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**The competitive effect of Electro-chlorination over chlorination for controlling
disinfection by-product formation in phenol and aniline enriched groundwater**

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Abstract:

Disinfection is an essential step to keep humans healthy from microorganisms present in drinking water. However, the formation of disinfection by-products (DBPs) is associated with adverse health effects, and the presence of organic pollutants in groundwater results in even more detrimental effects. Therefore, a better treatment technique is required to disinfect and remove organic pollutants simultaneously to control the formation of DBPs. Electro-chlorination (EC) was carried out using graphite electrode at the current density of 0.54–1.09 mA/cm² and sodium chloride for in-situ hypochlorite generation to treat groundwater contaminated with phenol and aniline. The comparative study between chlorination and EC showed a significant level of oxidation of phenol and aniline, resulting in their reduction up to 98.48% and 99.47%, respectively, in the EC process. Due to the higher mineralization rate of aniline, both chlorination and EC method are found to be effective. However, only the EC method is found to be appropriate and effective for treating phenol-contaminated water as the chlorination method resulted in the formation of complicated phenolic by-products. Gas-Chromatography/Mass-Spectrometry (GCMS) was used to assess the by-product formation of chlorination and EC in contaminated groundwater through the full-scan.

Keywords: Electro-chlorination; Disinfection By-products; Health Risk Assessment; Organic pollutant; Groundwater

1. Introduction

The existence of anthropogenic organic contaminants in groundwater has been the subject of profound studies in recent years worldwide. Anthropogenic organic pollutants in surface water, sewage and groundwater, and potable water have been identified as contaminants (Postigo and Barceló 2015; Lapworth et al., 2015). Pesticides and pharmaceuticals with metabolite, steroid, industrial additive, hormone, water treatment by-products, personal care products, fire retardants, and food additives are the most prominent of these pollutants (Stuart et al., 2012). Several of them may have a detrimental effect on human health and the environment, emphasizing that they need to consider their environmental role more effectively. In addition, coke-based factories are deemed responsible for generating large amounts of wastewater containing extremely hazardous, mutagenic as well as carcinogenic contaminants, including phenol and aniline (USEPA 2012; Mohanta and Mishra 2020). Because of its life-form solid toxicity, chemical uncertainty, high water-solubility, and volatility, the US Environmental Protection Agency (USEPA) recognizes them as its priority contaminants. They are also vulnerable to subsurface propagation and pose a significant health hazard that can affect the cardiovascular system, neurological processes, and even kidney failure (Wen et al. 2015; USEPA 2014; Mustapha et al., 2020; Mohanta and Mishra 2020).

As per Central Pollution Control Board (CPCB), usually, groundwater doesn't need advanced treatment processes unless harmful pollutants are present in it, unlike surface water which is typically susceptible to higher contamination and an advanced treatment process is mandatory. Mostly, only disinfection is done in groundwater to kill pathogens present in them. Chlorination, due to its efficacy and affordability, is the most popular form of disinfection of groundwater. However, groundwater contaminated with organic pollutants requires more disinfection effective techniques due to the formation of several regulated and unregulated DBPs in conventional chlorination techniques (Richardson and Postigo 2015; Dong et al.,

2018). Pan and Zhang (2013) identified four new groups of aromatic halogenated DBPs, which can be decomposed to form trihalomethanes (THMs) and haloacetic acids (HAAs) while chlorinating drinking water. Their formations are highly influenced by $[HOBr]/[HOCl]$. The presence of natural organic matter (NOM) with high aromatic content is responsible for aromatic halogenated DBPs. Ding et al., (2013) has identified occurrence patterns of 28 DBPs, including THMs, HAAs, haloacetonitriles (HANs), and emerging iodinated THMs (i-THMs) in the treated water, which was found to be cytotoxic and genotoxic in nature.

