ELECTROCHEMICAL DEGRADATION OF CONTRAST MEDIA

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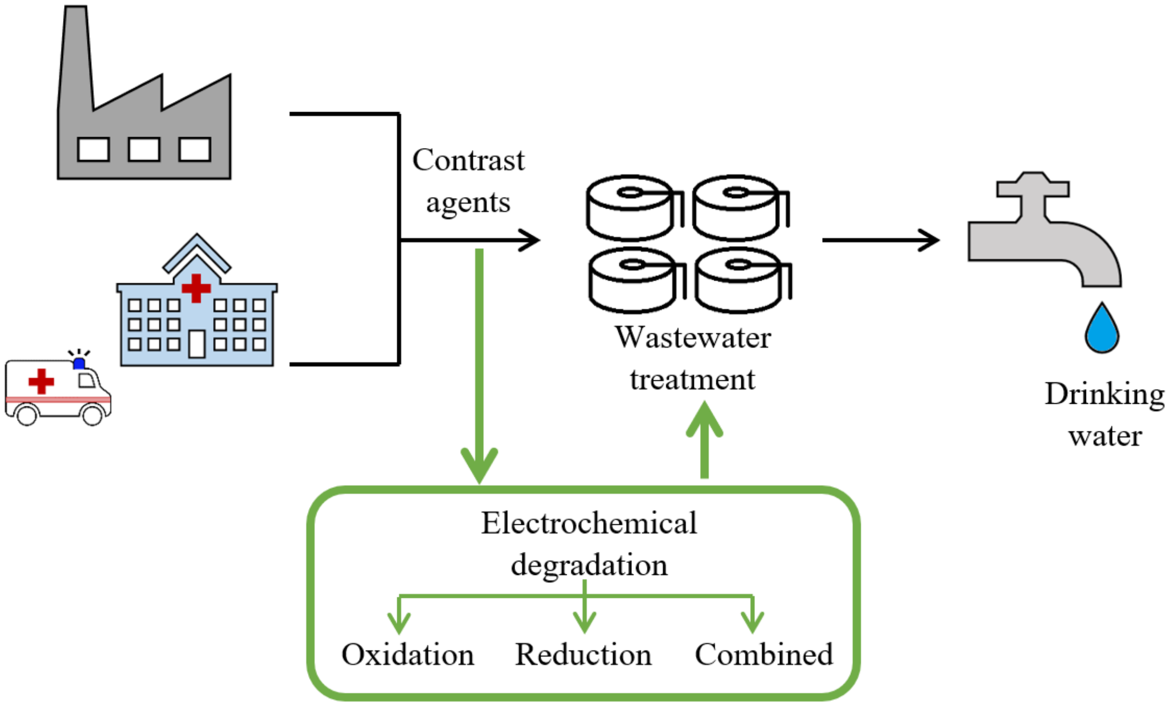
KEYWORDS

Iodinated contrast media, Gadolinium-based contrast agents, Contrast media remediation, Electrochemical water remediation, Advanced oxidation processes, Reductive dehalogenation.

HIGHLIGHTS

- Contrast media in water can be successfully removed using various electrochemical oxidation, even in complex matrices.
- Electrochemical reduction can help in removing iodine atoms from Iodinated contrast media, making them more biodegradable.
- The combination of electrochemical oxidation and reduction showed a good mineralisation of the compounds.

GRAPHICAL ABSTRACT



ABSTRACT

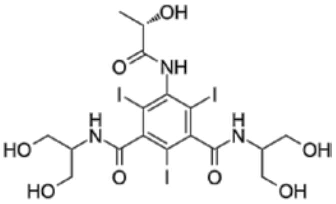
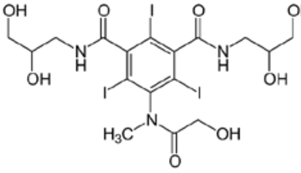
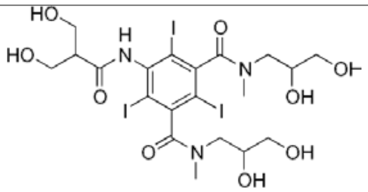
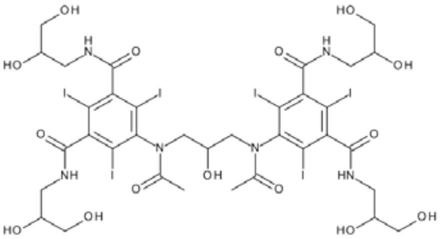
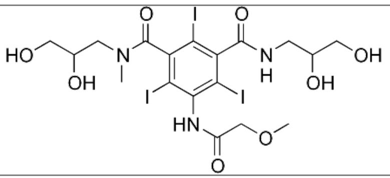
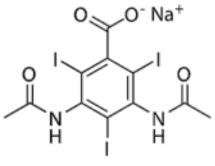
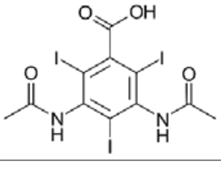
This work provides a critical review about the most recent works in electrochemical remediation of wastewater containing contrast media, very concerning pollutants resistant to conventional treatments in wastewater treatment plants. The focus is on iodinated contrast media and gadolinium-based contrast agents (GBCAs). After a short introduction in which non-electrochemical methods are presented, electro-oxidative and electro-reductive methods are discussed in the former case. A short section is also dedicated to methods based on a combination of the two. In the case of GBCAs, a brief presentation of non-electrochemical techniques is also reported, followed by some electrochemical treatments for Gd^{3+}. Considering the lack of literature on the use of electrochemical methods for the removal of this type of magnetic resonance imaging contrast agents, the potential of electrochemistry for the degradation in this field is then explored.

