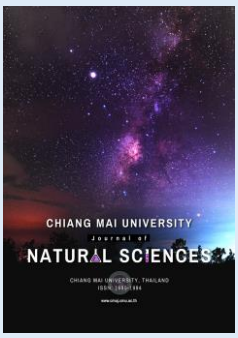

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Reviewed article

Chlorine and Chlorinated Compounds Removal from Industrial Wastewater Discharges: A Review

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Abstract Adsorption techniques for industrial wastewater treatment rich in heavy metals and aqueous solutions of water-soluble such as Cl^-, F^-, HCO^{3-}, NO^{3-}, $SO^{2-}{}_4$, and $PO^{3-}{}_4$, often include technologies for toxicity removals. The recent advancement and technical applicability in the treatment of chlorine and chlorinated compounds from industrial wastewater are reviewed in this article. Chlorine and chlorinated compounds are among the common discharged constituents from numerous industries. They can be carcinogenic or naturally toxic and can pose issues to aquatic ecosystems and human beings. Thus, elimination of chlorides and chlorinated compounds from water or wastewater is inevitable to get rid of the problem. Several techniques are being applied for the reduction of chlorine and chlorinated compounds in water. These include biodegradation, photochemical, adsorption, chemical, electrochemical, photo-electrochemical, membrane, supercritical extraction and catalytic method. Chlorine can react with various organic and inorganic micro-pollutants. However, the potential reactivity of chlorine for specific compounds is small, and only minor variations in the structure of the parent compound are anticipated in the water treatment process under typical conditions. This paper reviews different techniques and aspects related to chlorine removal, the types of chlorine species in solution and their catalyst, chlorine fate and transport into the environment, electrochemical techniques for de-chlorination of water, kinetics, mechanisms of reduction of chlorinated compounds, and kinetics of the electrochemical reaction of chlorine compounds.

Keywords: Industrial waste, Kinetics, Wastewater, Water purification

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INTRODUCTION

Enormous industrial effluent pollutants contaminated wastewater, bearing heavy metals and aqueous solutions of water-soluble, such as Cl^-, F^-, HCO_3^-, NO^{3-}, SO^{2-}_4, and PO^{3-}_4, may be entered and accumulated in the food chain and then human body, therefore, they can cause serious health disorders as well as unsuitable for human consumption or irrigation (Tilley et al. 2016; Xiong et al. 2019; Eunice et al., 2020). Chlorinated compounds, for example, have an adverse effect on human and animals. Agency for Toxic substances and Disease Registry (ATSDR, 2019) listed these compounds among the top 20 substances that need urgent remediation. Human consumption of chlorinated water results in several organs cancer such as the bladder, kidney, and rectal (Mahvi, et al. 2009; Ghoochani et al., 2017). Also, they affect reproduction outcome.

The treatment of certain industrial mine wastewater rich in soluble chloride salts leads to increased chlorine concentrations as well as an enrichment of undesirable elements such as F^-, Ca^{2+}, HCO^{3-}, NO^{3-}, SO^{2-}_4, and PO^{3-}_4 and certain heavy metals (Al-Hwaiti et al. 2015; Al-Hwaiti et al. 2016; Al-Hwaiti et al. 2018; Masixole et al. 2019). The conventional treatment processes have a significant faced problem due to incomplete removal anion or metal from inorganic effluent mine wastewater (Eccles, 1999). These treatment techniques are chemical precipitation, ion exchange, and electrochemical.

Nowadays, the adsorption technique can be applied for wastewater treatment in order to improve mine water effluent. However, this technique has shown significant advantage, which includes low-cost treatment, and high efficiency and convenient operation (Flávia et al., 2018). Kurniawan et al. (2005) reported that most solid adsorbents such as industrial wastes, zeolites, biomass materials, agricultural wastes, and polymeric materials might be used for the reduction of inorganic effluent mine water. Among various water and wastewater treatment technologies, process techniques including physicochemical treatment techniques for wastewater (Solimana and Moustafa, 2020), electrodialytic process by various fly ashes for treating heavy metals (Pedersen et al., 2003), photocatalytic (Skubal et al., 2002), coagulation-flocculation process (Hakizimana et al., 2017; Emad et al., 2020), water and wastewater treatment by flotation(George et al., 2018), biological filtration process (Shuokr et al., 2016), ion exchange process for wastewater treatment (Nirali et al. 2016), biodegradable processes of sewage by an aerobic and anaerobic process (Anijiofor et al., 2017; Wang et al., 2020), water and wastewater purification using photochemical Advanced Oxidation Processes (Marta and Natalia, 2010), solvent extraction and adsorption for wastewater effluent (Aswathy et al. 2016), water treatment and purification by adsorption processes(Adrián et al. 2017; Alshammari et al., 2020), electrolytic treatment of wastewater (Vinod Kumar, 2017; Jannatul et al., 2020), activated microbial sludge treatment for wastewater (Yongkui, 2020), chemical reduction of chlorinated organic compounds (Rodrigues et al., 2020), a catalyzed by laccase in aqueous solution (Asadgol et al., 2014); green synthesis iron oxide nanoparticles (Ehrampoush et al., 2015); Magnetic heterogeneous catalytic ozonation (Shahamat et al. 2014); ultrasound waves and ultraviolet irradiation; carbon nanotubes: kinetic and equilibrium studie (Mahvi et al., 2009); magnetic adsorption separation process (Dehghani et al. 2015); electro-coagulation process using iron and aluminum electrodes (Azari et al. 2017).

