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# Electrochemical hydrogenation for water purification made easy

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1 **WASTEWATER TREATMENT**

2 **Electrochemical hydrogenation for water purification made easy**

3 *The design of an electrochemical system without electrolytes allows hydrogenation of oxidized*  
4 *contaminants in water without the introduction of additional chemicals*

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9 The rise of water demand through agriculture, industries and domestic activities, combined with the  
10 water stress that is associated with climate change, is already leading to increased usage conflicts [1].  
11 The water crisis produces by the increased demand and reduced availability of clean water represents  
12 one of the biggest challenges of the 21<sup>st</sup> century and is part of the sustainable development goal  
13 addressed by the United Nations [1].

14 Among the various approaches to temper the problems created by water scarcity, the reuse of the  
15 treated wastewater for agriculture (e.g. irrigation), for industry or even for drinking water is a  
16 palatable solution [1,2]. However, most of the wastewater treatment plants (WWTPs) currently in use  
17 are based on biological processes and are not designed to completely eliminate recalcitrant pollutants  
18 such as pesticides, pharmaceuticals and cosmetics. These contaminants are found at trace levels (ng/L  
19 to µg/L) in natural water, and even at such ranges of concentration they can pose substantial  
20 environmental and health risks [3].

21 Physico-chemical treatments for wastewater could be an attractive alternative to biological process  
22 to remove persistent pollutants [4]. Before they can widely employ however, these technologies  
23 advance to the stage where they require low cost and they provide high level of efficiency.  
24 Furthermore, it is essential that they operate without the substantial need of chemicals that can pose  
25 additional environmental risks to the ones they are intended to reduce, and research is currently in  
26 progress to achieve these conditions. Now writing in Nature Water, Yinghua Xu et al. report an  
27 electrochemical system that could be used to treat wastewater without the substantial introduction of  
28 chemical that could become water contaminants [5].

29 Electrochemical systems are arising growing interest, because only electrons ( $ne^-$ ) are involved to  
30 eliminate the water pollution [6]. This can be done in two main ways. The first possibility is that the  
31 pollutants can be electro-oxidized or electro-reduced with a direct electron transfer at the anode or

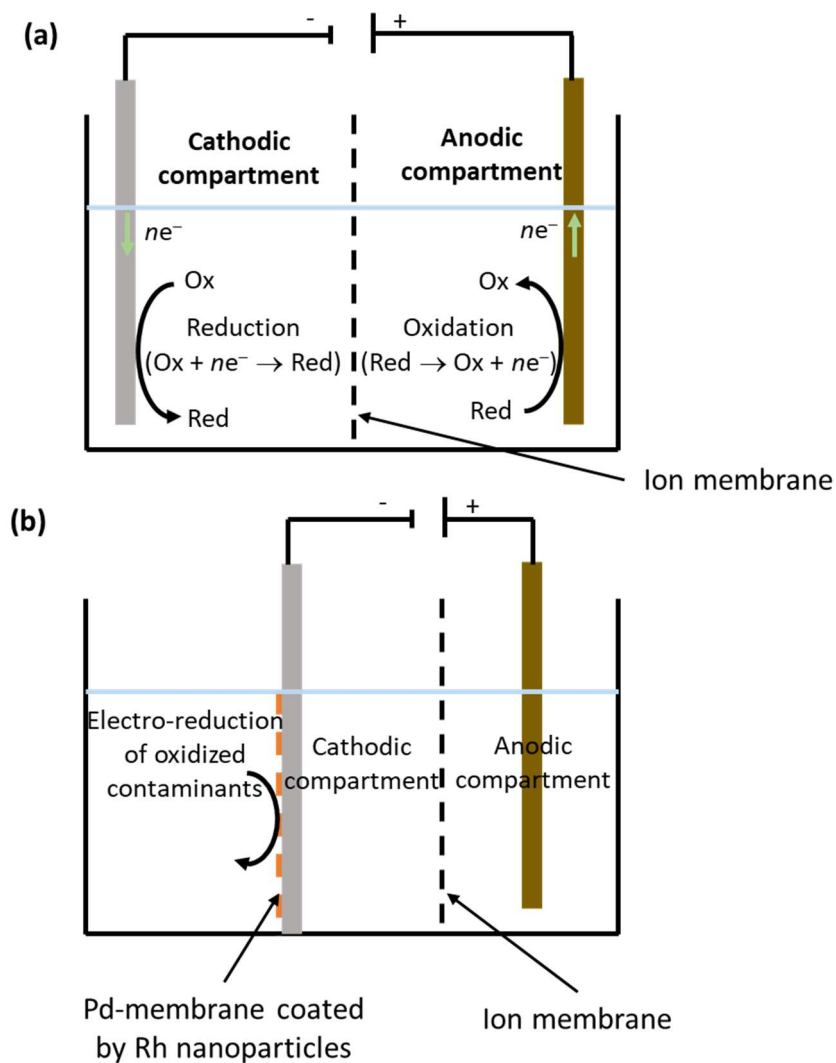
32 cathode surface, respectively (Figure 1a). The second path is the electro-oxidation or electro-  
33 reduction of the solvent (H<sub>2</sub>O in this case) and/or of other ionic species (e.g., SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>) that can then  
34 form strong oxidants (e.g., hydroxyl radicals (<sup>•</sup>OH), sulfate radical (SO<sub>4</sub><sup>•-</sup>), chlorine radical (Cl<sup>•</sup>))  
35 and/or reductants (aqueous electron (e<sup>-</sup><sub>(aq)</sub>)) that will eliminate the water pollution. This is called the  
36 indirect oxidation or reduction. Electrochemical technologies can also be flexible, easily scalable and  
37 allow operating numerous separation and conversion systems [7]. According to the operating  
38 conditions (e.g. applied current density, reactor design, type of electrode materials, water  
39 characteristics), high oxidation or reduction power can be obtained. This can lead to very high  
40 conversion rates and yields (>99%), as defined by the difference of initial concentration of the  
41 compounds to be removed with concentration at time *t*, divided by the initial concentration. However,  
42 the solution to treat need to be conductive enough to power the electrolysis. In many effluents, and  
43 particularly in municipal WWTPs, the ion content is not high enough so that the addition of  
44 supporting electrolyte is required. Moreover, the oxidative treatments often produce unwanted by-  
45 products (e.g. chlorate, perchlorate, nitrate) in presence of chloride ions (Cl<sup>-</sup>) and/or nitrogenous  
46 species that are ubiquitous in water. This problematic with intermediates is inherent with all  
47 conversion systems. In addition, some of the organic pollutants are at too high oxidation state (e.g.  
48 haloacetic acid, chlorophenol), meaning that a reduction technique is preferable [8].

