Electronic Supplementary Information

Advanced oxidation processes for the removal of [bmim][Sal] third generation ionic liquid: Effect of water matrices and intermediates identification

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Table S1. ICP-MS scan signal intensities for different types of water.

Proposed structures of intermediates for the photolitic degradation of [bmim][Sal]

Table S2. Proposed structures of intermediates for the photolitic degradation of [bmim][Sal] with the relative abundance of their product ions.

Fig. S1 Evolution of various ionic liquid (c_0 = 0.38 mmol L^{-1}) degradation after 60 min in presence of SS radiation. Applied AOPs: 7.2Fe/TiO_2 (1.67 g L^{-1}) + 45 mmol L^{-1} H_2O_2 + 70 µL h^{-1} H_2O_2 at pH 2.8. $[TBA]^+$ and Cl^- degradation could not be monitored by using HPLC-DAD technique.

Table S1. ICP-MS scan signal intensities for different types of water.

Origin of water samples	Element											
	B	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Cu
	Counts per second											
	$\times10^3$	$\times10^7$	$\times10^6$	$\times10^3$	$\times10^5$	$\times10^3$	$\times10^3$	$\times10^3$	$\times10^4$	$\times10^4$	$\times10^5$	$\times10^5$
Tap	2.14	8.25	1.58	-	1.47	1.14	0.14	9.00	6.07	0.26	1.19	0.56
Condensate	-	0.02	0.06	1.43	0.14	-	1.71	5.14	3.70	0.04	0.85	6.45
Pond	0.43	0.14	0.41	1.71	0.29	0.14	1.14	4.57	100.05	0.96	1.24	2.07
River	0.71	2.21	5.26	1.14	1.90	1.86	1.43	13.58	84.54	2.27	0.72	1.15
Rain	-	0.10	0.12	1.28	0.06	0.57	1.71	3.57	9.38	0.33	0.61	2.05

Origin of water samples	Element											
	Zn	Ga	As	Br	Sr	Sn	I	Ba	Mn	Ni	Ag	Pb
	Counts per second											
	$\times10^4$	$\times10^4$	$\times10^4$	$\times10^3$	$\times10^5$	$\times10^4$	$\times10^4$	$\times10^4$	$\times10^4$	$\times10^3$	$\times10^5$	$\times10^6$
Tap	1.21	-	2.99	3.43	1.96	4.76	5.61	4.19	1.87	-	-	-
Condensate	3.26	-	-	0.71	-	3.33	-	0.56	-	-	1.81	1.14
Pond	1.38	-	-	1.43	0.69	4.18	0.47	1.63	3.00	9.57	-	-
River	1.94	1.30	0.64	5.43	5.52	4.00	2.83	6.70	-	-	-	-
Rain	1.72	-	-	1.43	0.34	3.95	0.63	1.59	5.80	-	-	-

Proposed structures of intermediates for the photolitic degradation of [bmim][Sal]

Identification of the intermediates was carried out using the HPLC–ESI–MS/MS technique. Based on their MS/MS fragmentation data, twenty-two intermediates originating from $[bmim]^+$ were identified in positive mode, and one intermediate originating from $[Sal]^-$ was identified in negative mode (Table S2, ESI^+).

P1 is a compound with M_{mi} = 137, which is 2 mass units lower than the molecular mass of 3-butyl-1-methylimidazolium (PI), indicating loss of two hydrogen atoms, most likely from butyl-chain. Several parallel fragmentation reactions were observed: loss of methane (Δ*m/z* = 16), ethene (Δ*m/z* = 28), ethane (Δ*m/z* = 30), propenyl radical (Δ*m/z* = 41) and propene (Δ*m/z* = 42) from butyl group. The most abundant fragments correspond to the loss of C_3-units (propene/propenyl) and were tentatively identified as 1-methylpyrimidin-1-ium (*m/z* = 95) and (1-methyl-1*H*-imidazol-3-ium-3-yl)methyl (*m/z* = 96).[1] The ease of C_1 and C_3 loss may indicate that the double bond is located between C-2 and C-3 of side chain, i.e. that **P1** is 3-(2-but-2-en-1-yl)-1-methyl-1*H*-imidazol-3-ium.

P2 and **P3** are ionic compounds with M_{mi} = 153. ΔM_{mi} of 14 indicates the presence of oxo group in both compounds. The absence of C_1-fragment loss implies oxygenation of butyl chain, i.e. both compounds represent 1-methyl-3-(oxobutyl)imidazolium, differing in position of oxo group. Fragmentation patterns of these compounds differ significantly. Fragmentation of **P2** starts with oxobutene loss (Δ*m/z* = 70), forming the methylimidazolium cation (*m/z* = 83). A parallel complementary reaction yields the oxobutyl or butirylium cation (*m/z* = 71), by loss of *N*-methylimidazole (*Δm/z* = 82), followed by loss of 28 units corresponding to either ethene or carbon monoxide (impossible to differentiate using low resolution MS) yielding either propyl or acetylium cation. MS^2 spectra of **P3** featured fragment with *m/z* = 95 as a base peak at higher collision energies, and only minor peak at *m/z* = 83. Ion *m/z* = 95 is formed by loss of C_3H_6O, most likely propanal (Δ*m/z* = 58), with one carbon from butyl moiety being retained on imidazolium. If α-cleavage on carbonyl group is assumed to be the underlying fragmentation mechanism, it seems likely that **P2** is 3-butanoyl-1-methyl-1*H*-imidazol-3-ium and **P3** is 1-methyl-3-(2-oxobutyl)-1*H*-imidazol-3-ium.