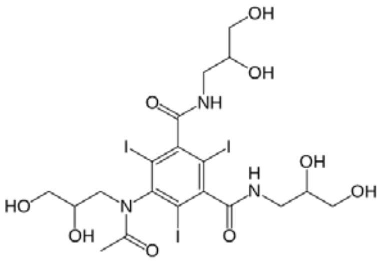
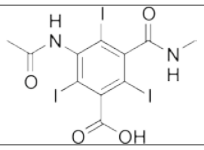
INTRODUCTION

In recent decades, the unprecedented increase in environmental awareness has led to a research effort in the field of remediation. To date, the general concern has shifted from classical pollutants such as solvents, additives and pesticides to the so-called pharmaceuticals and personal care products (PPCPs). Although they have remained invisible for long, their potential impact on the environment is significant. Among the PPCPs, contrast media, widely used worldwide and resistant to conventional biological wastewater treatment processes, are a concerning issue for environmental safeguarding.

Contrast media are a group of chemical agents developed to help characterise pathologies by improving the contrast resolution of an imaging modality in the medical field and can be classified based on the imaging modalities where they are used. The most common contrast agents are based on X-ray attenuation, increasing the radiodensity in a target tissue or structure, or on magnetic resonance signal enhancement, without employing cell-damaging ionising radiation [1]. For radiography, iodine-based contrast media (ICM) are the most used (some relevant examples are reported in **Table 1**).

Table 1: *Some of the most used ICM.*

Chemical	**CAS number**	**Formula**	**Structure**
Iopamidol	62883-00-5	$C_{17}H_{22}I_3N_3O_8$ MW: 777.09 g mol^{-1}	
Iomeprol	78649-41-9	$C_{17}H_{22}I_3N_3O_8$ MW: 777.09 g mol^{-1}	
Iobitridol	136949-58-1	$C_{20}H_{28}I_3N_3O_9$ MW: 835.15 g mol^{-1}	
Iodixanol	92339-11-2	$C_{35}H_{44}I_6N_6O_{15}$ MW: 1550.18 g mol^{-1}	
Iopromide	73334-07-3	$C_{18}H_{24}I_3N_3O_8$ MW: 791.11 g mol^{-1}	
Amidotrizoate sodium	737-31-5	$C_{11}H_8I_3N_2NaO_4$ MW: 635.90 g mol^{-1}	
Diatrizoic acid	117-96-4	$C_{11}H_9I_3N_2O_4$ MW: 613.91 g mol^{-1}	

Iohexol	66108-95-0	$C_{19}H_{26}I_3N_3O_9$ MW: 821.14 g mol^{-1}	
Iotalamic acid	2276-90-6	$C_{11}H_9I_3N_2O_4$ MW: 613.91 g mol^{-1}	

ICM are derivatives of 2,4,6-triiodobenzoic acid and are characterised by high-water solubility and stability against human metabolism. They are typically administered in high doses (up to 200 g per patient) and, after their application, are excreted in the patient's urine in their original, non-metabolized form [2]. As a result, ICM enter receiving waters and have been detected in municipal wastewater at relatively high concentrations (up to 100 μg L^{-1}), with hospitals serving as their main source [3], and have been frequently encountered in drinking water as well [4]. ICM compounds themselves should not impose a high risk for human health owing to their low eco-toxicity, but the role of degradation products formed during treatment processes is still unclear (in some instances metabolites have shown mutagenic effects) [5], and on the basis of precautionary principles, drinking water should be free of ICM [6].

Magnetic resounance imaging (MRI) contrast agents, and in particular gadolinium-based contrast agents, generate the same concern as ICM.

Currently, the U.S. Food and Drug Administration (FDA) has clinically approved nine gadolinium-based contrast agents (GBCAs). They are based on Gd^{3+} linear (DTPA = diethylenetriaminepentaacetic acid) or macrocyclic (DOTA = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) chelators (**Figure 1**) with nine coordination sites, with an octadentate polyaminocarboxylate chelator on eight positions, and an inner-sphere water molecule on the ninth site [7].