49 Xu et al. propose to avoid the addition of a supporting electrolyte by implementing a divided cell in  
50 which the electrochemical reactions occur behind the electrode, rather than in between cathode and  
51 anode like in a conventional reactor (Figure 1b) [5]. They also used palladium (Pd) membrane  
52 modified with rhodium (Rh) nanoparticles placed in the cathode chamber to catalyze the reduction of  
53 oxyanions (chlorate, perchlorate, bromate, nitrite, nitrate), haloacetic acids and chlorophenols by  
54 hydrogenation. They succeeded to reach conversions yield higher than 99%, except with nitrate and  
55 perchlorate. The high selectivity towards acetic acid is attributed to the Rh nanoparticles that favor

56 their adsorption compared to Pd, as noticed with Density Functional Theory calculation. The  
57 performance is confirmed in real tap water with around 85% decrease of trichloroacetic acid, and lead  
58 to a level of contamination below the threshold value (60 µg/L) set by the USEPA.

59 The results of Xu et al. are promising; however, some challenges remained to be solved. The lifetime  
60 of this kind of membrane electrode has to be tested over a long period (e.g. several months). This  
61 parameter is important, particularly in terms of costs, since it requires the use of expensive metals.  
62 This will be a prohibitive solution at larger scale if the assays failed. Moreover, scale up studies will  
63 have to be performed to further assess the efficiency at pilot scale. Furthermore, the cathode scaling  
64 is often encountered with solution that contain calcium and carbonates, which is the case of numerous  
65 effluents. So, the polarity reversal technique will need to be tested with such electrode materials,  
66 otherwise passivation issues will be encountered in continuous mode and at large scale. Finally, the  
67 control of selectivity in the aim at producing reduced valuable compounds could even be of higher  
68 interest.

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70  
 71 **Figure 1.** (a) schematized conventional divided electrochemical reactor (Ox: oxidant, Red:  
 72 reductant,  $e^-$ : electron,  $n$ : number of electrons transferred), (b) schematized reactor design proposed  
 73 by Xu et al. to operate without supporting electrolyte and for the electro-reduction of oxidized  
 74 organic (haloacetic acids and chlorophenols) and inorganic (chlorate, perchlorate, bromate, nitrite,  
 75 nitrate) contaminants in water [5].

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107 The authors declare no competing interests.

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