P4 and **P5** are ionic compounds with M_{mi} = 155. Mass difference of 16 units suggests hydroxylation. MS^2 spectra of both compounds were almost identical, the only difference being the higher abundance of ion *m/z* = 45 in **P4** spectra, making differentiation of two compounds difficult. Methylimidazolium cation (*m/z* = 83) represents the base peak in all spectra, leading to conclusion that the hydroxyl group is introduced into butyl part of molecule i.e. compounds represent 3-(hydroxybutyl)-1-methyl-1*H*-imidazol-3-ium. Fragments of methylimidazolium – 1-methyl-1*H*-azirenium (*m/z* = 56) and 1*H*-azirenium (*m/z* = 42) – are also observable at higher collision energies.[2] In addition, several fragments originating from complementary pathway – loss of methylimidazole, with charge retention on C_4 side chain – were present in both spectra. $C_4H_9O^+$ (protonated hydroxybutene or butyraldehide) at *m/z* = 73, was observable only in low-energy spectrum of **P5**, while two fragments corresponding to loss of H_2O (at *m/z* = 55) and loss of CO (at *m/z* = 45) from $C_4H_9O^+$ were present in spectra of both compounds. Abundant fragment at *m/z* = 45, and relatively abundant *m/z* = 55, could indicate that compound **P4** is 3-(1-hydroxybutyl)-1-methyl-1*H*-imidazol-3-ium, since *n*-butylideneoxonium ion ($C_4H_9O^+$) could easily undergo H_2O and CO loss. On the other hand, the loss of CO in spectra of compound **P5** is less prominent, but still present, which may indicate 3-(4-hydroxybutyl)-1-methyl-1*H*-imidazol-3-ium.

P6 and **P7** are isobaric compounds with M_{mi} = 171, which is 32 units higher than the monoisotopic mass of 3-butyl-1-methylimidazolium (PI), indicating the presence of two hydroxyl groups. Fragmentation patterns of two compounds bear no resemblance, suggesting different structures.

P6 could possibly represent 3-(3,4-dihydroxybutyl)-1-methyl-1*H*-imidazol-3-ium. In that case, the observed fragmentation pattern could be rationalized by a series of parallel reactions. The dominant pathway starts with loss of terminal CH_2OH unit as methanol (Δ*m/z* = 32), yielding 1-methyl-3-(3-oxopropyl)-1*H*-imidazol-3-ium (*m/z* = 139) that further fragments by loss of CHO (Δ*m/z* = 29) or CH_2CH_2CHO (Δ*m/z* = 57) giving ions at *m/z* 110 and 82, respectively. The alternative pathway begins with loss of water (Δ*m/z* = 18) from side chain C-3 hydroxyl, which – after keto-enol tautomerization – yields 1-methyl-3-(4-oxobutyl)-1*H*-imidazol-3-ium (*m/z* = 153). This ion can further fragment by loss of $CH_2CH_2CH_2CHO$ (Δ*m/z* = 71, giving product at *m/z* = 82), CH_2O or CHO (Δ*m/z* = 30 and 29, giving products at *m/z* = 123 and 124).

Fragmentation pathway of **P7** starts with loss of ethanol (Δ*m/z* = 46), yielding ion at *m/z* = 125 as a base peak at lower collision energies. This ion further fragments via loss of CO, CHO or CH_2O (Δ*m/z* = 28, 29 and 30, respectively), with 1-methylpyrimidin-1-ium (*m/z* = 95) as the most abundant fragment. Alternatively, 2-oxoethyl radical is lost (Δ*m/z* = 43), giving minor ion with *m/z* = 82. The ease of loss of terminal C_2-unit could indicate hydroxylation in C-2 and C-3 positions of side chain, i.e. that **P7** is 3-(2,3-dihydroxybutyl)-1-methyl-1*H*-imidazol-3-ium. In that case, ion at *m/z* = 125 would represent 1-methyl-3-(2-oxoethyl)imidazolium. The alternative ion, 3-acetyl-1-methylimidazolium (that would originate from C-1, C-3 dihydroxylated isomer) is less probable, since it would further fragment by loss of ketene (Δ*m/z* = 42) yielding methylimidazolium at *m/z* 83, which is absent.

Compounds **P8** and **P9** both have M_{mi} = 173. The monoisotopic mass, 34 mass units greater than that of 3-butyl-1-methylimidazolium, points out to the presence of two hydroxyl groups and either reduction of one double bond in imidazolium ring or ring cleavage. Both compounds share very similar PI MS^2 spectra. However, there is a slight difference in fragmentation patterns of these two compounds.