Recent research reviewed by (Adeola, 2018), suggests that chloride and other compounds released from industrial waste effluent are harmful to aquatic ecosystems and human health. This is because they form a stable compound, especially when they linked to alkali and alkali earth elements such as Na, K, Ca and Mg (Malcolm et al. 2017).

Although numerous reports showed that chloride enriched in municipal wastes and other industrial activities might be increased the chloride content in fresh and wastewater (Sarzamin and Jawad, 2018). Vít and Petr (2019) have investigated different chlorine species initiated in saline solution such as hypochlorites $HOCl/OCl^-$, chlorites ClO_2^-, chlorates ClO_3^-, chlorine dioxide ClO_2. Chlorine is among the highest commonly applied disinfectants in water purification; therefore, chlorine can be applied

in gas form or in solution as sodium hypochlorite or calcium hypochlorite to remove or reduce microorganism in water treatment (Enric et al., 2015). Chlorine species have subjected under regulation to low allowable concentration levels. The ion ClO_{2-} (chlorite) comes from the decomposition of ClO_2, being the most common DBP from ClO_2. Current research reports indicate that chloride mostly flows into wastewater treatment facilities from industry effluents. According to Scott et al. (2018), there are three softening processes such as scrutinized, reverse-osmosis, and lime softening are used for treating chloride at Wastewater Treatment Plants. György et al. (2018) Deborde and Von Gunten (2008) have used kinetics and mechanisms process in order to examine chlorine interactions in organic and inorganic mixtures. The results revealed that possible pathways of reaction are electrophilic substitution reactions with organic compounds.

The effects of structural and thermodynamic on process kinetics are adopted by Wolfgang et al. (2016). They used the Butler-Volmer equation for the reduction of chlorinated species reaction rate constant by mass transfer. The main objective of this paper is reviewing chloride and chlorinated compounds removal from water and wastewater, with emphasized on the reactivity kinetic and mechanisms on chloride and chlorinated compounds through water and wastewater effluent.

Types of chlorine species in solution and their catalyst

The aqueous chemistry of chlorine with respect to chlorination of water and wastewater has been reviewed by several investigators (Abarnou and Miosse, 1992; EPA, 2013; Cristina et al., 2012). The following review summarizes the chemistry of chlorine relevant to the discharge of chlorinated waters and wastewaters to the environment. Thorben et al. (2019) used the cathodic electrode processes included in metallic corrosion in chlorinated saline seawater for reduction of chlorine species in the chlorinated water system. Adna et al. (2017) and Wang et al. (2018) reported that chlorinated species have controlled by reactant concentrations, pH, temperature, reaction rates and equilibria. Bromide and iodide, if present even at low concentrations, are oxidized by chlorine forming oxidation products such as hypobromous acid (HOBr) and iodine (I_2). Hypobromous acid may, in turn, react with ammonia, if present, to form bromamines analogous to chloramines. Bromine and iodine-containing oxidants become increasingly significant with increasing bromide and iodide concentrations in estuarine and marine waters (Guanghui et al. 2006). Although generally of little consequence in waters at near-neutral pH values, molecular chlorine and nitrogen trichloride are also usually analyzed as free chlorine. Thus, chlorine has a higher oxidation potential than chlorine compounds such as (NH_2Cl), ($NHCl_2$), Nitrogen trichloride (NCl_3), and other organic compounds. Hypobromous acid and hypoiodous acid are distinguished by the usual analytical methods as free chlorine. HOBr reacts with ammonia to produce bromamines that are also detected as free chlorine. Thus the terminologies "free oxidant" and "combined oxidant" are more apt than free chlorine and combined chlorine when solutions containing bromide or iodide (e.g., seawater) are the subject of analysis. Nonetheless, present analytical approaches may not differentiate between free and combined bromine species. EU (2017) classified chlorine into different forms, such as chlorine gas, calcium hypochlorite, sodium hypochlorite. Table 1 shows the oxidation state of various inorganic oxidized forms of chloride and their stability in water.

Table 1. The oxidation state, free energy and stability of chloride forms in water.

Formula	Name	Oxidation state	Free energy change $\Delta_f G°$ (kJ/mol)	Stability in water	References
Cl^-	chloride	-1	-131	stable	Kang *et al.* (2006) and EurChlor (2004)
ClO^-	hypochlorite	+1	-37	unstable*	Kang *et al.* (2006) and EurChlor (2004)
ClO_2^-	chlorite	+3	17	unstable*	Kang *et al.* (2006) and EurChlor (2004)
ClO_3^-	chlorate	+5	-3	stable	Kang *et al.* (2006) and EurChlor (2004)
ClO_4^-	perchlorate	+7	-9	very stable	Kang *et al.* (2006)

Notes:*Chlorite and especially hypochlorite react with many reducing species and disproportionate under receiving environmental water conditions

Daniel and Vallero (2019) have reported that in the gas phase, Vinyl chloride gas may be absorbed into particles rather than into the aerosol phase as the particle phase is expected to be relatively small. Most delicate of chlorine is main source cause of toxicity, with a mean critical acute concentration (LC_{50}) of about 2,500 mg / L and a mean critical chronic concentration (IC_{25}) of around 720 mg/L. Chloride levels may always be required to verify whether chloride is toxic in the wastewater effluent (William et al., 2000; Mount et al., 1997).

