Catalytic hydrodehalogenation of halogenated disinfection byproducts for clean drinking water production: A review

Ali K. Ilunga *, Bhekie B. Mamba, Thabo T.I. Nkambule

Institute for Nanotechnology and Water Sustainability (iNanoWS), University of South Africa, UNISA Science Campus, Florida (Johannesburg), P.O. Box 392, Pretoria 0003, South Africa

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ABSTRACT

Water treatment plants applied large amount of chlorine to eliminate microorganisms and prevent future microbial contamination of drinking water. Electrophilic substitution and electron transfer activities between natural organic matter (NOM) and free chlorine resulted in the formation of chlorinated disinfection byproducts (DBPs). Chlorinated DBPs' consumption and exposure provoked severe health risks susceptible to cause death and/or lifetime illness. Conventional water treatment approaches such as membrane filtration, adsorption, sedimentation, and coagulation are much appropriated to eliminate chlorinated DBPs' precursors with a percentage removal estimated at 70. At the lowest concentration of chlorinated DBPs, conventional water treatment approaches fail to eliminate chlorinated DBPs in drinking water. In this review, we discussed catalytic hydrodehalogenation as an efficient approach to advance a complete eradication of chlorinated DBPs in drinking water. Metal nanocatalysts contributions were reviewed to understand the chemical pathways throughout the catalytic hydrodehalogenation of chlorinated DBPs. Palladium received much attention as metal nanocatalysts to facilitate the catalytic hydrodehalogenation of chlorinated DBPs. Catalytic investigations through novel nanocatalysts exploration should be intensified to gain insights in catalytic hydrodehalogenation of chlorinated DBPs and advance its possible incorporation in water treatment technology.

1. Introduction

Water treatment technology concentrates much energy to protect and prevent the depletion of natural potable water. Water scarcity faced by humanity constitutes a major concern because of the negative impact on the ecosystem and human lives. About 80% of planet earth is covered by surface water and groundwater such as rivers, sea, lake, and ocean. Surface water and groundwater contain chemical and biological substances such as heavy metals, organic compounds, and microorganisms which prohibited its direct consumption. Water treatment process combined series of physicochemical techniques to improve the quality of surface water before its consumption. Surface water and groundwater pollutants are diverse and varied with climate, geographic location, and socio-economic activities [1-3]. In nowadays, socio-economic activities such as mining, manufacturing, and agriculture are prevalent causes of surface water contamination [4-7]. Strong regulations must be implemented to regulate the socio-economic activities to protect surface water.

Conventional water treatment approaches such as coagulation, membrane filtration, adsorption, and sedimentation are systematically performed to remove chemical pollutants in surface water. Organic pollutants known as natural organic matter (NOM) are frequently tackled during water treatment process due to their diversity and toxicity capable to cause severe clinic threats to the water consumers. NOM consists of a heterogeneous mixture of organic compounds originated from decayed plants and animals, and chemicals dissolved in surface water. NOM can be partitioned into three fractions, hydrophilic (humic), hydrophilic (non-humic), and transphobic [8]. Hydrophobic fraction composed of fulvic and humic acids constituted the largest fraction about 75% of total NOM in surface water. Novel techniques have been advanced to facilitate the splitting of NOM such as the modified polarity assessment method (mPRAM) reported by Nkambule et al. which allowed NOM to split into fractions under middle conditions [9]. Conventional water treatment approaches led to about 70% removal of NOM in surface water [10-12]. Studies are going on to elucidate NOM complexity and genesis which constitute the fundamental steps to its complete removal in surface water.

Microorganisms such as bacteria, archaea, fungi, protozoa, algae,
and viruses in drinking water present severe health risks susceptible to lead to lifetime illness and cancers [13,14]. Water disinfection is basically performed at the last stage of water treatment process to eliminate pathogen substances in drinking water before the discharge in delivery networks. Several water disinfection methods were advanced to annihilate infectious microorganisms in drinking water namely, ultraviolet disinfection [15,16], ozone disinfection [17,18], chlorine disinfection [19,20], silver for water disinfection [21,22], and photocatalytic disinfection [23,24]. Chlorine disinfection method gained much attention compared to the others owing to its efficacy, affordability, and accessibility. It is critical to mention that most of water treatment plants applied water chlorination as a disinfection method. Chlorine is applied in excess for an effective water disinfection and to prevent future reinfection of disinfected water. Excess Chlorine defined as free chlorine assured the consumption of microbe-free water.