Fragmentation of **P8** starts with loss of hydroxypropyl radical (Δ*m/z* = 59), suggesting that one hydroxyl group is introduced into butyl part of molecule. Formation of cation radical with *m/z* = 114 indicates that hydroxyl is not bonded to position 1 of the butyl group. However, the position of the hydroxyl is impossible to determine using low resolution MS. On the other hand, if second hydroxyl group was on the reduced imidazolium, loss of water would be expected.

Contrary to this, fragments with *m/z* = 72 and 57, corresponding to *N*-formyl-*N*-methylmethaniminium and *N*-methylideneformamide, respectively, are observed. Further fragmentation by loss of *m/z* = 28, 30 and 31 yields compounds with *m/z* = 44, 42 and 41, respectively. This indicates the cleavage of imidazolium ring and presence of oxo group in the structure, i.e. that **P8** likely stands for [formyl(methyl)amino]-*N*-(hydroxybutyl)-*N*-methylmethaniminium.

On the other hand, fragmentation of **P9** starts with loss of 1-butene (Δ*m/z* = 56), followed by water loss (Δ*m/z* = 18), yielding compounds with *m/z* = 117 and 99, respectively. Hydroxy-1-methylimidazolium (*m/z* = 99) is then simultaneously fragmented by loss of HCN (Δ*m/z* = 27) and *N*-methylmethanimine radical (Δ*m/z* = 42), yielding compounds with *m/z* = 72 and 57, respectively. This all suggests that both oxo and hydroxyl group are on the cleaved imidazolium ring. Like in **P8**, *N*-formyl-*N*-methylmethaniminium (Δ*m/z* = 72) undergoes further fragmentation into compounds with *m/z* = 44, 42 and 41. Thus, **P9** is likely *N*-butyl[formyl(methyl)amino]-*N*-(hydroxymethyl)methaniminium.

Although compounds **P10**, **P11** and **P12** have identical monoisotopic masses of M_{mi} = 187, their fragmentation patterns suggest that they have various distribution of three hydroxyl groups (Δ*m/z* = 48) present in them.

In PI MS^2 spectra of **P10** and **P11**, intact methyl-imidazolium (*m/z* = 83) is present, leading to conclusion that the three hydroxyls are bonded either to butyl or N-methyl moiety. Fragmentation of **P10** starts with the loss of water, Δ*m/z* = 18, confirming this assumption. Position of one of the hydroxyl groups is determined by loss of formaldehyde (Δ*m/z* = 30), leading to conclusion that it was bonded to methyl group on position 1 of imidazolium. Parallel loss of 56 (propenal) and 44 (water + ethyne) mass units form 3-methyl-1*H*-imidazol-3-ium (Δ*m/z* = 83) and its ethenyl isomer (Δ*m/z* = 95), respectively. This indicates that the third hydroxyl is also on the hydroxybutenyl moiety. Accordingly, **P10** likely stands for 3-(dihydroxybutyl)-1-(hydroxymethyl)-1*H*-imidazol-3-ium.

Intermediate **P11** was identified as 1-methyl-3-(trihydroxybutyl)-1*H*-imidazol-3-ium. Initial loss of 62 mass units can be attributed to loss of methoxymethanol, confirming that two hydroxyls are on the butyl moiety. Formed 3-(hydroxyethenyl)-1-methylimidazolium (*m/z* = 125) then simultaneously losses ethenone (Δ*m/z* = 42), yielding 1-methylimidazolium (*m/z* = 83), and *N*-ethynylmethanimine (Δ*m/z* = 53), followed by imidazolium ring cleavage.

P12 is also a trihydroxy derivative of 3-butyl-1-methylimidazolium, with specific fragmentation pattern. Fragmentation of basic peak (*m/z* = 187) yields ion with *m/z* = 141, by loss of either formic acid or ethanol (Δ*m/z* = 46). Since ion *m/z* = 127 is also present in the spectra, derived by loss of acetic acid (Δ*m/z* = 60), it is concluded that two of the hydroxyls are bonded to the butyl part of the molecule. The third hydroxyl is on the imidazolium ring, which is evident from the loss of CO (Δ*m/z* = 28). However, the position of this hydroxyl is not possible to determine by low resolution MS spectra. Thus, it is only possible to say that **P12** likely stands for 3-(dihydroxybutyl)-1-(hydroxymethyl)-1*H*-imidazol-3-ium.

P13 and **P14** both correspond to compounds with monoisotopic mass M_{mi} = 189,50 mass units higher than the molecular mass of 3-butyl-1-methylimidazolium. Based on their PI MS^2 spectra and specific patterns of fragmentation, it was concluded that these compounds could have either three hydroxyl groups and reduction of one double bond in imidazolium ring, or cleavage of imidazolium ring with hydroxyl and oxo group attached, along with another hydroxyl on butyl or N-methyl moiety.