Chlorine fate and transport into the environment

Several investigators have reported the ecological fate of chlorine in water are understood, and it not remain in the environmental system for a long time (Truhlar et al. 2006; Zheng et al., 2015; Cotton et al., 1999). Researchers have indicated that chlorine photolysis is naturally present in seawater through fate and transport of aerosols (Knipping and Dabdub, 2003; Saeed et al., 2015; Amy et al., 2017). When the chlorine gas reacts with water, it is immediately changed into different forms such as hypochlorous acid, chloride ion, and hypochlorite; however, hypochlorite is formed when pH falls below 4 (Farr et al., 2003). Furthermore, chlorine also occurs mostly as the chloride anion (Cl^-), and then Cl^- can fate and transport into the soil through water flows. The fate of chlorite stabilities and persistent or non-persistent in the aquatic environment is indicated in several literature sources (Table 2).

Table 2. The literature reviewed for chlorate (ClO_3^-) stability in the aquatic environment.

Source	Stability	Martyrdom
GBCA (2002)	unstable	Chlorate is a strong oxidizing agent and should be non-persistent in organic water. Chlorate anion is unstable in water and decomposes to form[hypochlorite] $OCl^-$and oxygen
Couture (1998)	unstable	Chlorate is a strong oxidant and is therefore not supposed to survive in the presence of easily oxidizable content.
Stauber (1998)	unstable	Because chlorate is easily biodegraded and reacts readily in sunlight with organic material, it is doubtful that it will survive in natural waters.
VanWijk and Hutchinson (1995)	unstable	Chlorate is highly soluble, non-persistent and does not adsorb to sediment particles or bioaccumulate in biota.
USEPA (1999)	stable	Chlorate is stable in finished drinking water once it has been formed. There are no known treatments for chlorate removal once it's formed.
Urbansky (1998)	stable	The chlorate anion is chemically stable under environmental conditions
WHO (1986)	stable	Once chlorate ions are present in water, they are very persistent and very hard to remove
Gallagher *et al.* (1994)	stable	Chlorate is stable in water.

The study made by Zoeteman (1980) assessed the level of NaCl and $CaCl_2$ concentrated in water ranged between 200–300 mg/L. The study revealed that chloride ion showed high mobility moved into water bodies, this is due to intensive weathering process for rocks rich chlorides content, and then chloride leached into the soil. Hu et al. (2013) determined the transfer of Cl^- from the soil to other ecosystem is controlled by several complex processes such as hydrogeochemical process, besides that, contaminated soil by Cl^- can be a significant source for the groundwater contamination, subsurface soil gas, atmospheric air, surface water, and sediments (Lu, 2010).

The fate of contaminants introduced into the environment by chlorine compounds is the result of various chemical industries and pharmaceutical industry activities discharged (Michałowicz and Duda, 2007; Mahendran et al. 2015; Atashgahi et al., 2018). reported that chlorophenols have a serious challenge in human healths. The transformation and fate of chlorophenols compounds may lead to increase toxicity or carcinogenic, damage gene products or DNA (Michałowicz and Duda, 2007; Etinosa et

al. 2013). However, these chlorophenols fates adsorption in soils is governed by acidic conditions (pH) and vice versa. Chlorophenols have long been known released from industrial waste and landfills into surface water or atmosphere through volatilization (Adeola, 2018; Philip et al., 2001). Chlorophenols fates and transports to the environment are influenced by several processes such as chemical, physical, biological transformations, volatilization, sorption, degradation, and leaching (Schummer et al., 2006). Federica et al. (2015) stated that chlorinated solvents have faced several problems in terms of fate and transport these chemicals into the environment. In the pure chemical state, most chlorinated solvent mixtures having densities greater than water, and aren't speciation into cations and anions in aqueous solution but dissolve as neutral species. Phenol is considered to be one of the organic industrial effluents that release water from various organic chemical industries. The general specifications of different industrial organic industrial effluent waters are described in (Table 3).

Table 3. The parameter of organic industrial effluent water.

Industrial categories	General contaminants	References
Steel and Iron	Concentrated BOD and COD, grease and gasoline, strong pH, toxins, phenols, cyanide, heavy metals such as Mn, As, Hg, Cd, Ti, V, Sb, Th, Pb	Bej *et al.* (2020)
Leather and textiles	High BOD, solids, sulphates	Bej *et al.* (2020)
Paper and pulp	Concentrated BOD and COD, solids, chlorinated organic compounds	Bej *et al.* (2020)
Refineries and petrochemicals	Mineral oils, BOD, COD, phenols, chromium	Bej *et al.* (2020)
Chemicals	Cyanide, carbon-based chemicals, heavy metal ions, SS, COD	Bej *et al.* (2020)
Non-ferrous metals	Fluorine, suspended solids	Bej *et al.* (2020)
Mining	Suspended solids, metals, acids, salts	Bej *et al.* (2020)
Wastewater treatment plant	Electrolytic removal of physicochemical parameters viz., colour, turbidity, EC, TSS, BOD, COD and wastewater heavy metals	Kumar (2017)

Technologies used for de-chlorination of water

Several techniques are used for treating chlorinated compounds from water. These include biodegradation (Baskaran and Rajamanickam, 2019; Frascari et al., 2019; Khan et al., 2019; Papazi et al., 2019; Pathiraja et al., 2019; Nivorlis et al., 2019; Serbent et al., 2019), photochemical (Liu et al., 2020; Ding et al., 2020; Li et al., 2019), adsorption (Dontriros et al., 2020; Du et al., 2020; Liang et al., 2020; Lo et al., 2020; Qian et al., 2020), chemical (Kim et al., 2020; Qian et al., 2020; Song et al., 2020; Wang et al., 2020), electrochemical (Du et al., 2020; McQuillan et al., 2020; Wang et al., 2020; Xu et al., 2020), photo-electrochemical (Liu et al., 2020) membrane (Abdel-Shafy et al., 2017; Du et al., 2020; Vlotman et al., 2019; Wan et al., 2020), supercritical extraction (Zhang and Zhang, 2020), electron selectivity (Wang et al., 2020), neural network modeling (Baskaran et al., 2019), and catalytic (Nieto-Sandoval et al., 2019; Ruan et al., 2019; Zheng et al., 2020) method. Related literature on the electrolytic treatment methods application for different types of wastewater is shown in Table 4.