To overcome these problems, a treatment technique is needed that will treat the organic loading as well as disinfect the water at the same time. Many scientists currently concentrate on electrochemical processes to oxidize organic pollutants, and the literature shows that the Electrochemical method individually is not economical; therefore, several organic contaminant oxidization electrolytes have been tested. Electrochemical oxidation methods are used by various researchers for successfully disinfecting drinking water depending upon electrolyte solution and ability to produce radicals by different electrodes such as boron-doped diamond (BDD), dimensionally stable anode (DSA), platinum, and hemin/graphite (Jeong et al., 2007, 2009; Maa et al., 2011). Electro-oxidation may occur either by direct oxidation by hydroxyl radicals produced on anode's surface or by an indirect process where oxidants like chlorine, hypochlorous acid, and hypochlorite are formed at the electrode (Särkkä et al., 2015). Hypochlorite as an electrolyte can be used in the electrochemical treatment of groundwater polluted with organic loading as it is the most potent oxidizing agent of the chlorine oxyanions (Singh et al., 2021). However, hypochlorite handling and storing is a complex operation, making it costlier to use and more challenging to store. Therefore, it should be generated on-site through the Electro-chemical process, using sodium chloride, which is readily available and very cost-effective (Key 2010). Negatively charged ions, such as hydroxyl, oxygen, and chloride ions, donate electrons at the anode to produce oxygen gas, chlorine dioxide,

hypochlorous acid, hypochlorite ion, and hydrochloric acid under direct current (DC) voltage. Positively charged ions, on the other hand, such as hydrogen, calcium, magnesium, sodium, and potassium ions, gain electrons at the cathode and form hydroxide and hydrogen gas (Ashokan and Subrmaniyan 2009; Yi et al., 2019).

(2)

Advanced Electro-oxidation techniques encourage complete mineralization of toxic organic pollutants in simpler forms, i.e., CO₂, water, and inorganic compounds (Karthikeyan et al., 2014).

The study aims to find a suitable and effective disinfection process that can treat microorganisms and organic pollutants in groundwater by controlling the formation of DBPs.

2. Materials and Methods

2.1. Collection and characterization of groundwater samples

Standard sampling protocols were used to collect and preserve groundwater samples in triplicates from a dug-well near a steel industry, Asansol, West Bengal, India, using the grab

sampling method (Neilsen and Neilsen 2006). Water samples were preserved in prewashed polypropylene bottles and stored at 4°C. Aniline and phenol concentrations were determined by UV/Vis Spectrophotometer at the absorbance 555 nm and 500nm respectively for samples before and after the disinfection process (Norwitz and Kellher, 1981; APHA 2017).

2.2. Risk estimation of water sample before and after treatment

The human health risk was estimated due to exposure to aniline and phenol-contaminated groundwater using USEPA 2005 method. Chronic daily intake (CDI) was evaluated as per IRIS 2009 in mg/kg-d for aniline and phenol by ingestion exposure route. Input parameters were adapted from the study on risk by Mohanta and Mishra, 2020.

$$CDI_{Oral} = \frac{C_w \times IR \times EF \times ED}{B_w \times AT} \quad (8)$$

$$CDI_{Dermal} = \frac{C_w \times SA \times PC \times F \times ET \times EF \times ED}{B_w \times AT} \quad (9)$$

$$CDI_{inhalation} = \frac{C_{air} \times VR \times AE \times ET \times EF \times ED}{B_w \times AT}$$

(10)

C_{air} was calculated by following equations proposed by Little's theory in terms of concentration of phenol and aniline in the bathroom (Mishra et al., 2014);

$$C_{air} = \frac{Y_{s(t)} + Y_{s(i)}}{2} \quad (11)$$

$Y_{s(i)}$ is the initial phenol and aniline concentration in the shower room (assumed as 0 mg/L),

$Y_{s(t)}$ is the phenol and aniline concentration in the shower room at time t (mins).

$$Y_{s(t)} = \left[1 - e^{-bt}\right] \times \frac{a}{b} \quad (12)$$

$$a = \frac{Q_L \times C_w (1 - e^{-N})}{V_s} \quad (13)$$

$$b = \frac{\left[\frac{Q_L}{H} \times (1 - e^{-N}) \right] + Q_G}{V_s} \quad (14)$$

$$N = \frac{K_{OL} A}{Q_L} \quad (15)$$

Whereas N is a dimensionless coefficient,

Q_L = Water flow rate in L/min; a = factor; b = factor; t = time of contact in min