Fragmentation of **P13** starts with loss of water (Δ*m/z* = 18), indicating the presence of alcoholic hydroxyl in its structure. However, the position of the hydroxyl cannot be determined. Subsequent simultaneous losses of propadiene (Δ*m/z* = 40) and butadiene (Δ*m/z* = 54) yield compounds of *m/z* = 131 and 117, respectively. Both of yielded ions can originate from reduced and hydroxylated imidazolium ring or cleaved imidazolium with oxo and hydroxyl group. Thus, it was not possible to further elucidate the structure of **P13**.

On the other hand, **P14** has different fragmentation pattern, which allows determination of its structure. Loss of ethanol (Δ*m/z* = 46) and yielding ion with *m/z* = 143 points out that one hydroxyl is bonded to butyl group, most likely on position 3. This is a possible reaction from both reduced and hydroxylated imidazolium ring and cleaved ring with oxo and hydroxy group attached. However, specific ion with *m/z* = 102, which is formed by loss of etenimine (Δ*m/z* = 41), is specific only to the structure of *N*-(hydroxymethyl)-*N*-methyl-2-oxoethaniminium. This is confirmed by loss of water (Δ*m/z* = 18), formaldehyde (Δ*m/z* = 30) and ethenone (Δ*m/z* = 42) from its structure, yielding ions with *m/z* = 84, 72 and 60, respectively. Accordingly, **P14** most likely stands for hydroxy-*N*-(3-hydroxybutyl)[methyl(2-oxoethyl)amino]methaniminium.

P15, **P16**, **P17**, **P18** and **P19** all have monoisotopic masses of M_{mi} = 203, indicating that they either have four additional hydroxyl groups in the 3-butyl-1-methylimidazolium structure, or cleaved imidazolium ring with two hydroxyl and two oxo groups attached. It is difficult to discriminate these compounds only by their fragmentation patterns, but some precious information can be gathered.

Fragmentation of **P15** starts with consecutive loss of two molecules of water (Δ*m/z* = 18) one after another, suggesting that it has two alcoholic hydroxyls in its structure, apparently on positions 1 and 3 of butyl part of the molecule. Ion with *m/z* = 187, formed by loss of the first water molecule further losses propadiene (Δ*m/z* = 40) from its structure, yielding ion with *m/z* = 145. Further fragmentation by loss of CO (Δ*m/z* = 28) corresponds either to two-hydroxylated imidazolium or cleaved imidazolium ring with two oxo groups. Further loss of water (Δ*m/z* = 18) and formaldehyde (Δ*m/z* = 30) from the yielded ion (*m/z* = 117) forms ions with *m/z* = 99 and 87, respectively. Thus, **P15** corresponds either to *N*-(1,3-dihydroxybutyl)-*N*-formyl[formyl(methyl)amino]methaniminium, or 3-(1,3-dihydroxybutyl)-4,5-dihydroxy-1-methyl-1*H*-imidazol-3-ium.

P16 first losses water molecule (Δ*m/z* = 18), followed by the loss of ethanol (Δ*m/z* = 46), yielding compound with *m/z* = 139. This suggests that two hydroxyl groups are bonded to butyl part of the molecule, although it is impossible to determine their position. Subsequent loss of 44 mass units i.e. acetaldehyde or CO_2 (alternative loss of propane is not plausible) suggests that one or two hydroxyls are bond to imidazolium. This suggests that imidazolium ring is not cleaved, but it was not possible to further elucidate the structure of **P16**. The fragmentation of **P17** starts similarly with loss of ethanol (Δ*m/z* = 46), followed by loss of alcoholic hydroxyl in the form of water (Δ*m/z* = 18), yielding compounds with *m/z* = 157 and *m/z* = 139, respectively. This leads to a conclusion that two hydroxyls are also on butyl group, while simultaneous losses of carbon dioxide (Δ*m/z* = 44) and ethenedione (Δ*m/z* = 56) during the cleavage of imidazolium ring, yield cations of *m/z* = 95 and 83, indicating the presence of two hydroxyls in imidazolium ring, like in **P16**. Therefore, it is concluded that both **P16** and **P17** are tetrahydroxy derivatives of 3-butyl-1-methylimidazolium.

Fragmentation patterns of **P18** and **P19** are very similar and it is almost impossible to determine the differences in their structures by low-resolution MS. However, valuable information can be gathered by identifying both of their PI MS^2 spectra together. Fragmentation starts with loss of water (Δ*m/z* = 18), indicating the presence of (at least) one alcoholic hydroxyl in structure, probably in butyl part of molecule. Yielded cation (*m/z* = 185) is then further fragmented into compound with *m/z* = 157, by loss of ethene or carbon monoxide (both Δ*m/z* = 28). Either way, the hypothesis of one hydroxyl on imidazolium moiety and three hydroxyls on butyl (or one on methyl) group is supported by this. Thus, the only difference between **P18** and **P19** is probably in the positions of the four hydroxyls, which cannot be determined with certainty.