Chlorinated compounds are readily degraded using several bioactive species from several strains such as *Pseudomonas guguanensis, Desulfomonile tiedjei, Methylobacterium, Methylophilus, Hyphomicrobium, Nitrosomonas europea, Pseudomonas cepacia, Escherichia coli, Alcaligenes denitrificans* and *Rhodococcus erythropolis.* The role of these strains is divided into two categories; co-metabolic conversions or conversions. The chlorinated hydrocarbons have a major carbon source to these strains where they act as electron acceptors in the respiratory process in solutions lack of oxygen. For example, trichloroethylene is readily degraded to CO_2 and lighter hydrocarbons using *Pseudomonas guguanensis* at a rate of degradation of 0.41 mg/L.h with 90% of removal efficiency (Han and Yan, 2016; Quan et al., 2017). Several methods are used for the degradation of trichloroethylene from aqueous water such as groundwater. These include dehalococcoides-containing microbial communities, polyethyleneimine-modified zero-valent iron nanoparticles, bysonophotolytic-activated

persulfate processes, and polyethyleneimine-modified zero-valent iron nanoparticles (Mao et al., 2017; Lin et al., 2018; Bahrami et al., 2018; Mdlovu et al., 2019).

Table 4. Different electrolytic treatment methods using various types of wastewater.

Wastewater	Experimental specification	Observations	References
Wastewater Treatment Plants in Industrial and Municipal Zones	Activated Sludge Microbial Community	Industrial WWTP sludge had impacted on nitrification and denitrification. Industrial WWTP sludge had high metabolic functions linked to xenobiotic and amino acid metabolism	Yongkui *et al.* (2020)
wastewater treatment	Electrolysis process modelling in wastewater treatment using various kinds of neural networks	The process' efficiency was quantified in the effluent of aerated lagoons by the final values of TSS, chlorophyll a, and COD. The experiments conducted in a pilot plant under different retention time conditions, the distance between electrodes, electrical current and the use of two types of electrodes allow for the determination of the conditions which lead to high chlorophyll-a, TSS and COD removal rates.	Silvia *et al.* (2011)
Industrial wastewater	Glass tank reactor with DC power supply, using iron electrodes.	99% reduction in cadmium occurs at 40 V after only 20 minutes.	Bazrafshan *et al.* (2006)
Bio refractory organic pollutants	Electrochemical reactor with integrated advanced electrochemical oxidation in a single cell, with fluidization by activated carbon (AC).	22%-30% COD removal with AC fluidization and 97.8% removal with integrated advanced, activated carbon (AC) electrochemical oxidation.	Zhou Ming-hua *et al.* (2004)
Domestic sewage from municipal sewers	Electrolytic treatment using Al and Fe electrodes.	Reduction of total phosphorus by 38 to 98 per cent and removal of COD by 10 to 63 %	Krzemieniewski and Dębowski (2005)
Domestic Wastewater	Induced air, electro, cavitational, and centrifugal flotation systems (CFS) flotation techniques.	Over 99% of total suspended solids (TSS), 80% of chemical oxygen (COD) and 95% of FOG (over 99.5% of suspended emulsified FOG) were removed.	Colic *et al.* (2007)
Domestic wastewater	Electrocoagulation (EC) process using Fe–Fe electrodes.	The removal efficiency of COD and SS, respectively, was obtained and showed to be over 60 and 70%.	Kurt *et al.* (2008)
Domestic wastewater	Electrocoagulation (EC) process using Fe–Fe electrodes.	The removal efficiency of COD and SS, respectively, was obtained and shown to be over 60 and 70%.	Kurt *et al.* (2008)
Effluents from lagoons	Continuous electro-coagulation reactor with three anodes of aluminium.	By applying a power input of about 550 W, total suspended solids (TSS) and chlorophyll-a removal reached as high as 99.5% and about 100%.	Azarian *et al.* (2007)
Papermill wastewater	Pulsed electro-coagulation treatment with aluminium electrodes	The EC, SS, COD and true colour reduction were 25.4, 97.1, 76.5, and 70.1% respectively.	Perng *et al.* (2007)
Pasta and cookie processing wastewater	Electrolysis at 3 - 8 pH range in a batch reactor that uses Al electrode for 60 minutes.	80 - 90% COD removal and 57% colour reduction.	Roa-Morles *et al.* (2007)
Poultry Slaughterhouse wastewater	A batch reactor at pH 6.1-6.5 using Electrodes Al and Fe for 60 minutes	Reduction of 80-84% in COD, 84-88% in BOD, 100% in oil and grease and 58-70% in TSS	Asselin *et al.* (2008)
RB4 dye wastewater	Reduction and oxidation of electrodes at reticulated vitreous carbon electrodes (RVC) and Ti / SnO_2 / SbO_x (3% mol)/RuO_2 (30% mol)	50% Colour removal at 0.6 V and 100% Colour removal at 2.4 V for 1 hour Electrolysis.	Patricia *et al.* (2003)

Table 4. Continued.