Chemical reactions between free chlorine and NOM formed chlorinated disinfection byproducts (DBPs) [25,26]. Typically, free halogen interacted with NOM to form halogenated DBPs such as chlorinated DBPs, brominated DBPs, and iodinated DBPs. Halogenated DBPs in drinking water are responsible for severe illness as well as cancers [27,28]. Among the closely monitored halogenated DBPs by water treatment technology, we can list trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), chlorophenols, and chlorite. The world health organization (WHO) imposed permissible concentration guidelines to minimize the consumption or exposure of halogenated DBPs in drinking water. The total THMs (comprising CHCl₃, CHBrCl₂, CHBr₂Cl, and CHBr₃) in drinking water should not exceed 100 μg/L [29]. The United States scale the permissible total THMs in drinking water at 80 μg/L, whereas Canada and Australia provide a guideline values of 100 μg/L and 250 μg/L of the total THMs, respectively [30–32]. The HAAs are also regulated in different countries namely, US with 60 μg/L permissible concentration and 80 μg/L guideline value in Canada. Diverse unregulated halogenated DBPs have been reported in water drinking distribution networks such as dichloroacetonitrile, trichloropropanone, and trichloronitromethane [33]. This indicated that more than to regulate halogenated DBPs permissible concentration, works should be conducted to achieve the complete eradication of halogenated DBPs in drinking water.

Dehalogenation process defined as carbon-halogen bonds cleavage constitutes the reliable chemical approach to promote for a complete removal of halogenated DBPs in drinking water. Radical and electronic cleavages are the evoked mechanism pathways to describe the carbon-halogen bonds cleavage during dehalogenation [34,35]. Dehalogenation always coupled with another chemical reaction such as hydrogenuation where the cleaved carbon linked with hydrogen (reductive dehalogenation), and Suzuki cross-coupling where carbon-carbon bonds were formed [34,36]. Mechanistic models such as dissociative electron attachment (DEA), desorption induced by electronic transition (DIET), and desorption induced by multiple electronic transition (DIMET) were developed to describe the electronic transfer process throughout dehalogenation of organic halide compounds [37–39]. Dutta et al. applied a hot electron transfer based on DEA model to elucidate the kinetic and mechanism behind the dehalogenation of brominated purine [40]. Yang et al. reported an efficient electrochemical dehalogenation of florfenicol based on electrochromic WOx [41]. The electrocatalytic dehalogenation of C–Cl and C–F bonds in florfenicol was estimated at 99.7% for 120 min reaction time.

The incorporation of nanomaterials in water treatment processes highly improved the physicochemical techniques applied to produce safe and clean water drinking [42–44]. Metal nanoparticles were broadly applied as nanocatalysts to facilitate the complete removal of halogenated DBPs following the reductive dehalogenation process under eco-friendly conditions. It is critical to underline that the absence of catalysts resulted in zero reductive dehalogenation activity. Reductive dehalogenation conducted in aqua phase can be referred as hydrodehalogenation. Metal nanoparticles fast agglomeration rate constituted a huge drawback for a suitable catalytic transformation. Several synthetic methods were advanced to produce robust metal nanocatalysts and evaluated their catalytic activities in hydrodehalogenation of halogenated DBPs [45–47]. In this work, we reviewed scientific publications related to the hydrodehalogenation of halogenated DBPs catalyzed by transition metal nanocatalysts and their potential applications in water treatment technology. Catalytic pathways were evoked to detail the interfacial interaction between halogenated DBPs and metal nanoparticles during catalytic hydrodehalogenation.

2. Halogenated DBPs' formation

Optical analytic methods were explored to depict NOM contents as well as to monitor NOM removal throughout water treatment process. Fluorescence excitation-emission matrix spectroscopy with parallel factor (FEEM-PARAFAC) analysis was recently developed and applied in South Africa to monitor NOM removals through coagulation [48,49]. The FEEM-PARAFAC analysis revealed that about 42% of the dissolved organic compounds were removed through coagulation. As aforementioned, about 70% of NOM can be removed through water treatment process. The optical analysis results indicated that a higher percentage of NOM aromatic fraction is removed compared to NOM aliphatic fraction during water treatment process [50,51]. This indicated that NOM aliphatic fraction constitutes the principal organic precursors interacting with free halogen to form halogenated DBPs.