P20, **P21** and **P22** all correspond to compounds with monoisotopic mass M_{mi} = 205, which is 2 units higher than compounds **P15** - **P19**. This leads to an assumption that these compounds have four hydroxyls and one reduced double bond in imidazolium ring, or two hydroxyls in butyl moiety and hydroxyl and oxo group bound to a cleaved imidazolium ring.

PI MS^2 spectra of **P20** and **P21** are almost identical, making it impossible to determine differences in their structures. Hence, all the valuable information is gathered from their spectral data together. Fragmentation starts with loss of water (Δ*m/z* = 18), forming ion with *m/z* = 187. Parallelly, loss of 32 mass units (methanol) yields product with *m/z* = 173. This product then losses another methanol (Δ*m/z* = 32) and ethanedial (Δ*m/z* = 58), leading to formation of products with *m/z* = 141 and 115, respectively. Parallel fragmentation of the two intermediates by subsequent loss of formic acid (Δ*m/z* = 46) and methanol (Δ*m/z* = 32) leads to formation of ions with *m/z* = 159 and 127, respectively.[22] Ion 127 can then lose 28 (CO) or 40 (propadiene) units, yielding *m/z* = 99 and 87. Although the fragmentation patterns for both **P20** and **P21** are well defined by the spectral information, it was not possible to further elucidate their structures.

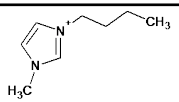
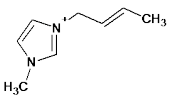
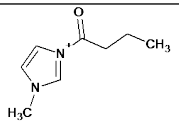
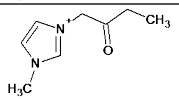
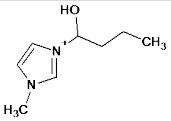
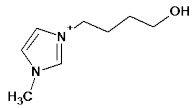
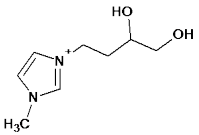
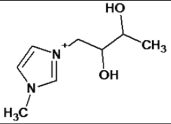
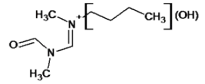
PI MS^2 of **P22** is not very informative since only few fragments are present. Fragmentation starts with loss of acetaldehyde (Δ*m/z* = 46), yielding compound with *m/z* = 159, followed by the loss of methanimine (Δ*m/z* = 29). Yielded cation (*m/z* = 130) then losses propenol or ethanedial (Δ*m/z* = 58), forming ion with *m/z* = 72. This fragmentation pattern gives limited information for identification of the intermediate **P22**.

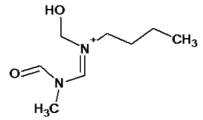
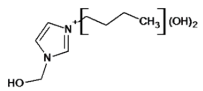
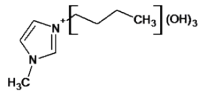
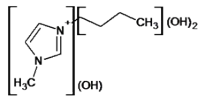
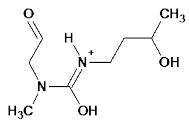
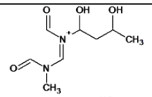
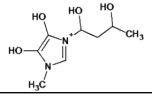
P23 is a compound with *m/z* = 153, identified in the NI mode. Its mass is 16 units higher than salicylate, indicating that one hydroxyl more is present in this molecule. Due to the specific stereochemistry, addition of hydroxyl group onto salicylate is only possible in meta- position (3- or 5-). Fragmentation starts with loss of CO_2 (Δ*m/z* = 44), yielding either 3-hydroxy-6-oxocyclohexa-2,4-dienide or 5-hydroxy-6-oxocyclohexa-2,4-dienide (*m/z* = 109). Next, loss of water (Δ*m/z* = 18) yields 2-hydroxycyclohexa-1,3-dien-5-ynide (*m/z* = 91). However, it is not possible to determine whether **P23** stands for 3-hydroxysalicylate or 5-hydroxysalicylate.

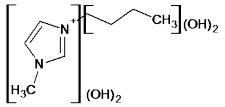
1 A. Lesimple, O. Mamer, W. Miao and T.H. Chan, *J. Am. Soc. Mass Spectrom.*, 2006, **17**, 85.

2 O.A. Mamer and A. Lesimple, *Rapid Commun. Mass Spectrom.*, 2005, **19**, 1771.

Table S2. Proposed structures of intermediates for the photolitic degradation of [bmim][Sal] with the relative abundance of their product ions.