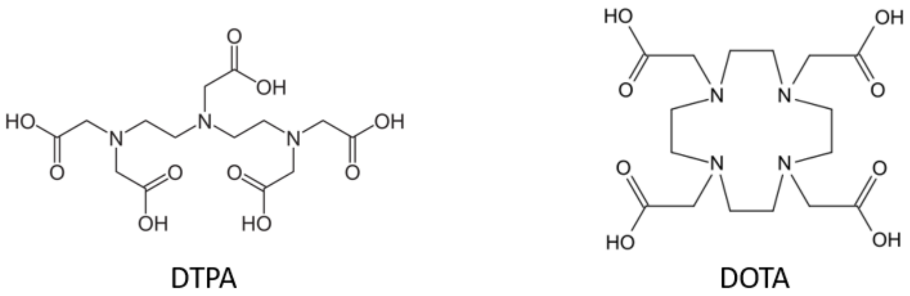


Figure 1: *Clinically approved GBCAs are based on the two ligand scaffolds DTPA and DOTA.*

As for ICM, their concentration in freshwater environments is increasing because after administration they are excreted unchanged and enter the sewage system, where they are released into surface waters [8,9], contaminating systems which provide drinking water resources [10,11]. It is not yet fully clear whether GBCAs themselves, their transformation products (TPs) or the release of free Gd are causing adverse health effects

[12], but even though actual GBCAs concentrations are still very low, their increasing makes the development of effective degradation methods crucial. For what concerns the toxicity of Gd-containing species, this is also a topic under investigation. While GBCAs are generally regarded as safe compounds, their administration to patients with decreased kidney function is associated with nephrogenic systemic fibrosis NFS; in those patients, an accumulation of insoluble Gd-containing deposits was detected in tissue samples [13]. Therefore, an increasing concentration of these species in natural waters might lead to adverse issues, likely in the long term.

In addition, we should consider that Gd, as all the rare earth elements, is among the 2020 Eu list of critical raw materials [14]. The list contains all the chemical elements characterised by an economic importance and supply risk: indeed, while their demand is continuously growing, their supply from natural deposits is getting limited, placing the focus on their recovery rather than their extraction.

In response to these concerns about ICM and GBCAs in water and wastewater, researchers have examined several treatment options, including electrochemistry-based ones, which are summarised in this review.

IODINATED X-RAY CONTRAST MEDIA

Researchers have examined several options to find effective approaches for water treatment able to eliminate ICM and their TPs. The removal of some of the ICMs has been unsatisfying using activated carbons [15], while using borate as a complexing agent and fixing the resulting adducts on ion exchangers has provided good results[16]. Reverse-osmosis membranes seem to effectively remove specific ICM, also coupled with microfiltration [17], as well as anoxic bank filtration that can reduce their concentration in raw drinking water [18]. However, even though effective, treatments based on the sorption or separation of ICM leave the iodinated molecule intact, leaving their degradation to subsequent treatments and not providing a permanent solution for the depollution. Degradative methods, able to destroy the contrast agents' molecules, are then preferable. Oxidation with ozone [19] was not efficient owing to low reaction rate, while other oxidation processes seem to be promising. Degradation using dual-wavelength UV-LED light (also combined with chlorine) [20], photocatalytic degradation with TiO_2 and UV-light [21], sonolysis [22], UV-peroxysulphate [23], photo-Fenton [24] and O_3/H_2O_2 [25] have reported good results, although sometimes generating toxic iodinated by-products [26,27].

Reductive processes exploiting zero-valent metals, such as Al and Fe [28–30], can deiodinate ICM even in a complex urine matrix, making them suitable for treating hospital wastewater.

However, among the successful oxidative and reductive treatments, electrochemical methods described in the following paragraphs (**Figure 2**) are among the most versatile and easily scalable. In addition, the use of inherently clean reactants such as electrons together with other properties (e.g. cutback of chemicals and mild reaction conditions), make them among the most sustainable treatments, in line with the principles of green chemistry. To date, limitations to the use of electrochemical methods are related to their applicability to real highly concentrated biological matrices, such as those coming from hospitals and factories which are the primary sources of this kind of pollutants. Indeed, more attention should be paid to optimising electrode materials, considering more sustainable and less expensive electrodes to promote the application of such treatments in real life. Particular attention should be paid then to the recovery of the inorganic iodine generated, as it represents a valuable resource.