Wastewater	Experimental specification	Observations	References
Textile indigo dye effluent	A batch-electrolyte-cell type electrochemical method hangs for 40 minutes Pt plates, DC power supply (40 V)	Reduced COD by 46% in textile effluents	Dogan and Turkdemir (2012)
Textile dye house factory wastewater	Electrochemical oxidation and membrane filtrations.	89.8% chemical oxygen demand (COD) removal, 100% TSS reduction and 98.3% turbidity elimination.	Xuejun Chen (2003)
Mixed liquor solution in wastewater	Electrocoagulation was done using perforated cylindrical iron electrodes.	In no more than 60 minutes, the electro-coagulation process achieved steady-state conditions. The steady removal efficiencies of COD and nutrients exceeded 89% at high voltage gradient (6 V / cm).	Al-Shannag *et al.* (2013)
Wastewater of wastewater treatment plant	Used a submerged membrane electro-bioreactor (SMEBR) is a new hybrid wastewater treatment technology that employs electrical field and microfiltration.	Ammonia (as NH^{3+}-N), phosphorus (as PO_4^{3-}-P), and COD removal efficiencies were 99%, 99%, and 92%, respectively.	Hasan *et al.* (2014)
Tannery wastewater	Electrocoagulation (EC) technique using iron and aluminium electrodes to treat tannery wastewater	Total chromium and colour removal efficiencies were achieved at optimum COD conditions as 63.3, 99.7, and 82% respectively.	Deghles and Kurt (2016a)
Tannery effluents	An electro-coagulation process with electrodes of either aluminium or iron	The removal efficiency of COD, NH_3-N, Cr and colour corresponds to a conductivity value of 0.371mS/cm at 45 minutes, respectively.	Deghles and Kurt (2016b)
Tannery effluent	Electrocoagulation treatment.	The TDS, BOD, COD and Cr, were significantly reduced under optimum operating conditions of 20mA cm^2.	Ramesh *et al.* (2007)
Livestock wastewater	Electrocoagulation (EC) process with Al electrodes at a pH of 8, 30 mA/cm^2 current density, 30 min electrolysis time.	The colour removal was 95.2%, and the COD 93%.	Bong-yul *et al.* (2015)

Pesticides such as DDT, DDE, Endrin and Lindane were totally diminished using *P. cepacia* at low concentration (0.05 ppm) and after 24 h exposure.

Zero-valent iron is used in chemical, photo-electrochemical and catalyst degradation of chlorinated compounds in the adsorption and degradation of chlorinated acid, where this rate decreases with increasing solution acidity (Mdlovu et al. 2018; Kim et al., 2020; Qian et al., 2020; Song et al., 2020; Wang et al., 2020). Furthermore, Pd/Al_2O_3 catalyst was used to remove chlorinated micropollutants from the water with a reduction rate constants 0.32–1.56 L/g.min (Nieto-Sandoval et al. 2019). Also, Pd/CeO_2 catalysts were applied to degrade bromochloroacetic acid from the liquid phase through the hydrogenation process (Zheng et al., 2020). Furthermore, 2,4-dichlorophenol can be de-chlorinated using by Fe/Ni nanoparticles (Ruan et al., 2019).

Photocatalytic and electrochemical methods were also adopted to catalyze chlorinated compounds to produce less harmful products such as carbon dioxide. Several photo-catalyst such as C_3N_4/NiO are used to degrade 70.4% of 2-chlorodibenzo-p-dioxin in the presence UV–vis light illumination (Ding et al., 2020). Also, tungsten oxides nano-film anode is used for chlorinated compounds. The removal efficiency of 4-chlorophenol is 85.5%, and 48% is obtained with tungsten photoanode electrochemical (Liu et al., 2020). The biocharcoal-based electrode is also used to achieve 86.7% removal rates of Cl^- from leather processing wastewater (Kim et al., 2020). Different carbon-supported iron was used for removal of chloramphenicol (Stryer 1988). Pd-TiO_2

catalyst is used as electrocatalyst for hydrodechlorination reaction for 2,4-dichlorophenol (Wang et al., 2020).

Mining wastewater treatment with a focus on a natural substrate or sorbent adsorption can be used to remove contaminants such as heavy metals and chlorinated compounds. A description of the most adsorption for mining wastewaters treatment is shown in Table 5.

