies using ozone at different pH and times (13 g/h ozone dose)

Time (min)	pH	Ace (%)	RC, ppb	Ac (%)	RC, ppb	Fl (%)	RC, ppb	Ph (%)	RC, ppb	Flu (%)	RC, ppb	Pyr (%)	RC, ppb	COD Rem. Ef.
		78 ^a	12.62	80 ^a	4.96	55 ^a	7.67	91 ^a	1.16	90 ^a	0.97	99 ^a	0.13	64 ^a
50	3.0	77	13.26	83	4.37	83	4.66	92	1.03	92	0.91	100	n.d.	81
20	4.0	63	21.36	83	4.23	83	4.23	86	1.03	86	1.7	99	0.13	81
80	4.0	78	12.61	85	3.88	81	3.29	92	0.94	91	0.95	99	0.13	90.4
8	6.5	79	12.43	84	4.04	76	4.07	89	1.42	90	0.97	97	0.45	81
92	6.5	80	11.97	85	3.91	88	2.08	84	2.02	89	1.11	96	0.61	98
50	6.5	79	12.00	85	3.93	88	2.06	91	1.1	91	0.94	99	0.13	93
50	6.5	80	11.73	85	3.84	87	2.18	93	0.85	91	86	100	0.07	89
50	6.5	80	11.86	83	4.22	87	2.23	90	1.22	91	0.87	100	0.09	90
20	9.0	76	13.74	84	4.00	^b n.a.		91	1.14	91	0.88	100	0.07	86
80	9.0	79	12.41	83	4.20	85	2.5	91	1.1	91	0.89	96	0.49	90.4
50	10.0	80	11.85	85	3.83	^b n.a.		91	1.19	91	0.93	99	0.14	93

RC, residual concentration; Rem. Ef., removal efficiency.

^aObtained removal efficiencies after pretreatment.

^bNot available.

Table 4 | Effects of pH and ozone time on the removal of organic COD and micropollutants

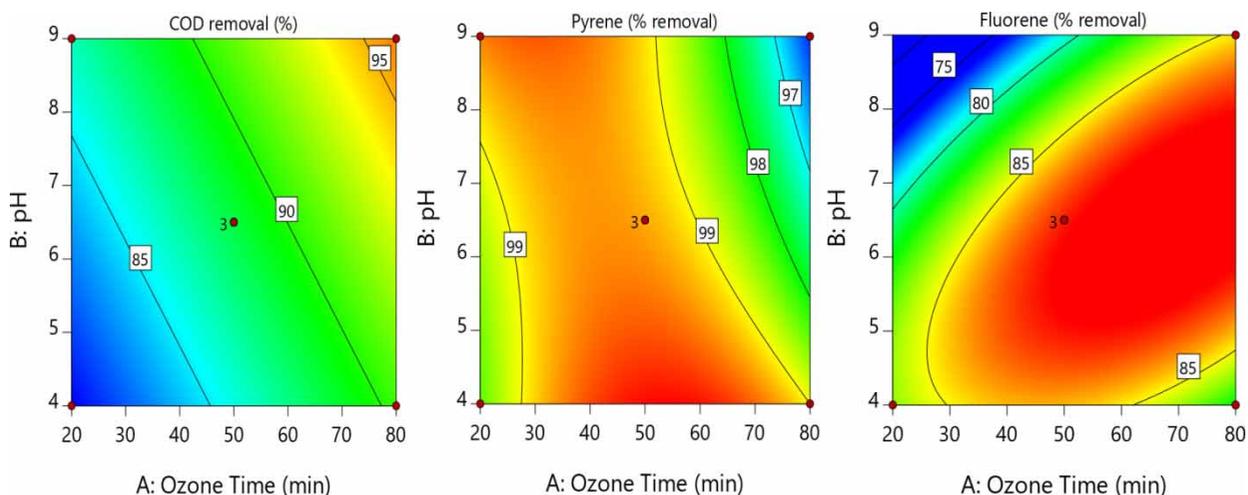
ppb	pH		Ozone time		Model		Model significance
	F-value	p-value	F-value	p-value	F-value	p-value	
COD (ppm)	6.25	0.037	19.21	0.002	12.73	0.003	significant
Py	3.56	0.12	8.96	0.03	10.11	0.012	significant
Fl	13.14	0.0361	62.76	0.0042	23.26	0.0132	significant
Ace	2.43	0.16	2.75	0.14	2.43	0.15	not significant
Ac	0.03	0.87	1.02	0.35	1.4	0.32	not significant
Ph	0.84	0.13	0.023	0.89	1.34	0.38	not significant
Flu	0.67	0.44	0.66	0.44	1.29	0.35	not significant

There was a statistically significant relationship between variables and Fl and Py. Also, the distributions were found as quadratic for both analytes. ANOVA results in terms of COD removal were found to be similar for OO and FO (Figure 3). SD, CV and AP were obtained as 195, 26.3% and 9.32, respectively.

CONCLUSION

In this study removal of six PAH micropollutants was investigated using combined treatment of CP, FO and OO respectively. CP was mainly used to reduce high organic contents (COD up to nearly 6,500 mg/L) of leachate by up to 30%, and it was observed that some micropollutant were also eliminated significantly at the same time (especially Py with a removal efficiency of 68%). FO as a second treatment after CP was used with the aim of breaking

down the hardly biodegradable PAH compounds. As a result of this process, all selected micropollutants were removed by more than 50% except Fl (33%). Also, Py was almost removed completely. Before OO, optimum operating conditions were determined based on residual COD values for CP (pH: 5.5, FeCl₃: 3.445 g/L) and FO (pH: 3, H₂O₂: 7.84 g/L and FeSO₄·7H₂O: 1.579 g/L) treatment methods. In the OO process, different operating conditions (pH and experiment durations) were applied in order to observe the removal rates of micropollutants. Additional increase in removal efficiencies of up to 32% was achieved with OO after FO. It can be concluded from these results that both FO and OO processes were demonstrated to be effective for degradation of the refractory pollutants in the leachate after being treated by a chemical process. Removal efficiencies between 80% and 100% were obtained for the selected micropollutants by combined treatment of CP, Fenton and ozonation. It can be said that this combined treatment

**Figure 3** | Distribution charts of COD, Fl and Py according to their removal efficiency.

method is a promising approach for eliminating the micropollutants.

Future outlook

Other compounds belonging to the PAH group and diverse subgroups of micropollutants such as pesticides, pharmaceuticals and phthalates should be investigated within this treatment approach. In addition, in order to determine the effectiveness of OO more accurately, ozonation studies should be carried out after CP or alone.

ACKNOWLEDGEMENTS

This research was supported by Selcuk University Scientific Research Fund (16101012). Authors also thank the Advanced Technology Research & Application Center (SU-ILTEK) for its contribution.

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First received 7 June 2018; accepted in revised form 17 August 2018. Available online 28 August 2018