Gaseous chlorine and/or hypochlorite compounds are the most preferable chlorine sources for water chlorination to eliminate microorganisms in drinking water [52]. A two-dimension quantitative plot defined as a chlorination plot can be constructed to monitor water chlorination [53]. Two variables, chlorine residual versus chlorine, constructed a chlorination plot and led to a chlorination curve. Fig. 1a illustrates a chlorination curve progression during water chlorination. Infectious substances extermination is achieved at breakpoint or dip. It is recommended to slightly exceed the breakpoint (more chlorine addition) during water chlorination to prevent the recontamination of disinfected water. March and Gual constructed a chlorination curve to monitor the chlorination of raw greywater with hypochlorite [54]. The chlorination curve indicated the typical hump-and-dip profile which assessed the formation and destruction of chloramine at 1.5 mol of hypochlorite. That indicated more than 1.5 mol of hypochlorite was required to effectively decontaminate raw greywater and prevent its recontamination. Fig. 1b showed a chlorination curve constructed throughout raw greywater chlorination with hypochlorite for an hour of contact time.

Excess chlorine interacted with NOM to generate chlorinated DBPs [55]. Two mechanisms have been advanced to explain the chemical pathway of chlorinated DBPs formation. First, chlorine fast hydrolysis produced hypochlorous acid (HClO) and hypochlorite ions (ClO⁻) [56]. Hypochlorous acid and hypochlorite ions interacted with NOM through electrophilic substitution and/or electron transfer mechanisms to form chlorinated DBPs [57–60]. A similar chemical pathway is invoked to describe the formation of halogenated DBPs. Bromine hydrolysis produced hypobromous acid/hypobromite ions (HBrO/BrO⁻) which reacted with NOM to form brominated DBPs [59]. Different free halogens led to competitive halogenation for the formation of halogenated DBPs [59,61]. The formation of brominated DBPs proceeded much faster than chlorinated DBPs ones.

The formation of halogenated DBPs has been reported during water treatment process. Water treatment process conducted membrane-based treatment to eliminate organic pollutants in surface water. However, particles-fouled faced by membrane-based treatment significantly reduced the fluidity of refresh water. Physical and chemical cleaning methods were developed to recycle the fouled membrane [62,63]. Chemical cleaning methods commonly applied chemical agents such as NH₂OH, H₂SO₄, peroxidase, and NaClO to reclaim membrane fluidity [62–64]. Long-recycling time and high concentration of sodium
hypochlorite throughout the reclaim of a fouled membrane was reported to generate chlorinated DBPs [65]. Ye et al. indicated that the presence of chlorine dioxide led to the formation of iodinated DBPs during oxidation of iodide-containing waters [66]. The use of chlorinated or halogenated compounds to reclaim the fluidity of a fouled membrane should be prohibited to prevent the risk of halogenated DBPs formation.

Peroxymonosulfate oxidation is one of the degradation processes widely conducted to mineralize organic pollutants in wastewater [67,68]. Xie et al. reported the formation of brominated DBPs during peroxymonosulfate oxidation due to free bromine presence [69]. Chu et al. demonstrated that water temperature influenced the formation of iodinated haloacetamides during persulfate oxidation [70]. This demonstrated that sulfate-based oxidation technologies in water treatment process should be applied with precautions. Fakour and Lo lately reported the formation of chlorinated DBPs in herbal spa pools [71]. Hydrolytic dissolution of herbal medicine releases organic substances which interact with free halogen and form halogenated DBPs. An extended conservation period of herbal spas in tape water can result in the formation of halogenated DBPs. Porcar-Santos et al. reported the formation of halogenated DBPs in stimulated seawater during photo-catalytic degradation of sulfamethoxazole catalyzed by TiO$_2$ nanoparticles [72]. This indicated that the photodegradation of organic pollutants in the presence of free halogen may generate halogenated DBPs.

Analytical and physicochemical techniques were widely reimaged to facilitate the quantification and identification of halogenated DBPs in drinking water. Tao et al. recently developed an analytic stepwise technique to detect halogenated DBPs in tap water using a liquid chromatography-high resolution mass spectrometry (LPHC-Q-Orbitrap-MS) [73]. The analytic stepwise technique unveiled the presence of the unknown halogenated DBPs (123 X-DBPs) in tap water. Saturated aliphatic and phenolic halogenated DBPs were equally identified through LPHC-Q-Orbitrap-MS analysis. Using UPLC/ESI-tqMS analysis, Gong et al. showed that the chlorination of saline wastewater effluents can result in the formation of unknown iodinated DBPs [74]. Shahar et al. constructed an enzymatic reflectance biosensor to detect halogenated DBPs [75]. The enzymatic halocarbon reflectance biosensor permitted 1,2-dichloromethane (50 mg L$^{-1}$) detection at 662 nm. The storage period of the enzymatic reflectance biosensor was estimated at up to 6 days at pH 8.0 and 4 °C. Table 1 lists recent analytic methods applied to detect halogenated DBPs. The detection and quantification of halogenated DBPs constituted the fundamental steps to achieve their effective removal for a safe drinking water production.