Table 5. Adsorption process for mining wastewaters treatment

Name of isotherm	Equation	References
Henry's law	$q_e = Kq_mC$	Dąbrowski (2001) and Evgenia et al. (2013)
Langmuir	$q_e = \frac{Kq_mC}{1+KC}$	Dąbrowski (2001) and Evgenia et al. (2013)
Freundlich	$q_e = AC^B$	Liu (2005)
Brunauer–Emmett–Teller (BET theory)	$q_e = \frac{Kq_eC_r}{[1+(K-1)C_r][1-C_r]}$	Maciej (2009)
Brunauer–Deming–Deming–Tellet (BDDT theory	$q_e = \frac{Kq_{mCr}\left[1+m(g-1)C_r^{m-1}+gC_r^{m-1}(2g-1)C_r^m\right]}{(1-C_r)\left(1+[K-1]C_r+K(g-1)C_r^m-gC_r^{m-1}\right)}$	Caurie (2006)
Redlich–Peterson	$q_e = \frac{Kq_mC}{(1+KC^B)}$	Wu et al. (2010)
Langmuir–Freundlich	$q_e = \frac{Aq_mC^B}{1+AC^B}$	(Azizian et al. (2007)
Sips	$q_e = q_m\left[\frac{AC}{1+AC}\right]^B$	Ahmed (2012)
Toth	$q_e = \frac{KC}{\left(1+\frac{C^B}{A}\right)+\left(1+\frac{C^B}{A}\right)^{\frac{1}{B}}}$, where $n_M = KA^{\frac{1}{B}}$	(Terzyk et al. (2003)
Yoon–Nelson	$\frac{C_e}{C_o} = \frac{1}{1+\exp[k_{YN}(r-(V/Q))]}$	Yazıcı et al. (2009)
Dubinin–Radushkevich	$q_e = q_m \exp*\left\{2\left[\left(\frac{k_oe}{b_o}\right)^2\right]\right\}$	Condon (2000)
Dubinin–Astakhov	$q_e = q_m \exp*\left\{-\left[\left(\frac{k_oe}{b_o}\right)^2\right]\right\}$	Condon (2000)
Temkin	$q_e = \frac{R_gT}{b_T}\ln(A_TC_e)$	Khan (2012)
Fritz–Schlunder	$q_e = \frac{q_mK_{FS}C_e^{n_{FS}}}{1+K_{FS}C_e^{m_{FS}}}$	Jossens et al. (1978)
BiLangmuir	$q_e = \frac{q_{m1}K_{BiL1}C_e}{1+K_{BiL1}C_e} + \frac{q_{m2}K_{BiL2}C_e}{1+K_{BiL2}C_e}$	Yamamoto et al. (1993)

The effect of support of these catalysts is investigated by studying the adsorption effect of several adsorbents on the uptake of these compounds. A $CuOx/Na_2CO_3$ porous sorbent is used to remove HCl from CO_2-rich mixture gases. The results show that 400,000 m^3/h of hydrochloric acid can be removed from flue gas using 500 tons sorbents (Marschner, 1995). Chloro-organic in synthetic and site groundwater was successfully remediated by Palladium/Fe nanoparticle integrated membranes (Wan et al., 2020). Immobilized clostridium butyricum in silica gel is also employed for de-chlorination of trichloroethene (Lo et al., 2020).

Electrochemical Techniques for de-chlorination of water

Different electrochemical techniques were used in electro redox reaction of chlorinated compounds (García-Armada, 1996; Fritz et al., 2013; Eduardo et al., 2014). Electrochemical method type Cyclic Voltammetry (CV) is used to measure the current adsorbed to an electrode in an electrochemical cell under conditions and to measure the current produced. The electrochemical potential is scanned linearly from initial to a final value, and the corresponding current is measured (Joshi and Sutrave, 2018). The measure upper and lower peaks of the current-potential curve represent the redox reaction of the existing species in solution. This technique is useful to provide

information about thermodynamic and kinetics of the redox reactions (Florica, 2014). This technique was used for de-chlorination in solution depends on different types of electrodes where the optimum condition for its electrochemical behaviour is monitored at pH 8. When boron-doped diamond (BDD) electrodes are used, the chloride ions exists for the anodic reaction as ClO^- (Michio et al., 2008). The coupled amperometric technique was employed to estimate chlorine concentration at a low concentration of 0.1-2 mg/L.

Linear sweep voltammetry technique was used graphite electrodes in order to determine chlorine concentrations with a range between (1.0-300.0 mg/dm^3), and ClO^- concentration less than (<1.0 mg/dm^3) (Pathiratne et al., 2008). The differential pulse voltammetric technique was used as a gold electrode to determine chlorine concentration ranged between 1 and 5 mg Cl/dm^3 (Sulistyo et al., 2010). The voltammetric potential sweep technique was also used different electrodes (e.g. platinum, gold, and glassy carbon disk) to measure chlorine concentration with a range of about 4-400mgCl/L, whereas a sensitivity concentration is 1.0mgCl/L (Fumihiro et al., 2005). Fumihiro et al. (2004) used Pt for electrode linear sweep-voltammetry in order to determine the hypochlorite ion. They also investigated physical, chemical factors, pH, temperature, sweep rate, dissolved oxygen and metal might be controlled electrochemical reaction. Cyclic voltammetry technique was used a pencil graphite electrode (PGE) to determine Polyvinyl chloride stability (Melih et al., 2019). The differential pulse polarography (DDP) technique was used to determine the electrochemical reduction of chlorite. The reaction condition investigated that concentrations of chlorite ranged from 19 µg/L-19 mg/L, pH ranged from 3.7 to 14, ionic strength range from 0.05–3.0 M (Nakareseisoon et al., 1988).

Mechanisms of reduction of chlorinated compounds

The most common reaction pathways for the electrochemical reaction of halogen ions and their compounds in aqueous solution and at the surface of electrodes are proposed by many researchers (Kraft, 2008; Radjenovic and Sedlak, 2015; Katsaounis and Souentie, 2014; Exner et al., 2016; Exner et al., 2018). These halogen ions have several oxidation states based on existence in their compounds. For example, chlorine has seven oxidation numbers that have values of -1, 0, +1, +3, +4, +5, or +7. When choline presents as free chlorine gas it has a 0 oxidation number; however, the most common oxidation number is -1 when reacts with hydrogen and mono- or divalent metals to produce hydrochloric acid and metal chlorides as shown:

$$H^+ + Cl^- \rightarrow HCl$$
$$M^+ + Cl^- \rightarrow MCl$$
$$M^{2+} + Cl^- \rightarrow MCl_2$$