Hazard Quotient (HQ) represents the non-cancer risk in humans. HQ for all the routes of exposure due to aniline and phenol contaminated groundwater was calculated according to the following formulas:

$$HQ_{Oral} = CDI / RfD_{Oral} \quad (16)$$

$$HQ_{inhalation} = CDI / RfC \quad (17)$$

$$THQ = HQ_{Oral} + HQ_{dermal} + HQ_{inhalation} \quad (18)$$

Where THQ stands for Total Hazard Quotient, which is defined as the sum of hazard quotients due to all three routes of exposure. RfD value (Reference dose) for phenol and aniline is taken as 0.3mg/kg-day and 0.00688 mg/kg-day respectively. The RfC (Reference concentration) for phenol and aniline is taken as 0.2 mg/m³ and 0.001 mg/m³ respectively (RSL 2016).

According to USEPA, the threshold limit is considered as 1 for HQ (Mohanta et al., 2020).

2.3.Chlorination and Electro-chlorination process

A comparison study was done to identify the suitable and effective method for chlorinating aniline and phenol-contaminated groundwater. The chlorine demand of the raw water sample

was calculated using the Iodometric method (4500-Cl, APHA 2017). The emergence of DBPs is allied to the elevated level of residual chlorine; therefore, regulation of available and residual chlorine needs to be done (Otter et al., 2020). In chlorination, estimated chlorine dosing of 1.8 mg/L was done (i.e., 1.6mg/L Chlorine demand + 0.2 ppm residual chlorine) and mixed thoroughly, which was then left for a contact period of 30 minutes in an open vessel.

In this study, EC has been executed to avoid the formation of chlorinated by-products, and its laboratory setup is shown in fig 1. The electrochemical remediation of phenol and aniline contaminated groundwater was carried out as batch type in a plexiglass reactor having a specific dimension of (160 × 120 × 120) mm. The distance amongst graphite electrodes was held at 25 mm based on the preliminary optimization. Throughout the procedure, the anodic surface area immersed in the solution was 110 cm². A precision DC power source was used (PowerPac™ HC power supply Bio-Rad laboratories the USA, model no. 164–5052), and the applied current was set between 60 to 120 mA, contributing to a current density of 0.54–1.09 mA/cm². Based on the stoichiometry, the chlorine dosing was done in the form of 2.96 mg/L sodium chloride, contributing to 1.8 mg/L chlorine (i.e., 1.6mg/L Chlorine demand + 0.2 mg/L residual chlorine) for a total contact period of 30 minutes. The concentrations of aniline and phenol were measured after that for both cases.

Fig 1. Schematic diagram of the electro-chlorination setup.

2.4.Calculation and energy consumption

As a function of electrolysis duration, the % removal efficiency of chlorination and EC for all contaminants was calculated using Eq. 19.

$$\eta = \frac{C_o - C_t}{C_o} \times 100 \quad (19)$$

Where C_0 and C_t are the initial and residual concentrations of phenol and aniline at times 0 and t , respectively.

In the electrochemical process, the quantity of energy consumed, which is a crucial economic parameter, was estimated according to Eq. 20.

$$E = \frac{U \times I \times T}{V} \quad (20)$$

Where E represents the electrical energy consumed (in kWh/m³); U is the voltage applied (in Volt); I is the current (in Ampere); T is the electrolysis time (in hours), and V is the volumes (in litres).

2.5. Analysis of By-product formation using GC-MS

To analyze the organic by-product formation due to chlorination and EC of all the samples, including raw water, Gas chromatography-mass spectrometry (GCMS) analysis was carried out. The organic compounds were extracted in the solvent dichloromethane using EPA 8270 method through the liquid-liquid extraction ion method (EPA 8270, 2018). The samples were then concentrated by evaporating in a water bath at 38 to 41°C, further concentrated using the nitrogen blowout technique.

These extracted samples were then analyzed through GCMS by a TG-5MS (30 m×0.25µm) GC column in GC (Thermo Fisher trace 1300) with TSQ Duo mass spectrometer equipment, under the operating condition of the standard EPA method. The oven temperature of 100°C was applied and then increased to 290°C after 2 minutes, with a ramp rate of 5°C. Other analytical conditions are as follows; Injection temperature –250°C; Solvent delay-2 min, and electron energy was 70 eV. Measurement mode: Scan; Mass range: m/z 50–550 and total run time 60 min. The carrier gas was pure helium (99.999%) at a 1.1 mL/min flow rate.