Epidemiology studies unveiled that the exposure and consumption of halogenated DBPs can provoke multiple types of cancer such as colon, rectum, stomach, brain, pancreas, lung, urinary bladder, and liver [81,82]. Halogenated DBPs toxicity pertained to halogen and can be classified as that iodinated DBPs > brominated DBPs > chlorinated DBPs [74,83]. Epidemiology reports indicated that human beings are confronted with adverse reproductive due to exposure or consumption of halogenated DBPs [52]. Mammals epidemiology trials unveiled an effective link between THMs and some biological toxicities such as neurotoxicity, reproductive toxicity, hepatoxicity, and nephrotoxicity.

Table 1 Analytic methods in use for the detection of halogenation DBPs.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Description</th>
<th>Halogenated DBPs</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Predictive model</td>
<td>Multivariate linear regressions models through basic water treatment parameters</td>
<td>Dichloroacetonitrile, Trichloroacetonitrile, Bromochloroacetonitrile</td>
<td>[33]</td>
</tr>
<tr>
<td>NOM DBP code</td>
<td>A new algorithm developed to improve organohalogens identifications using ultrahigh-resolution mass spectrometry (URH-MS)</td>
<td>Brominated DBPs, Chlorinated DBPs</td>
<td>[76]</td>
</tr>
<tr>
<td>FT-ICR/MS and LC-Orbitrap MS</td>
<td>Non-target Fourier transition ion cyclotron resonance mass spectrometry combined with liquid chromatography</td>
<td>Trichloroacetic acid, Dichloroacetic acid</td>
<td>[77,78]</td>
</tr>
<tr>
<td>UPLC/ESI-tqMS</td>
<td>Ultra-performance liquid chromatography/electrospray ionisation-triple quadruple mass spectrometry combined with high-resolution mass spectrometry.</td>
<td>Dibromoacetic acid, Bromoaetic acid</td>
<td>[79]</td>
</tr>
<tr>
<td>ESI FT-ICR MS</td>
<td>Ultra high resolution Fourier transformation ion cyclotron resonance mass spectrometry.</td>
<td>Unknown iodinated DBPs</td>
<td>[80]</td>
</tr>
</tbody>
</table>
The skin exposure on halogenated DBPs was found responsible for melanoma cancer [85–87]. Clinic risks associated with consumption and exposure of halogenated DBPs are countless. Scientific researchers and governments must join efforts to develop and implement sustainable strategies for the elimination of halogenated DBPs in drinking water.

### 3. Catalytic dehalogenation

Biological and chemical approaches were explored to address catalytic dehalogenation of halogenated organic compounds. Microbial hydrodehalogenation consisted of enzymatic dehalogenation where dehalogenase promoted carbon-halogen bonds cleavage. Owusu et al. reviewed the potential role of dehalogenase-producing halophilic bacteria in decontamination of marine environment [88]. Microbial and chemical dehalogenation can be combined to advance the cleavage of carbon-halogen bonds. Synergistic effect generated by dehalogenase bacteria and iron nanoparticles was found to enhance the microbial anaerobic dechlorination of perchloroethene [89]. The use of microbial dehalogenase to eliminate halogenated DBPs could not be acceptable for the production of safe and clean drinking water. Therefore, chemical approach using metal nanocatalysts to advance catalytic dehalogenation constitutes the viable technology to achieve safe and complete removal of halogenated DBPs.

Water chlorination is commonly conducted at the last stage of water treatment process before the discharging of drinking water for consumption. Conventional water treatment approaches served to eliminate the organic precursors (NOM) of halogenated DBPs and pre-formed halogenated DBPs in surface water [90–92]. At the lowest concentration of halogenated DBPs, conventional water treatment approaches failed to remove the halogenated DBPs [93]. This shows the necessity of alternative removal approaches for an effectively elimination of halogenated DBPs in drinking water and subsequently cut off clinic risks associated with its consumption. Catalytic dehalogenation emerged as an efficient approach for the removal of halogenated DBPs in drinking water [94,95]. Metal nanoparticles were often applied as nanocatalysts to improve the catalytic dehalogenation of halogenated DBPs. In this review, attention is given to understand the chemical activity generated by the mutual interaction between nanocatalysts and halogenated DBPs during catalytic dehalogenation.