In the presence of oxygen, chloride ion can have positive oxidation number, and its value increases with increasing oxygen in the compound according:

The oxidation number of +1: $Na^+ + ClO^- \rightarrow NaClO$
The oxidation number of +3: $Na^+ + ClO_2^- \rightarrow NaClO_2$
The oxidation number of +4: ClO_2
The oxidation number of +5: $Na^+ + ClO_3^- \rightarrow NaClO_3$
The oxidation number of +7: $Na^+ + ClO_4^- \rightarrow NaClO_4$

In electrochemical cell reaction, these compounds are either oxidized to produce free chlorine gas at the surface of cell anode or reduced to produce chloride ions on cathode according to the reactions shown in Table 6 and Table 7. The values of standard oxidation potential E^O, are varied from 0.89 to 1.584 V versus Standard Hydrogen Electrode (SHE). During the oxidation process of some of these chlorination compounds, other electrochemical reactions related to water reduction or oxidation takes place based on solution acidity as Table 7.

Table 6. Standard reduction potential for various chlorinated compounds vs SHE.

Oxidizing agent	Reaction	E^o	Reference
$HClO_2$	$HClO_2 + 3H^+ + 4e^- \rightarrow Cl^- + 2H_2O$	1.584	Kaczur *et al.* (1996)
ClO_2	$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O$	1.504	Kaczur *et al.* (1996)
ClO_3^-	$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$	1.450	Kaczur *et al.* (1996)
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.358	Kaczur *et al.* (1996)
ClO_4^-	$ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O$	1.287	Kaczur *et al.* (1996)
ClO^-	$ClO^- + 2e^- + H^+ \rightarrow Cl^- + OH^-$	0.890	Kaczur *et al.* (1996)
$HClO$	$HClO + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.490	David (2006)

Table 7. The standard reduction potential of water vs SHE.

Reaction	E^o	Reference
$2H_2O + 2e^- \rightarrow H_2 + OH^-$	-0.828	Amikam *et al.* (2018)
$0.5O_2 + H_2O + 2e^- \rightarrow 2OH^-$	-0.401	Amikam *et al.* (2018)

On the surface of the catalytic electrodes chloride ions undergoes adsorption by the surface of the anode as per Figure 1 (Liang et al., 2020). First chloride ions first diffuse to the surface of the electrode and get adsorbed as

$$Cl^- \rightarrow Cl^*$$

Then the adsorbed chloride ion undergoes electrochemical oxidation reaction to form chlorine gas as

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

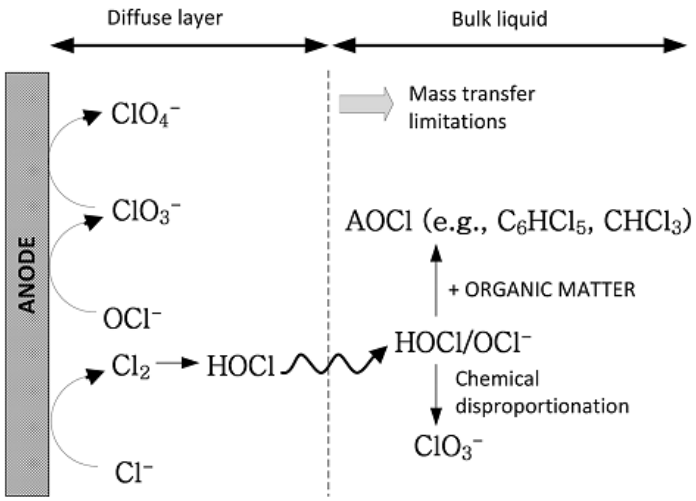

Figure 1. Adsorption/electrochemical reaction of chloride ions and related compounds on the electrode surface.

Depending on solution acidity (Figure 2) chlorine gas evolved from solution at low pH; however, it undergoes oxidation reaction to form *HClO* which in turn its ions ClO^- is

further undergoes adsorption/electrochemical reactions to form ClO_3^- and ClO_4. Some of the produced $HClO$ diffuses back into solution with its base to disproportionate to O_3.

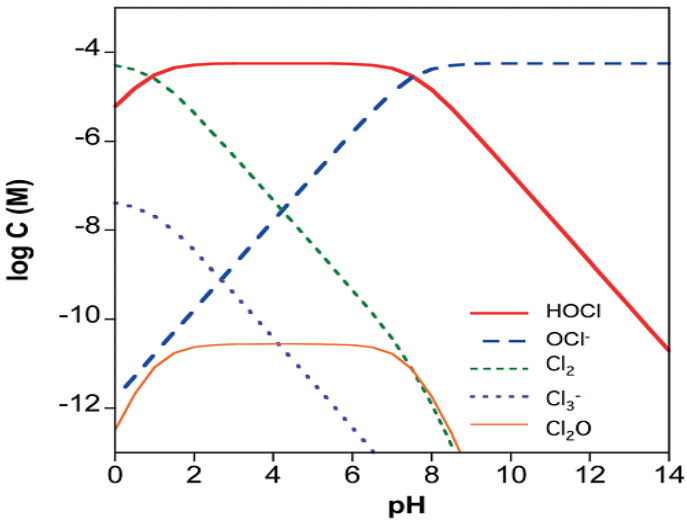

Figure 2. Speciation of Chlorine and its species at various pH values (Remucal and Manley 2016)

Kinetics of Electrochemical Reactions of chlorine compounds

While there are many chlorine species exists in the electrochemical cell such as Cl^-, ClO^-, ClO_2^-, ClO_3^- , ClO_4^- , and $HClO$, and other counter species such as OH^- and H^+, their existence affect the electrochemical reaction to liberate chlorine from solution. The rate of the electrochemical reaction of chloride ions on the surface electrode has therefore regulated the reaction rate between chloride ions and their solution types, as well as the electrical potential gap between electrode surface and solution. Exner et al. (2016) used DFT to study the kinetics reaction of chlorine at aRuO2(110) Model Electrode. They found that Volmer–Heyrovsky mechanism significantly influenced the adsorption of chloride ions on the active oxygen atoms of RuO_2 lead to further reaction to liberate chlorine gas from solution. The rate of development of the produced chlorine is linearly proportional with current density.