3. Results and discussions

3.1. Effect of chlorination and electro-chlorination in aniline and phenol concentration

In the raw groundwater sample, the aniline and phenol concentrations were found to be 0.34 and 0.271 mg/L, respectively, which is 58.4 and 292 times higher than the desired limit in drinking water (IS: 10500, 2012; ATSDR 2002). For EC, sodium chloride was chosen for on-site generation of Sodium hypochlorite, which is approximately 5.08 times cheaper than using it as chlorination dosing (Key 2010). An optimization study was done primarily, and it was found that the current density of 0.818 mA/cm² resulted in maximum removal of aniline. In comparison, maximum phenol removal from contaminated groundwater was achieved at a current density of 0.91 mA/cm². The amount of maximum electrical energy consumed for maximum reduction of phenol and aniline was estimated to be 1.35 kWh/m³ and 1.51 kWh/m³, respectively. Residual chlorine after chlorination and EC process was assessed and found to be 1.9 mg/L and 2.1 mg/L, respectively, therefore meeting the regulations for residual chlorine in portable water.

In chlorination, aniline and phenol concentrations were reduced by 92.35% and 6.27%, respectively. The very low removal efficiency of total phenol was achieved due to the formation of several phenol-based chlorination by-products such as 2-Oxo-4-phenyl-6-(4-chlorophenyl)-1,2-dihydropyrimidine, 5-chloro-4,6-diphenyl-, 2,3,4,6-tetrachlorophenyl ester, etc. The formation of chloro-phenols due to the chlorination of phenols present in the water was also reported by Jiang et al., (2020). While, in the case of electro-chlorination, removal efficiencies of 99.47% and 98.48% were achieved for aniline and phenol concentrations, respectively, because of their oxidation into simpler forms. Pillai and Gupta (2016) also attained more than 99% phenol removal efficiency using NaCl as an electrolyte at all pH ranges. It clearly suggests lesser by-product formation in the EC process than that of conventional chlorination methods, making it an environmentally friendly and sustainable technology (Yi et al., 2019). The in-situ production of hypochlorite due to electrolysis of NaCl

may initially result in the formation of p-chlorophenol, which will assist in a higher degradation rate of phenol, as its degradation rate is much higher than phenol (Sathish and Vishwanath 2005). phenol degradation exhibits pseudo-first-order kinetics, and the indirect oxidation of active chlorine at anode enhances the degradation and mineralization, resulting in their removal through electrochemical oxidation of chlorine (Tasic et al., 2014; Villegas et al., 2016; Tawabini et al., 2020). The degradation rate of phenol is reported to be faster in an alkaline medium, and its proposed possible pathway is shown in figure 2. Sathish and Vishwanath 2005 have reported a similar decomposition pathway for phenol in alkaline medium.

Fig 2. Removal efficiencies of phenol and aniline at a different applied current

Fig 3. Pathway for decomposition of phenol during Electrolysis with NaCl as electrolyte

3.2.Human Health Risk assessment for Chlorinated and Electro-chlorinated groundwater

Exposure to aniline and phenol-contaminated groundwater may result in various health hazards, including damage to the cardiovascular and neurological systems. To assess the extent of risks to human health, Hazard Quotient was evaluated before and after the chlorination process, as shown in table 1. HQ due to phenol contaminated groundwater via ingestion route of exposure was found to be 0.055, 0.049, 0.06 for men, women, and children, respectively. Lower HQ values were due to the high RfD value of phenol, i.e., 0.3 mg/Kg-day. HQ via dermal and inhalation routes of exposure was found to be very low, i.e., up to 2.55E-04 and 2.50E-06, respectively, therefore contributing negligible weightage to the total hazard quotient. In the case of chlorination, there was an insignificant reduction in HQ, while a considerable reduction was observed compared to the electro-chlorinated water sample. Many phenolic compounds with complicated structures were present in the raw water. Simple chlorination resulted in the formation of even more complex by-products of phenolic compounds. However,