Catalytic dehalogenation consisted of low-cost and eco-friendly chemical transformations proceeded at middle conditions. In the absence of catalysts, dehalogenation of halogenated DBPs can’t be achieved due to the remarkable energy bond describing carbon-halogen bonds [96]. Shen et al. conducted a redox-mediated electro-Fenton process for the complete dechlorination and mineralization of chlorophenol catalyzed by an in-situ-formed PdFe nanoalloy catalyst [97]. Reductive sites on the surface of PdFe improved hydrogen adsorption and oxygen molecular reduction. Oxygen species such as hydroxide radicals were found responsible for the complete mineralization of chlorophenol. Oxygen species (oxygen radicals and sulfate radicals) were reported to favor the formation of halogenated DBPs [69]. The uncontrollable state of oxidative dehalogenation pathways provoked the formation of halogenated DBPs. This supported the lack of interest in oxidative dehalogenation to eliminate halogenated DBPs in drinking water.

Reductive dehalogenation has been explored as an alternative removal approach for a sustainable elimination of halogenated DBPs to improve the quality of drinking water. Reductive dehalogenation of halogenated DBPs can be detailed as such the carbon-halogen bond cleaved to release halogen and hydrogen species substituted the released halogen to form a carbon-hydrogen bond. Reductive dehalogenation has been numerously conducted in synthetic chemistry and chemical-engineering transformations [98,99]. Scheme 1 illustrates reductive dehalogenation of halogenated DBPs catalyzed by metal nanocatalyst. Reductive dehalogenation consisted of selective and effective approaches to eliminate halogenated DBPs in drinking water. A large discussion on reductive dehalogenation or hydrodehalogenation for the removal of halogenated DBPs will be articulated in the following paragraphs.

### 4. Reductive catalytic dehalogenation

Heterogeneous nanocatalysts are usually constructed with solid supports to accommodate activity metal nanoparticles. Mesoporous transition metal oxide materials were majorly solicited as solid supports owing to their porosity and thermal stability. Recent scientific reports indicated that mesoporous transition metal oxide materials expanded their interests in heterogeneous nanocatalysis as solid supports to active nanocatalysts [100,101]. Mesoporous transition metal oxide materials as catalysts were not much explored for the hydrodehalogenation of halogenated DBPs. Recently, Patra et al. designed a highly ordered mesoporous metal oxide materials (MFT-1) composed of TiO$_2$-Fe$_2$O$_3$ using sodium dodecyl sulfate as a structured-directing agent [102]. The MFT-1 showed great catalytic activity during the reductive dehalogenation of diverse halogenated compounds. Our literature searches revealed that so far only MFT-1 has been tested as a catalyst for the reductive dehalogenation of halogenated compounds. Experiments are needed to gain much insights about mesoporous transition metal oxide materials as heterogeneous catalysts in reductive dehalogenation of halogenated DBPs. A successful ending will certainly lead to low-cost and efficient removal of halogenated DBPs which will highly enhance the quality of drinking water.

Metal nanoparticles supported on solid supports have been explored as nanocatalysts in countless chemical transformations. The interfacial
interaction between metal nanoparticles and solid supports was found to generate physical effects such as charge transfer, synergist, and spill-over [103–105]. Those physical effects were of great interest for the improvement of catalytic activity and chemical transformations. Zheng et al. reported a synergistic effect from palladium nanoparticles-metal oxide supports catalysts during hydrodehalogenation of bromochloroacetic acid [106]. A precipitation method was followed for the synthesis of transition metal oxide supports (CeO$_2$, Al$_2$O$_3$, activated carbon (AC), and SiO$_2$). A precipitation-deposition approach was performed to deposite Pd nanoparticles onto the transition metal oxide supports. Pd/SiO$_2$ indicated a negligible reaction rate progression compared to the rest of the supported nanocatalysts. Pd/CeO$_2$ led to the complete mineralization of bromochloroacetic acid where hydrodehalogenation was observed for Pd/Al$_2$O$_3$ and Pd/AC. Several hypotheses can be invoked to interpret bromochloroacetic acid mineralization in the presence of Pd/CeO$_2$. High adhesion energy on the surface of CeO$_2$ facilitated hydrogen spilling over on Pd nanocatalyst and lattice oxygen mobility on CeO$_2$ are the reliable catalytic pathway responsible for the complete mineralization of bromochloroacetic acid in the presence of Pd/CeO$_2$ [107,108].