Dickinson and Wynne-Jones (Dickinson et al., 2016) studied the rate of chlorine gas formation at the platinum electrode. They proved that the rate is inhibited by the oxide that makes on the electrode surface where the order of reaction was unity at low chlorine concentration. Isai et al. (2013) performed Tafel analysis on chloride ions oxidation on the platinum electrode and showed that the mechanism of the reaction is influenced by the dissociative electrochemical adsorption of chlorine species and chemical recombination of the adsorbed Pt–Cl.

Nicoson et al. (2002) studied the mechanism and the kinetics of the electrochemical reaction of chlorine gas and hypochlorite ions produced in acetate buffer solution. The reaction was first order in $[Cl_2]$ and $[ClO_2^-]$, with a rate constant of k1 = $(5.7 \pm 0.2) \times 10^5$ M^{-1} s^{-1} at 25.0 °

Therefore, the target electrochemical reaction of chloride ions on the surface of the electrode is governed by

$$O + ne^- \leftrightarrow R$$

Where O represent the free chlorine in solution, Cl_2, R is the chloride ions, Cl^- in solution, and ne^- are the number of electrons transfer in the electrochemical cell.

Some of the produced chlorine can future reacts with oxygen to produce hypochlorous acid (HClO) in solution according to the general equation

$$R \rightarrow Y$$

Hypochlorous acid may dissociate on the surface of the electrode to produce hypochlorite ions (ClO^-) as

$$Y \rightarrow P + H^+$$

Further series reactions on the surface of the electrode such as

$$ClO^- \rightarrow ClO_3^- \rightarrow ClO_4^-$$

On a planner electrode, the rate of oxidation of chloride ions is related to the rate of change of these ions within a distance, x, from the electrode surface according

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2}$$
$$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} - k_R C_O^n$$

Where C_O and C_R are the concentration of oxidized (Cl_2) and reduced (Cl^-) species in solution and their diffusion coefficients are denoted as D_O and D_R, respectively. k_R is the reaction constant. The side reaction of hypochlorous acid to hypochlorite ions is assumed n^{th} order.

These equations are solved simultaneously coupled with bellow initial and boundary conditions to provide the variation of concentration of chloride ions and produced chlorine with time and at a given distance from the electrode surface.

$$C_R(x, o) = C_R^* \,,\; C_R(x, o) = o$$
$$\lim_{x\to\infty} C_R = C_R^*, \lim_{x\to\infty} C_O = 0$$

At the surface of the electrode

$$D_R \frac{\partial C_R}{\partial x} = D_O \frac{\partial C_O}{\partial x}$$

And $$\frac{C_R}{C_R} = e^{\frac{nF}{RT}\eta}$$

Where F and R are the Faraday and ideal gas constants, respectively. η is the cell overpotential that represents the difference between the applied, E potential and reaction equilibrium potential, E^O.

CONCLUSION

In this review, adsorption techniques have been reviewed for the removal of chlorine and chlorinated compounds in water and wastewater, and biodegradation, photochemical, adsorption, chemical, electrochemical, photo-electrochemical, membrane, supercritical extraction and catalytic methods may be used. In addition, types of chlorine species in solution such as chlorine (Cl_2), hypochlorous acid (HOCl), hypochlorite ion (OCl^-), monochloramine (NH_2Cl), dichloramine ($NHCl_2$), nitrogen-trichloride (NCl_3), monochloramine (NH_2Cl), dichloramine ($NHCl_2$), nitrogen-trichloride (NCl_3), and chlorophenol. Numerous industrial usages and production of chlorine and chlorinated compounds has resulted in the discharge of different types of chemicals into the environment and have a serious challenge in the health sectors.

The fate and transport of chlorophenol compounds may lead to an increase in toxicity that may damage DNA or gene products as well as that may mutagenic and carcinogenic for living organisms. The primary processes involving transport, mobility and distribution of these chemicals in the environment at various environmental parameters such as chemical, physical, and biological transformations, sorption,

volatilization, degradation, and leaching were discussed. However, further study is necessary to comprehend the mechanisms of reduction of chlorinated compounds, which has electrochemical cell reaction, chlorine compounds are either oxidized to produce free chlorine gas at the surface of cell anode or reduced to produce chloride ions on cathode according to the reactions. Moreover, the kinetics of the electrochemical reaction of chlorine compounds, which has many chlorine species exists in the electrochemical cell such as Cl^-, ClO^-, ClO_2^-, ClO_3^-, ClO_4^-, and HClO, and other counter species such as OH^- and H^+, their existence affect the electrochemical reaction to liberate chlorine from solution.

The scientific research to develop novel technology for solid adsorbent processes, either for the rate of the electrochemical reaction of chloride ions on the surface electrode is controlled the rate of reaction between chloride ions and their species in solution, as well as, the electrical potential difference between electrode surface and solution.

CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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