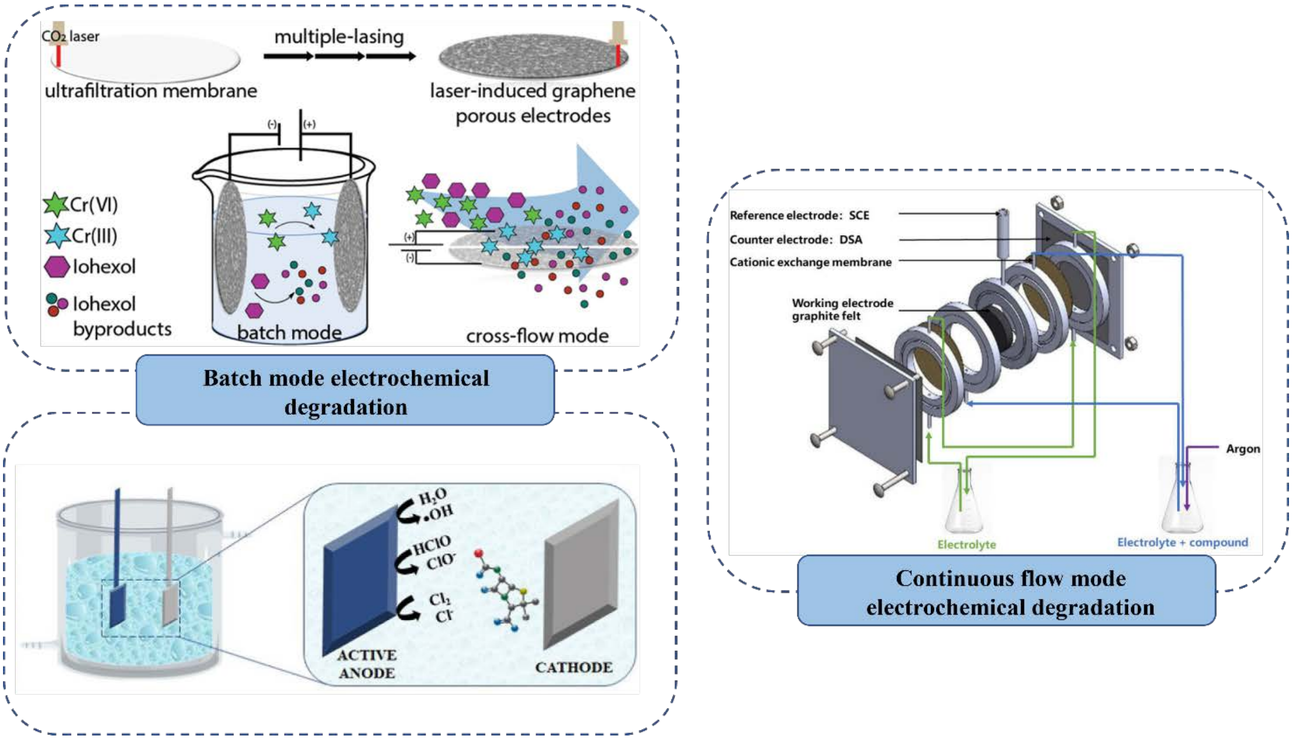


Figure 2: *Examples of batch and flow electrochemical degradation of ICM. Pictures reproduced with permission from refs.* [31–33]

Electrochemical Oxidation of ICM

Electrochemical oxidation (EO) processes are the most widely used in water remediation because they generally lead to the total degradation of the organic pollutants [34,35], and their industrial application to ICM, such as iomeprol and iopromide, has already reported good results [36]. The mineralisation often involves indirect oxidation based on the *in situ* generation of strong oxidants, mainly hydroxyl radical ·OH, through Eqs. (1) and (2):

$$\mathrm{M} + \mathrm{H_2O} \rightarrow \mathrm{M}(\cdot\,\mathrm{OH}) + \mathrm{H^+} + \mathrm{e^-} \tag{1}$$

$$\mathrm{R} + \mathrm{M}(\cdot\,\mathrm{OH}) \rightarrow \mathrm{M} + \mathrm{CO_2} + \mathrm{H_2O} \tag{2}$$

where M is the metal surface and R is the organic pollutant. “Non-active” electrodes with high oxygen evolution overpotential, such as boron-doped diamond (BDD), are the most suitable for this application [35]. Bocos *et al*. tested BDD for the mineralisation of diatrizoic acid (DIA), and its degradation was easily achieved [37].

The use of an electro-Fenton process in the same conditions enhanced the previous results. Electro-Fenton process is based on the electrocatalytic *in situ* formation of ·OH via the Fenton reaction:

$$\mathrm{H_2O_2} + \mathrm{Fe^{2+}} \rightarrow \mathrm{Fe^{3+}} + \mathrm{OH^-} + \cdot\,\mathrm{OH} \tag{3}$$

Both H_2O_2 and ferrous iron are generated and regenerated respectively through electro-reduction at the cathode:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad (4)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (5)$$

A BDD anode was also tested for iohexol oxidation by Tissot *et al.* [38]. This time, mineralisation analysis revealed that working in galvanostatic conditions, using either the initial limiting current density or half of it, leads to the complete degradation of the iohexol. The difference in the two cases is that the first condition allows a lower formation of intermediates, while the second one has higher current efficiency.

In 2017, Schneider *et al.* demonstrated that electrochemical treatment with BDD electrodes is effective for the removal of six ICM: diatrizoate, iotalamic acid, iopromide, iohexol, iopamidol and iomeprol [39]. Degradation of at least 90% was achieved for all six ICM in separate experiments. High mineralisation rates of 60 to 80% were also obtained, with the exception of iomeprol, indicating the formation of organic transformation products. During electrochemical degradation, dehalogenation occurs and iodate is the main product, confirming the mechanism presented by Bocos *et al.*, where ·OH is supposed to undergo *ipso* attacks on the iodine sites. After the substitution of the three iodine atoms by hydroxyl groups, the hydroxylation products can undergo other reactions, such as de-acetylation and de-carboxylation, leading to the final aromatic intermediate and then to carboxylic acids.