The kinetic models such as the Langmuir-Hinselwood kinetic model have been often solicited to confirm the interfacial interaction between halogenated DBPs and metal nanocatalyst throughout reductive dehalogenation [97,109]. For a fast-reductive dehalogenation process, halogenated DBPs sorption onto metal nanocatalyst surface constituted the rate-determining step. Most of the kinetic data generated from reductive dehalogenation of halogenated DBPs fit with the Langmuir-Hinselwood kinetic model [109–111]. This indicated that the reaction rates during reductive dehalogenation of halogenated DBPs depended on the interfacial interaction between the catalyst and substrates. Fig. 2 shows the Langmuir-Hinselwood kinetic model fit of bromochloroacetic acid hydrodehalogenation catalyzed by Pd nanocatalyst deposited on ceria [106]. Halogenated DBPs concentration linearly progressed along with the reaction rate which showed that halogenated DBPs adsorption on metal nanocatalyst surface governed the reaction rate of reductive dehalogenation.

Wu et al. conducted a hydrodehalogenation of 4-chlorophenol catalyzed by palladium phosphide nanoparticles (Pd$_3$P$_{0.95}$/SiO$_2$) using hydrogen gas as hydrogen sources [112]. The Langmuir-Hinselwood kinetic model indicated that the adsorption of substrates on palladium phosphide nanoparticles surface consisted of the rate-determining step enhancing the catalytic rate of 4-chlorophenol hydrodehalogenation. Phosphides played an essential role in adsorption control minimizing the adsorption of chlorine and sulfur ions on palladium surface while improving 4-chlorophenol adsorption. The adsorption control enhanced the turnover rate of 4-chlorophenol hydrodehalogenation. Fig. 3(a-c) pictures the turnover rate variation based on the adsorption of substrates (4-chlorophenol, chlorine, and sulfur) on the surface of palladium phosphides nanocatalysts [112]. The equilibrium constant established by 4-chlorophenol and palladium nanoparticles was higher than the ones from chlorine ions and palladium nanoparticles (Table 2).

Our literature search indicated that palladium nanoparticles have been largely explored as metal nanocatalysts to facilitate the reductive dehalogenation of halogenated DBPs. However, no clear reports have been found to support a real application in water treatment plants. Nevertheless, we highly believe that hydrodehalogenation constitutes an efficient scientific approach in the removal of halogenated DBPs in drinking water. Cai et al. lately reported hydrodechlorination of trichloroacetic acid assisted by palladium nanoparticles deposited on H$_2$-transfer membranes [109]. The reaction rate was governed by the adsorption of substrates on palladium surface as the rate-determining step in the hydrodechlorination of trichloroacetic acid. Mechanism pathway of trichloroacetic acid hydrodechlorination is illustrated in Scheme 2, where hydrogen species on palladium interface interacted with adsorbed chlorinated DBPs to initiate the hydrodechlorination. Table 3 lists scientific publications wherein transition metal nanocatalysts were involved in the reductive dehalogenation of halogenated DBPs.

A remarkable catalytic activity exhibited by palladium nanoparticles during reductive dehalogenation of halogenated DBPs is unquestionable and leads to a fast reaction rate for a complete halogenated DBPs removal. Wu et al. conducted a deposition method to design a hydrogen-based membrane palladium-film reactor (H$_2$-MPFR) [122]. The hollow-fiber membrane containing palladium nanoparticles was evaluated in continuous-flow hydrodehalogenation of 2,4-dichlorophenol. Palladium-film nanocatalyst indicated an exceptional efficiency estimated at 87% of chlorinated DBPs reduction. The modified hollow-fiber membrane prevented the migration of organic substances to clean water. Palladium-film nanoparticles improved the anti-fouling ability of the modified membrane also led to a complete hydrodechlorination of chlorinated DBPs. Scheme 3 schematised the catalytic pathway 2,4-dichlorophenol hydrodehalogenation using of palladium-film nanocatalyst. This investigation demonstrated that reductive dehalogenation can perfectly be incorporated in water treatment plants and highly improved the reduction of total halogenated DBPs percentage in drinking water.

Fig. 2. a) Hydrodehalogenation at a varied concentration of bromochloroacetic acid catalyzed by Pd/CeO$_2$. b) The Langmuir-Hinselwood kinetic model fitting curve [106].
4.1. Hydrogen sources