Compound	t_R (min)	M_{mi}	Molecular formula	Name of compound	Structure	Mode	Vcol (V)	Product ions *m/z* (relative abundance)
$[bmim]^+$	2.88	139	$C_8H_{15}N_2$	1-methyl-3-butyl-1*H*-imidazol-3-ium		PI	10 20 30 40	139(44), 83(100), 57(6) 139(8), 83(100), 57(7), 42(7), 41(12) 83(100), 56(13), 42(39), 41(31), 39(7), 29(7) 83(71), 56(28), 42(100), 41(64), 39(36), 29(13)
P1	2.58	137	$C_8H_{13}N_2$	3-(2-but-2-en-1-yl)-1-methyl-1*H*-imidazol-3-ium		PI	10 20 30 40	137(100) 137(100), 96(24), 95(24) 137(56), 121(12), 107(15), 96(64), 95(100), 81(22) 107(20), 96(29), 95(100), 81(57), 55(23), 54(60), 42(33)
P2	2.41	153	$C_8H_{13}N_2O$	3-butanoyl-1-methyl-1*H*-imidazol-3-ium		PI	10 20 30 40	153(91), 83(100), 71(20), 43(26) 153(16), 83(100), 71(13), 43(89) 83(49), 43(100), 42(8) 83(23), 43(100), 42(15)
P3	2.54	153	$C_8H_{13}N_2O$	1-methyl-3-(2-oxobutyl)-1*H*-imidazol-3-ium		PI	10 20 30 40	153(100), 96(27), 95(8), 83(15) 153(34), 96(83), 95(100), 83(36), 43(20) 96(14), 95(100), 83(11), 68(6), 43(11) 95(100), 68(17), 43(14), 42(10)
P4	2.37	155	$C_8H_{15}N_2O$	3-(1-hydroxybutyl)-1-methyl-1*H*-imidazol-3-ium		PI	10 20 30 40	155(100), 83(96), 55(14), 45(7) 155(9), 83(100), 55(23), 45(22), 42(5) 83(100), 55(22), 45(54), 42(24) 83(69), 56(22), 55(20), 45(100), 43(10), 42(56), 29(12)
P5	2.47	155	$C_8H_{15}N_2O$	3-(4-hydroxybutyl)-1-methyl-1*H*-imidazol-3-ium		PI	10 20 30 40	155(72), 83(100), 73(7), 55(12) 155(6), 83(100), 55(26), 45(6), 42(6) 83(100), 56(10), 55(31), 45(13), 42(26) 83(100), 56(26), 55(30), 45(35), 43(18), 42(94), 41(20), 39(13), 29(14), 28(10)
P6	2.55	171	$C_8H_{15}N_2O_2$	3-(3,4-dihydroxybutyl)-1-methyl-1*H*-imidazol-3-ium		PI	10 20 30 40	171(25), 153(9), 139(79), 123(9), 110(100), 96(12), 82(76) 139(46), 110(10), 96(9), 95(7), 83(14), 82(100) 139(12), 95(13), 83(24), 82(100), 55(13) 95(20), 83(28), 82(100), 81(24), 55(31), 54(17), 42(21)
P7	2.76	171	$C_8H_{15}N_2O_2$	3-(2,3-dihydroxybutyl)-1-methyl-1*H*-imidazol-3-ium		PI	10 20 30 40	125(100), 96(8) 125(100), 97(25), 96(24), 95(19) 125(52), 97(46), 96(61), 95(100), 56(20) 97(8), 96(24), 95(100), 68(8), 56(8)
P8	2.82	173	$C_8H_{17}N_2O_2$	[formyl(methyl)amino]-*N*-(hydroxybutyl)-*N*-methylmethaniminium		PI	10 20 30 40	173(85), 114(61), 72(100), 57(34), 44(12) 114(23), 72(100), 57(88), 44(52), 42(27), 41(27) 72(44), 57(78), 44(100), 42(58), 41(68), 29(19) 57(29), 44(100), 42(97), 41(100), 29(36)