Mixed metal oxide (MMO) electrodes, such as Ti/SnO_2-SbBi and Ti/TiO_2-NT/SnO_2-SbBi, were also tested for removing iopromide, iohexol and diatrizoate and their degradation performances were compared with those of BBD [40]. The work by Moura de Salles Pupo *et al.* demonstrated similar, if not better in some cases, oxidation rates for MMO. A laser-made Ti/RuO_2-TiO_2 anode was then tested by Bomfim *et al.*, removing 95.5% of iohexol with a very high kinetic rate and low energy consumption [33].

Another kind of anode successfully tested for ICM degradation is a graphene sponge modified with borophene in which the production of oxidant species, namely ozone and ·OH, is enhanced, improving the degradation of highly polar contaminants such as iopromide and diatrizoate [41].

In a very recent work by Moratalla *et al.*, the combined electro-oxidation (EO) and dehalogenation by zero-valent iron (ZVI) process have proved to improve both the efficiency and the kinetics of the single electrochemical process to degrade iopamidol (IPM) in synthetic urine [42]. Three different electrochemical set up were tested: electro-oxidation (EO), electro-oxidation preceded by a pre-treatment with ZVI (ZVI-EO) and electrochemical treatment coupled with a fluidised bed with ZVI (EO/ZVI).

Results showed that EO was less efficient than EO/ZVI and ZVI-EO. Removal percentage was 74.9%, 86.7% and 99.5% respectively. These results are related to the higher quantity of oxidants produced during the reactions involving ZVI. EO/ZVI process promotes the production of a larger amount of ·OH through the Fenton reaction (Eqs. 3-5), enhancing the degradation rate of iopamidol. ZVI pretreatment in ZVI-EO processes favoured instead the 95% decrease of IPM by forming the deiodinated product, decreasing the amount of oxidants required to remove IPM and other related oxidation products.

To the electro-oxidation of organic matter can also contribute the presence of sulphate ions. It is well known that BDD anodes can produce persulphate oxidising sulphate. This oxidation is considered a two-step process involving the formation of sulphate radicals $SO_4^{\cdot -}$ (Eqs. 6-8) in the first one and their recombination in the second one (Eq. 9).

$$SO_4^{2-} \rightarrow SO_4^{\cdot -} + e^- \tag{6}$$

$$HSO_4^- + \cdot OH \rightarrow SO_4^{\cdot -} + H_2O \tag{7}$$

$$H_2SO_4 + \cdot OH \rightarrow SO_4^{\cdot -} + H_3O^+ \tag{8}$$

$$SO_4^{\cdot -} + SO_4^{\cdot -} \rightarrow S_2O_8^{2-} \tag{9}$$

Sulphate radicals are strong oxidants, with a redox potential similar to that of hydroxyl radicals at acidic pH and both of them have been reported to react with many pharmaceuticals. Considering that wastewater usually contains sulphate and that $SO_4^{\cdot -}$ and $\cdot OH$ tend to react differently with organic matter (the former *via* electron transfer and the latter *via* addition to unsaturated bonds or H-abstraction), Farhat *et al.* investigated the role of sulphate radical species and nonradically activated persulphate in diatrizoate and iopromide oxidation [43], using a BDD anode anodically polarised. The experiments demonstrated that degradation performance in the presence of sulphate was 10-15 times higher with respect to the inert matrix. This significant contribution to ICM degradation is probably due to their continuous regeneration at the anode surface. In addition, electrogenerated $SO_4^{\cdot -}$ may react with active sites at the electrode surface to form chemisorbed intermediates that stabilise the radicals. The non-radical activation of the formed persulphate *via* a ternary system consisting of the organic compound, BDD and persulphate also contribute to the degradation.

The effects on the transformation pathways of diatrizoate and iopromide in the presence of sulphate ions were studied by Radjenovic *et al.* [44]. Using almost the same experimental conditions of the previous work, they demonstrated that sulphate anolyte yielded higher mineralisation. In addition, only three TPs were identified for electro-oxidation in nitrate electrolyte for iopromide, while several TPs were detected in sulphate anolyte. In particular, two hydroxylamine derivatives of iopromide and a nitro derivative of diatrizoate were observed and being their formation due to a one-electron charge transfer, their presence could be assigned to electro-oxidation mediated by sulphate radicals.

Electrochemical Reduction of ICM

In recent years, electrochemical reduction (ER) has been successfully applied for the dehalogenation of several organic compounds, focusing on the study of electrocatalytic materials and innovative setups [45–48]. In the case of ICM, the reduction is particularly interesting because the cleavage of C-I bonds requires much less energy than the cleavage of other C-X bonds, leading to cheaper processes [49]. In addition, the removal of organically bound iodine is the key process to remove adsorbable organic halogens (AOX) compounds and to make the transformation products more biodegradable and less bioaccumulative. AOX, defined as the sum of all halogenated compounds which can be absorbed on activated carbon, are in fact very well known for their widespread distribution, potential toxicity and bioaccumulation [50].