Hydrogen sources are of great interest in reductive dehalogenation and should demonstrate eco-friendly properties and market accessibility. Transition metal nanocatalysts facilitated the cleavage of carbon-halogen bond and hydrogen sources provided hydrogen species to substitute the cleaved halogen. Hydrogen gas has been broadly applied as hydrogen sources to advance the reductive dehalogenation of haloacids. Lan et al. applied hydrogen gas as a hydrogen source to achieve chlorophenol hydrodechlorination under ambient condition in the presence of deposited palladium nanocatalyst [123]. Carbon nanotubes, aluminum oxide, activated carbon, and graphene were used as supports and conventional impregnation method was performed to deposit palladium nanocatalyst on each support. All the deposited palladium nanocatalysts exhibited exceptional catalytic activity throughout chlorophenol hydrodechlorination. Pd nanocatalyst deposited on carbon nanotubes exhibited the highest catalytic activity compared to all the rest. Carbon nanotubes large porosity was the reason for catalytic activity increase by permitting the substrates and product-free mobility throughout hydrodehalogenation reaction. Hydrogen gas as hydrogen sources allowed a clean hydrodehalogenation of halogenated DBPs which is highly motivating for water treatment technology.

Hydrogen gas inflammability demands rigorous safety management that might restrain its interest for reductive dehalogenation of halogenated DBPs in water treatment technology. Alternative hydrogen sources with much stability, eco-friendly, and market accessibility such as borohydride compounds have been explored for a prompt hydrodehalogenation of halogenated DBPs. Adhikary et al. reported the reductive dehalogenation of haloacetic acids (Tri-, di-, mono-bromoacetic acids and tri-, bi-, and mono-chloroacetic acids) using sodium borohydride as a hydrogen source [124]. Using sol-gel entrapped gold and silver nanocatalysts, haloacetic acids were dehalogenated under reductive conditions. The product compositions pertained to the additional rate of sodium borohydride. A fast addition of sodium borohydride resulted in complete dehalogenation of halogenated DBPs. Borohydride ions as hydrogen sources for reductive dehalogenation of halogenated DBPs offered diverse possibilities which allowed the control of reaction-rate and product formation.

Hydrogen gas and borohydride ions are the preferable hydrogen sources for a sustainable reductive dehalogenation of halogenated DBPs. This can be justified by their eco-friendly descriptions which favored the
hydrolysis released hydrogen ions at lower pH which can serve as halogenated DBPs in the absence of external hydrogen sources. Water hydrogenations were reported to advance the hydrodehalogenation of its implementation in water treatment technology. Direct and indirect understand the hydrodehalogenation of halogenated DBPs and promote system [109]. The contrary observation can be explained by the absence of external hydrogen sources such as sodium borohydride.

4.2. Reaction medium

Aqueous medium is of great interest in the current discussion to understand the hydrodehalogenation of halogenated DBPs and promote its implementation in water treatment technology. Direct and indirect hydrogenations were reported to advance the hydrodehalogenation of halogenated DBPs in the absence of external hydrogen sources. Water hydrolysis released hydrogen ions at lower pH which can serve as hydrogen sources. Duan et al. analyzed the hydrodehalogenation pathways of trichloroacetic acid using hydrogen gas and sodium borohydride as hydrogen sources [109,125]. Cai et al. conducted a successful hydrodechlorination of trichloroacetic acid catalyzed by palladium nanocatalyst using hydrogen gas as a hydrogen source [109]. Dichloroacetic and monochloroacetic acids were identified as intermediaries before obtaining acetic acid as a final product. On the other hand, Adhikary et al. showed that non-intermediaries were formed (only acetic acids) throughout hydrodechlorination of trichloroacetic acid catalyzed by gold nanocatalyst using sodium borohydride as a hydrogen source [125]. Scheme 4 briefs the hydrodechlorination pathways of trichloroacetic acid catalyzed by gold nanocatalyst using hydrogen gas and sodium borohydride as hydrogen sources based on [109,125] report. Those two reports indicated that hydrogen sources influenced the chemical pathways throughout the hydrodehalogenation of halogenated DBPs. Intermediary products formation or partial hydrodehalogenation throughout hydrodehalogenation of halogenated DBPs should be avoided to prevent their clinic risks in drinking water.

4.3. Electroreductive dehalogenation

The electrochemical system has been explored as an alternative approach for halogenated DBPs reduction without the use of chemical reductants. In some cases, hydrogen species formations using chemical reductants can result in undesirable byproducts throughout the reducive dehalogenation of halogenated DBPs. Electroreductive dehalogenation has been advanced to achieve a reductant-free hydrodehalogenation of halogenated DBPs. Metal semiconductors were largely explored as electrocatalysts to assist the electroreductive dehalogenation of halogenated DBPs [132–134]. Electronic excitation of metal semiconductors generated active hydrogen species which initiated the reduction of halogenated DBPs. Escobedo et al. reported an electroreductive dehalogenation of 2-chlorophenol using dealloyed nanoporous Pd/Ti cathode as an electrocatalyst [135]. Electroreductive analysis unveiled that electronic reduction of hydrogen molecular on the surface of dealloyed nanoporous generated hydrogen species which initiated the hydrodechlorination of 2-chlorophenol.