P9	2.92	173	$C_8H_{17}N_2O_2$	*N*-butyl[formyl(methyl)amino]-*N*-(hydroxymethyl)methaniminium		PI	10 20 30 40	173(100), 117(10), 114(27), 99(7), 90(8), 72(51), 57(18), 44(7) 173(30), 117(17), 114(21), 99(17), 72(100), 58(20), 57(65), 44(53), 42(27), 41(34) 99(16), 72(40), 58(22), 57(63), 44(100), 42(56), 41(83), 29(18) 72(17), 58(15), 57(18), 44(100), 42(88), 41(96), 39(26), 29(21)
P10	2.30	187	$C_8H_{15}N_2O_3$	3-(dihydroxybutyl)-1-(hydroxymethyl)-1*H*-imidazol-3-ium		PI	10 20 30 40	187(28), 169(14), 139(100), 128(14), 125(21), 123(19), 96(51), 72(71), 71(19) 169(15), 139(100), 125(18), 96(57), 95(38), 83(35), 72(58), 71(48), 44(24), 43(25) 139(39), 123(13), 96(40), 95(100), 83(66), 82(21), 72(23), 71(40), 44(40), 43(83), 42(26) 96(18), 95(100), 83(43), 82(21), 71(11), 44(38), 43(77), 42(39), 41(11)
P11	2.41	187	$C_8H_{15}N_2O_3$	1-methyl-3-(trihydroxybutyl)-1*H*-imidazol-3-ium		PI	10 20 30 40	187(19), 129(13), 128(20), 125(13), 83(10), 72(100), 71(24), 59(7), 44(6) 125(12), 83(23), 72(100), 71(57), 59(9), 44(37), 43(39), 42(12), 30(13) 95(12), 83(23), 72(46), 71(41), 58(14), 44(73), 43(100), 42(36), 30(12) 95(15), 83(14), 44(44), 43(100), 42(47)
P12	2.73	187	$C_8H_{15}N_2O_3$	3-(dihydroxybutyl)-1-(hydroxymethyl)-1*H*-imidazol-3-ium		PI	10 20 30 40	187(6), 141(100), 127(8), 113(9), 111(8), 100(8) 141(100), 127(23), 113(44), 100(39) 141(30), 113(100), 100(67), 99(27), 82(44), 70(29), 56(25), 55(38) 113(43), 100(47), 99(25), 82(74), 70(53), 56(50), 55(100), 54(34)
P13	2.36	189	$C_8H_{17}N_2O_3$	-	-	PI	10 20 30 40	189(59), 171(14), 131(17), 130(15), 117(19), 100(18), 72(100) 189(12), 131(10), 117(11), 73(13), 72(100), 58(12), 55(60), 44(32), 42(16) 72(41), 55(100), 45(27), 44(45), 42(26) 72(28), 55(100), 45(57), 44(80), 43(25), 42(58)
P14	3.23	189	$C_8H_{17}N_2O_3$	hydroxy-*N*-(3-hydroxybutyl)[methyl(2-oxoethyl)amino]methaniminium		PI	10 20 30 40	143(100), 114(9), 102(33), 100(10), 84(11), 72(22), 60(32), 57(18) 143(36), 102(77), 84(17), 72(25), 60(100), 57(69), 46(26), 44(18), 42(16) 102(29), 84(10), 72(8), 60(100), 57(81), 46(48), 44(30), 42(40), 41(32) 84(12), 60(100), 57(62), 46(63), 44(53), 42(95), 41(80), 29(21)
P15	2.13	203	$C_8H_{15}N_2O_4$	*N*-(1,3-dihydroxybutyl)-*N*-formyl[formyl(methyl)amino]methaniminium or 3-(1,3-dihydroxybutyl)-4,5-dihydroxy-1-methyl-1*H*-imidazol-3-ium	 	PI	10 20 30 40	203(16), 145(15), 144(31), 126(11), 126(11), 117(23), 99(14), 87(51), 72(100), 43(11) 126(18), 117(22), 99(25), 87(100), 72(98), 44(18), 43(43) 87(20), 72(21), 45(100), 44(53), 43(82), 42(36) 86(9), 70(14), 69(10), 45(100), 44(56), 43(69), 42(32), 41(20)

P16	2.20	203	$C_8H_{15}N_2O_4$	tetrahydroxy derivate of BMIM		PI	10	203(35), 185(17), 144(25), 139(47), 126(18), 117(41), 96(16), 87(48), 72(94), 72(100)
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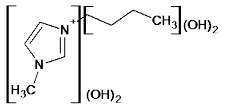
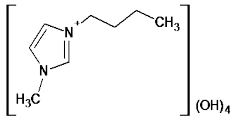
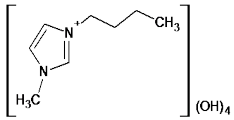
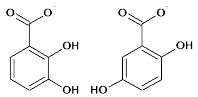
							30	96(30), 95(58), 83(24), 72(90), 72(50), 58(34), 45(100), 44(50), 43(46), 42(36)
							40	95(74), 45(53), 43(100), 42(34)
P17	2.47	203	$C_8H_{15}N_2O_4$	tetrahydroxy derivate of BMIM		PI	10	158(18), 157(38), 139(100), 130(18), 129(16)
							20	157(13), 139(100), 129(13), 83(15), 71(27), 60(12)
							30	139(63), 95(21), 83(100), 82(13), 71(19), 70(48), 60(33), 43(12), 42(43), 30(12)
							40	95(31), 83(73), 82(24), 70(32), 60(49), 56(41), 55(23), 46(23), 43(32), 42(100), 41(20)
P18	2.57	203	$C_8H_{15}N_2O_4$	tetrahydroxy derivate of BMIM		PI	10	157(100), 140(12), 129(33), 125(28), 116(12), 88(17), 87(18), 72(13), 71(17), 60(14), 59(12)
							20	129(48), 125(53), 88(28), 71(100), 60(86), 59(28), 42(40)
							30	125(28), 96(29), 95(25), 71(93), 70(25), 60(100), 56(30), 44(55), 43(41), 42(79)
							40	95(44), 71(24), 71(20), 60(63), 56(15), 46(18), 44(59), 43(65), 42(100), 30(16)
P19	2.67	203	$C_8H_{15}N_2O_4$	tetrahydroxy derivate of BMIM		PI	10	185(17), 157(17), 140(12), 129(17), 125(100), 83(17)
							20	185(13), 129(10), 125(100), 111(11), 97(26), 96(14), 83(23), 71(23), 60(15)
							30	139(21), 139(18), 125(80), 111(12), 97(89), 96(100), 95(75), 83(56), 81(23), 71(22), 60(19), 59(11), 56(48), 44(17), 43(56), 42(42)
							40	125(10), 97(16), 96(37), 95(100), 83(16), 81(16), 68(19), 60(10), 56(11), 43(14), 42(17)
P20	2.49	205	$C_8H_{17}N_2O_4$	-	-	PI	10	173(82), 144(46), 141(49), 127(34), 115(100), 100(16), 99(47), 87(21), 72(17)
							20	173(100), 141(77), 127(47), 115(93), 100(30), 99(64), 87(56), 74(51), 72(74), 71(29), 60(58), 44(26), 42(35)
							30	141(48), 127(61), 99(70), 87(63), 74(38), 72(78), 60(99), 46(39), 44(51), 43(33), 42(100)
							40	99(37), 74(22), 72(42), 60(47), 57(24), 46(29), 46(26), 44(53), 43(26), 42(100)
P21	2.63	205	$C_8H_{17}N_2O_4$	-	-	PI	10	173(96), 159(27), 144(48), 141(12), 127(34), 115(100), 99(11), 87(20), 74(14), 73(11), 72(16), 60(12), 44(11)
							20	173(93), 159(25), 141(16), 127(66), 115(100), 99(20), 87(67), 74(48), 72(87), 60(70), 44(23), 43(16), 42(23)
							30	173(14), 127(33), 115(15), 99(25), 87(40), 74(50), 72(100), 60(71), 57(22), 56(18), 46(25), 44(37), 43(18), 42(69)
							40	87(21), 74(24), 72(42), 60(44), 46(36), 44(51), 42(100)