in the EC process, these compounds were dissociated into simpler forms, resulting in a drastic reduction of phenol content. THQ due to aniline contaminated groundwater was found to be 3.08, 2.73, and 3.33 for men, women, and children, respectively. High HQ value even for lower aniline concentration was due to its lower Reference dose (RfD) value, i.e., 0.0068 mg/Kg-day, representing a higher probabilistic non-cancer risk to the exposed population. However, a remarkable reduction in HQ was observed in the case of both the chlorination and EC process (table 1). In chlorinated water, THQ was found to be 2.35E-01, 2.09E-01, and 2.55E-01, while for EC water, it was found to be 1.63E-02, 1.44E-02 and 1.77E-02 for men, women and children, respectively. It was evident that for aniline, any treatment method can be used due to its higher mineralization rate. Although the THQ values were reduced for Phenol and Aniline contaminated water after chlorination, but still, the formation of toxic DBPs will lead to considerable carcinogenic and non-carcinogenic risks. For all the cases, it was observed that children were at the highest non-cancer risk due to their lower body weight concerning ingestion rate (Laxmi Mohanta et al., 2019, Mohanta and Mishra 2020).

Table 1: Hazard Quotient of water samples before and after chlorination.

3.3. Analysis of by-product formation by GC-MS

The organic compounds in the raw and treated groundwater were studied and calculated using the mass spectral library database of the National Institute of Standards and Technology (NIST) (Fig 3). The results showed that organic pollutants found in groundwater were evidently degraded, and only Decanedioic acid was found in abundance in EC treated water, which is neither toxic nor hazardous in nature. Phenol was found in all the samples; however, its relative abundance was found to be negligible in the case of EC treatment. Many new by-products such as 2-Hydroxybiphenyl, 2,3,4,6-tetrachlorophenyl ester, 6-Fluoro-2-trifluoromethylbenzoic acid, 2-Phenylamino-5,6(4H) dihydro-1,3-thiazine, 5-chloro-4,6-diphenyl-, 2-

Hydroxybiphenyl, 2-Oxo-4-phenyl-6-(4-chlorophenyl)-1,2-dihydropyrimidine, etc were formed in chlorination process (Table 2). In the EC process, phenol present in the water sample was converted into a carboxylic acid, carbon dioxide and water, as shown in fig 2, and was found at the low relative abundance in the form of 1,4-Benzenedicarboxylic acid. Some of these compounds are corrosive, toxic and may cause environmental as well as health hazards. Aniline was present in the form of 2-Chloroaniline-5-sulfonic acid in raw water; however, it was not identified in the chromatograms of both the treated groundwater due to its higher mineralization rate into the end product and intermediate products (Singh et al., 2021).

Fig. 4: GC-MS analysis chromatograms (a) Raw groundwater (b) chlorinated water (c) electro-chlorinated water

Table 2. GC-MS Analysis of groundwater treated using chlorination and electro-chlorination

Conclusion

This study focused on evaluating an effective treatment technique that will disinfect the groundwater as well as oxidize the organic pollutants such as phenol and aniline at the same time by controlling the formation of DBPs. The comparative study between chlorination and EC process with respect to oxidation of phenol and aniline and by-product formation showed profound results. HQ due to phenol in groundwater showed negligible reduction for chlorination, which resulted in the formation of a number of complicated by-products. In contrast, the drastic reduction was observed in the case of EC as its degradation and mineralization system efficiency was enhanced by indirect oxidation of chloride ions formed at the anode. However, HQ due to aniline reduced significantly for both the chlorination and election-chlorination, because of its higher mineralization rate. Several harmful chlorination and other by-products formations were observed in the case of chlorination, making the contaminated groundwater even more toxic to consume. However, only one non-toxic by-

product, i.e., Decanedioic acid was found in the case of EC. If the only aniline is present in groundwater, both chlorination and election-chlorination can be opted. However, if phenol is present, then EC is found to be effective and safe for human health. Further detailed study may also be needed for quantitative study of DBPs formation and associated risks.

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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 paper.

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Figures

Figure 1

Schematic diagram of electro-chlorination set up.

Figure 2

Removal efficiencies of phenol and aniline at different applied current

Pathway for decomposition of Phenol during Electrolysis with NaCl as electrolyte

Figure 4

GC-MS analysis chromatograms (a) Raw groundwater (b) Ex-situ chlorinated water (c) In-situ electro-chlorinated water