In 2009, Zwiener *et al.* studied the electrochemical reduction of iomeprol, aiming to evaluate the mechanism through the identification of the TPs in a divided cell using a reticulated nickel foam as a cathode [51]. Electrolysis were carried out using both an aqueous solution ($NaClO_4$ 0.1 M) and urine as matrix. In the former case, iomeprol was completely degraded, but no mineralisation of the carbon skeleton of the molecule was detected. In urine, the time required for the degradation is the same, but the energy needed is higher. Identified TPs are those due to the subsequent formal substitution of iodine with hydrogen in IMP, leading to IMP-1I, IMP-2I and IMP-3I. A further transformation product is due to the electrochemical reduction of the side chain with the loss of C(=O)=CHOH. The advantage of such a process is the possibility of being used for the pretreatment of concentrated solutions before their discharge into the sewage system and the fact that no additional reactive chemicals are required. However, in this work, the release of iodine is suggested to occur as solvated iodide ions, in accordance with the theoretical models developed so far for dehalogenation [52,53]. Yan *et al.* studied the electrochemical reductive dehalogenation of diatrizoate and iopamidol and proposed that the mechanism for the dehalogenation is instead radical-based (Eq. 10), where the concerted transfer of 3 electrons occurs [54].

$$\mathrm{ICM} + 3\,\mathrm{e}^- \rightleftarrows 3\,\mathrm{I}\cdot + \mathrm{products} \tag{10}$$

This hypothesis is confirmed by performing an RRDE (Rotating Ring-Disk Electrode) experiment, where the reductive dehalogenation occurred at the disc while the ring potential is set at a value sufficient for iodide oxidation. In the presence of organic species able to react with active iodine, the ring current is suppressed.

The study of Del Moro *et al.* about the degradation of iopamidol, iobitridol, iodixanol, iopromide, amidotrizoate and iomeprol proposed instead a different reduction of the sidechains with respect to the one presented by Zwiener *et al.* [55]. Even though the aromatic ring deiodination is still presented as the fastest reaction, where the aromatic ring is said to play a key role in capturing one electron and then iodide is expelled, the alkyl aromatic amides reduction is considered as the other important process. This would bring to a different product with respect to the one presented by Zwiener *et al.*, where the chain lost is the $-CH_2-CH-OH-CH_2-OH$. However, experimental conditions were quite different.

Zhang *et al.* studied the electrocatalytic reduction of iohexol exploiting vitamin B12 as a catalyst [56]. It is well known in fact that some transition metal complexes can favour the selective reduction of the carbon-halogen bonds of pollutants. The electrocatalytic activity of vitamin B12 was demonstrated and the electrocatalytic conditions were optimised to promote the electrocatalytic process over direct reduction. Total dehalogenation of iohexol was achieved with a current efficiency of 49%, which can be improved by immobilising the catalyst on the electrode.

Coupled electrochemical reduction and oxidation of ICM

Considering the good results of electrochemical methods both in the oxidation and reduction of ICM, researchers have also proposed treatments based on the coupling of the two. It is known that halogen groups tend to exhibit a negative inductive effect that decreases the electron density at the benzene ring, thus increasing oxidation resistance [43]. The difficulty to oxidise several ICM can therefore be reduced by shifting towards the degradation of pre-electrochemical deiodinated molecules, also leading to the complete mineralisation. In addition, electrochemical reduction coupled with electrochemical oxidation has already shown good results, reaching the mineralisation of the reduced products [57,58].

Radjenovic *et al.* studied the electrochemical reduction and successive oxidation methods for the removal of diatrizoate [3] using a BDD anode and a cathode of graphite felt (or Pd-nanoparticle-loaded graphite felt). Reductive and oxidative processes were successfully combined in a three-compartment electrolytic cell to allow the separation of iodide ions formed during the electrolysis in the central compartment by electrodialysis, whereas diatrizoate and its reduction products accumulated in the cathodic cell.

In another study by Zhang *et al.*, electrochemical reduction followed by oxidation of diatrizoate allowed total deiodination and improvement of the biodegradability of the solution, achieving a mineralisation yield of 60% instead of 5% obtained for the non-treated diatrizoate solution [32]. The study aimed to combine the benefit of selective electrochemical pretreatment and low-expensive biological treatments to reach the complete mineralisation of ICM [59,60]. First, the electrochemical reduction of diatrizoate was performed using a flow cell with a graphite felt electrode, reaching complete deiodination. The following electrochemical oxidation, at different potentials, was carried out. Finally, four different biological treatments were realised to complete the degradation process. The study highlighted that the mineralisation yield increased from 41% to 60% when electrochemical oxidation was implemented after electroreduction [32]. Simultaneous electro-reduction and oxidation have been tested on iopromide by Lütke *et al.* using a single-compartment cell equipped with a BBD anode and a platinum cathode [61]. A very high degradation efficiency was achieved, up to 96% of mineralisation, and the exhibited toxicological relevance of the TPs was negligible. Laser-induced graphene (LIG) electrodes were also tested for the degradation of iohexol in an undivided cell showing good results [31]. **Table 2** summarizes the results discussed for ICM degradation through electrochemical oxidation, reduction and a combination of the two.