The designing and maintenance of electrochemical reactors are
investigations have been expanded to develop robust and efficient electrocatalysts for consecutive electroreductive dehalogenation to improve the utility of electrochemical reactors. Transition metal nanocatalysts exceptional physicochemical properties promoted their interest in several electroreductive dehalogenation processes [118,136,137]. Mechanism pathway analysis through scavenging experiments indicated that electrocatalysts’ surface served as a platform on top of which hydrogen species and halogenated DBPs interacted to produce the dehalogenated products [135].

Dauda et al. conducted a cathodic reductive dehalogenation of halogenated DBPs catalyzed by cobalt-molybdate (Co-MoS₂) electrocatalyst using a single electro-reactor [136]. The hydrothermal method was adapted for the synthesis of Co-MoS₂ electrocatalyst. The cathodic reductive dehalogenation led to the 90% removal of halogenated DBPs namely, CHCl₃, CHBr₃, and CHBr₂Cl in aqua phase. Scheme 6(a) displays the single electro-reactor applied to electro-reduce halogenated DBPs using Co-MoS₂ electrocatalyst. The interfacial interaction between substrates and electrocatalyst constituted the rate-determining step from which generated synergist effect and improved percentage removal of halogenated DBPs in aqua phase. The Co-MoS₂ electrocatalyst was stable and reusable for several recurring electroreductive dehalogenations. Liu et al. constructed a composite electrocatalyst of cobalt-phosphorous/oxide (Co-P/O) and evaluated that as an electrocatalyst for the electroreductive dehalogenation of halogenated antibiotics [138]. The dual synergistic effect between Co-P/O electrocatalyst and chlorine, and Co-P/O electrocatalyst and hydrogen species were found responsible for the reductive dehalogenation of halogenated antibiotic substances. The synergistic effect of metal-halogen and metal-hydrogen interaction is shown in Scheme 6(b) [138]. This illustrated that the synergist effect generated by interfacial interaction between halogenated DBPs and electrocatalyst represented an essential step and governed the electrocatalytic rate of halogenated DBPs reduction.

5. Conclusion

Microorganisms in drinking water cause severe health risks susceptible to lead to lifetime illness and/or death. Water treatment technology promoted chlorine disinfection as an affordable and reliable approach to disinfect drinking water before the discharge in the distribution channels. Excess chlorine is used throughout chlorine disinfection to achieve a complete extermination of microorganisms. That allowed free chlorine or free halogen in drinking water which interacted with natural organic matters and generated halogenated DBPs. Epidemiology and clinic analyses assessed that halogenated DBPs consumption and exposure provoked severe health risks. Catalytic hydrodehalogenation constitutes the viable scientific approach for complete and eco-friendly removal of halogenated DBPs in drinking water. The use of metal nanocatalysts accelerated the carbon-halogen bonds cleavage opening the way to carbon-hydrogen bonds formation throughout a hydrodehalogenation process. Palladium nanocatalysts received tremendous solicitation to facilitate the hydrodehalogenation of halogenated DBPs. Hydrogen gas and sodium borohydride are the prevalent hydrogen sources applied for the formation of hydrogen species to achieve a fast hydrogenation of the cleaved halogen. Electroreductive hydrodehalogenation is of great interest in water treatment technology to advance redundant-free hydrodehalogenation of halogenated DBPs for the production of clean drinking water. Halogenated DBPs and metal nanocatalysts engaged into an interfacial interaction which played a critical role in the progression of carbon-halogen bonds cleavage towards the hydrogenation. Academic efforts are needed to investigate other transition metal nanoparticles and mesoporous metal oxide materials as efficient catalyts to achieve fast hydrodehalogenation of halogenated DBPs and produce safe and clean drinking water. Chemical engineering trials in real water treatment plants are critical to establish the efficiency of catalytic hydrodehalogenation to eliminate halogenated DBPs in drinking water.
Scheme 3. Catalytic pathway of 2,4-dichlorophenol hydrodehalogenation catalyzed by H₂-MPFR [122].

Scheme 4. Trichloroacetic acid hydrodehalogenation using hydrogen gas and sodium borohydride as hydrogen sources.

Scheme 5. Mechanism pathways on Cu monometallic and Cu/Fe bimetallic surface during 4-chlorophenol hydrodehalogenation at low pH in water media [126].
Declaration of competing interest

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

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