P22	2.79	205	$C_8H_{17}N_2O_4$	-	-	PI	10 20 30 40	159(100), 130(35), 72(9), 71(15) 159(100), 130(9), 100(17), 72(79), 71(40), 60(15), 44(13), 42(7), 30(11) 159(17), 72(100), 71(15), 60(20), 44(27), 42(30) 72(71), 60(33), 44(92), 42(100), 30(18)
$[Sal]^-$	9.60	137	$C_7H_5O_3$	salicylate		NI	10 20 30 40	137(6), 93(100) 93(100) 93(100), 65(9) 93(100), 75(5), 65(56), 41(8)
P23	7.75	153	$C_7H_5O_4$	3- (or 5-) hydroxy salicilate		NI	10 20 30 40	109(100) 109(100), 108(38) 109(7), 108(100), 91(48) 108(100)

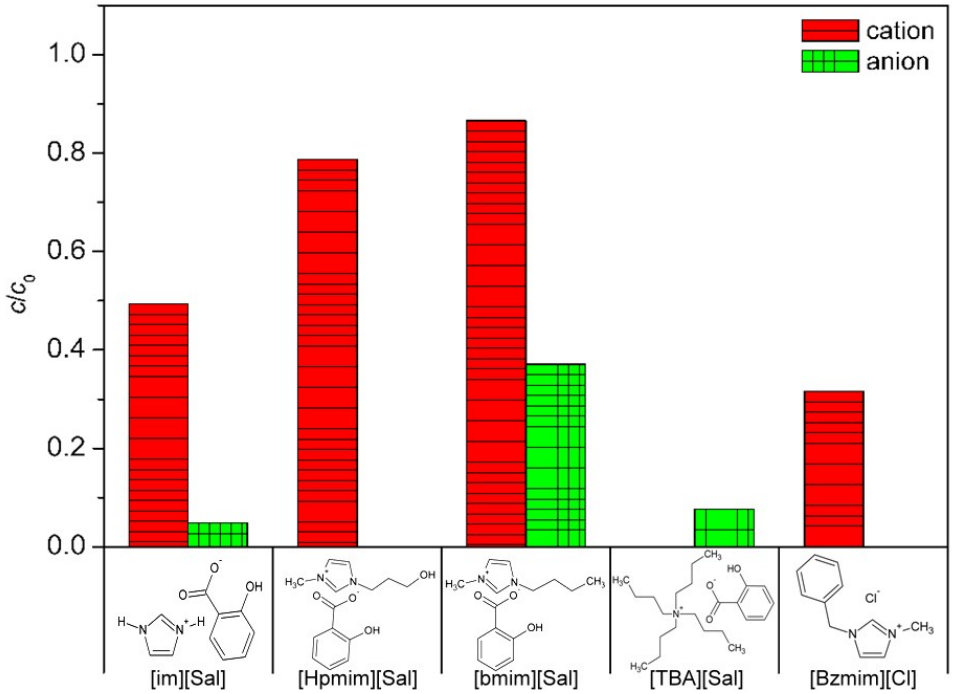


Fig. S1 Evolution of various ionic liquid (c_0 = 0.38 mmol L^{-1}) degradation after 60 min in presence of SS radiation.
Applied AOPs: 7.2Fe/TiO_2 (1.67 g L^{-1}) + 45 mmol L^{-1} H_2O_2 + 70 µL h^{-1} H_2O_2 at pH 2.8.
$[TBA]^+$ and Cl^- degradation could not be monitored by using HPLC-DAD technique.