Table 2: *Summary of the described electrochemical methods for the degradation of ICM.*

Electrochemical method	Target substrate	Degradation
EO with BDD anode [37]	Diatrizoic acid	Complete
EO with BDD anode [38]	Iohexol	Complete
EO with BDD anode [39]	Diatrizoate, iotalamic acid, iopromide, iohexol, iopamidol and iomeprol	90%
EO with BDD anode EO with Ti/SnO_2-SbBi anode EO with Ti/TiO_2-NT/SnO_2-SbBi anode [40]	Iohexol, iopromide, diatrizoate	~ 84%
EO with laser-made Ti/RuO_2–TiO_2 anode [33]	Iohexol	95.5%
EO with graphene sponge RGO functionalised with borophene [41]	Iopromide and diatrizoate	95% and 89%
EO/ZVI [42]	Iopamidol	86.7%

ZVI-EO [42]	Iopamidol	99.5%
EO with BDD anode and sulphate species [43,44]	Diatrizoate and iopromide	Complete
ER with nickel foam cathode [51]	Iomeprol	Complete
ER with graphite felt anode and vitamin B12 catalyst [56]	Ioxehol	Complete
ER + EO with graphite felt cathode and BDD anode [3]	Diatrizoate	Complete
ER + EO + biodegradation with graphite felt cathode [32]	Diatrizoate	60%
ER + EO with Pt cathode and BDD anode [61]	Iopromide	96%
EO + ER with LIG anode and cathode [31]	Iohexol	50%

EO = electro-oxidation, BDD = boron-doped diamond, NT = nanotubes, EO/ZVI = electrochemical treatment coupled with a fluidised bed with zero valent iron, ZVI-EO = electro-oxidation preceded by a pre-treatment with zero valent iron, ER = electro-reduction, LIG = laser-induced graphene.

MRI CONTRAST MEDIA

The degradation of GBCAs is still a limited explored research area and, despite the several advantages of electrochemical degradations, there is still poor literature on their application to GBCA. To date, the research has mainly been focused on their separation from the environment as a preliminary step to a further degradation.

Bendakovska *et al.* presented the sorption of two different GBCAs by active carbon, humic acids and other materials [62]. They found promising outcomes for sorption by active carbon as a confirmation of the results achieved by Elizalde-Gonzales' group, which studied the pH-dependent sorption of GBCAs by active carbon in aqueous solution and model urine [63]. A notable finding is a decrease in the absorbed amount in urine caused by competitive absorption. Recently, Sommer *et al.* explored the interaction between Gd chelates and humic substances, both for linear and macrocyclic GBCAs [64]. They stated that only the linear molecule reacted to form Gd-humic acid adducts. Macrocyclic chelates are indeed more stable, favouring their accumulation in the environment. Progress has also been gained in the uptake of dissolved Gd^{3+} in specific absorbent and reusable materials. This method could be used to remove those few highly toxic cations released by GBCAs to an aqueous environment, or after an ideal treatment for the separation of Gd^{3+} from the organic chelating ligands. Some research groups turned their attention to Gd-imprinted polymers, highly selective materials produced using Gd^{3+} as a template ion. Zheng *et al.* produced three-dimensional macroporous imprinted chitosan films [65], while Li's group obtained imprinted magnetic chitosan/carbon nanotube composites [66]. Those materials showed to be stable and effective for the reversible Gd^{3+} adsorption from an aqueous solution. Lee ***et al.*** instead synthesised and studied a stable metalorganic framework known as Cr-MIL-101-PMIDA, showing good selectivity for the absorption of Gd^{3+} among rare elements' cations [67]. Furthermore, with regard to liquid-liquid extraction of Gd^{3+} from aqueous phase, ionic liquids showed to be promising extracting agents: for instance, the use of N-methyl-N,N,N-trioctyl ammonium-bis-(2-ethylhexyl) phosphonate (MTOABEHP), synthesised by Dutta *et al.*, allows an almost quantitative separation and recovery of Gd^{3+} cations [68].

Regarding non-electrochemical degradation techniques, Cyris *et al.* considered advanced oxidation as a step of an advanced wastewater treatment, which could degrade gadolinium chelates [69]. Advanced oxidation was performed on GBCAs through the reaction with hydroxyl radicals produced by the application of ozone and hydrogen peroxide, and successfully degraded the gadolinium chelates, obtaining different Gd^{3+} non-toxic species (still complexed with ligands deriving from chelates degradation) in a very short time. The effect of the application of UV radiation to GBCAs was investigated by Birka *et al.*, observing a general high stability towards it. Only in the case of Gd-BOPTA (gadobenate dimeglumine) they detected Gd-containing transformation products formed after the exposure, demonstrating partial degradation by UV radiations [70].

Lately, the electrochemistry of rare elements has gained importance being studied to develop new methods for the recovery of those rare metals from different matrixes.

The electrodeposition of metallic Gd on a substrate used as cathode is known to be challenging in water, due to the too negative potentials required for the reduction of Gd^{3+} to Gd. Some examples are present in literature, but they are usually performed under hard conditions, such as in the case of Bermejo *et al.*: a fixed potential was applied to $GdCl_3$ dissolved in molten LiCl-KCl eutectic under Ar atmosphere at 748 K. When an inert working electrode made of tungsten was used, the electroreduction occurred in a single step, and the nucleation of Gd crystals on the substrate was studied [71]. Bagri's research group, although under inert atmosphere, managed to electrodeposit Gd and other rare earth elements (REEs) metals at room temperature using a new class of specific ionic liquids as solvents, made of rare earth salts dissolved in trimethyl phosphate [72]. Ionic liquids often allow to widen the electrochemical potential window thus enabling rare earth elements' electroreduction. Aghazadeh *et al.* succeeded in the electrodeposition of Gd hydroxide on a stainless steel cathode by electrogeneration of hydroxide ions [73]. The galvanostatic experiment was performed on a solution of Gd nitrate maintained at a low temperature.

Recently, Couto *et al.* made up an electrodialytic process to recover rare earth elements from coal ashes [74]. With the REE-containing coal ash placed into the anode compartment of a two-compartments electrodialytic cell kept at low pH, the application of a current led to the REEs solubilisation and migration towards the cathode. After three days, 70% of REEs were effectively extracted and dissolved in high concentrations in the catholyte.

Considering the promising results of these preliminary studies and the advantages that electrochemistry offers in the degradation of ICM, it is highly desirable to extend the application of electrochemistry also to GBCAs' degradation. As a starting point, the most effective electrochemical degradation techniques developed for ICM could be tested on GBCAs. Oxidation through the electro-production of hydroxyl radicals could represent a promising approach. Other interesting fields of investigation are performing advanced oxidations and electrodialytic processes or finding improved conditions for the electrodeposition of rare metals. It will also be crucial to dig deeper into rare elements' electrochemical behaviour and the degradation of Gd chelates to recover that critical element.

CONCLUSIONS

In this review, we summarised the current state of ICM and MRI degradation, highlighting the main features of electrochemical treatment processes, which offer considerable advantages compared to conventional ones. Indeed, they provide ease of on-demand operations, the possibility of complete automation of water treatment and little or no need to use externally stored chemicals. Other benefits include the possibility to control and adjust the EC potential of the working electrode(s) to optimise the degradation of target compounds and a wide range of EC reactor configurations and available electrode materials, including those with electrocatalytic properties. Electrochemistry does represent an intrinsically green and economically affordable technique if we consider the prospective availability of renewable energy sources. Future research should be focused on providing novel approaches for reducing the concentrations of ICM and MRI in wastewater in a cost-effective manner. The best option should be to eliminate contrast media through a localised action before they can enter the aquatic environment. Thus, collecting urine from all patients following ICM and MRI examinations could be a promising strategy to reduce their increasing concentrations in drinking water systems, allowing at the same time to recover the technologically critical element gadolinium and the valuable iodine, in a circular economy perspective. The development of methods able to work with high pollutants concentration should be the focus of the next research.

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ANNOTATED REFERENCES

* Paper of special interest
** Paper of outstanding interest

Radjenovic [3]****:** The authors demonstrated the potential of electrochemical reduction and oxidation coupled in a three-compartment reactor operated in a continuos mode, also combined with the recovery of the released iodide ions electrodialyzed in a central compartment.

Bocos [37]****:** This work demonstrate that electrochemical mineralization performances are enhanced by exploiting the Fenton reaction also in the case of hardly oxidizable molecules such as ICM.

Moratalla [42]***:** Synthetic urine polluted with iopamidol was treated by electrochemical oxidation, also coupled with chemical dehalogenation through ZVI, demonstrating the possible use of such a treatment in real hospital matrix.

Farhat [43]***:** This interesting work analyzes the influence of the presence of sulphate ions on the oxidation of recalcitrant pollutant. They are in fact commonly detected in wastewater but often neglected when dealing with oxidative processes. Here a demonstration of the enhanced oxidation by the activation of sulphate.

Yan [54]****:** In this study, the radical mechanism for the dehalogenation of ICM is demonstrated by the use of RRDE. This mechanism is in contrast with the one accepted for halogeneted compound in general, giving a particular relavence to the work.

Cyris [69]***:** This work demonstrates that the degradation of gadolinium chelates via hydroxyl radical is effective. Since no effect of free Gd was detectable in toxicity test, the reaction produced (yet unknown) ligands capable of binding Gd ions.

Couto [74]****:** This work shows an effective electrodialytic process for the recovery of rare earth elements from coal ashes. Applying 50 mA and adjusting the pH to 2, REEs at the anode compartment are solubilized and more than 70% are extracted and concentrated at the catholyte.