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Effluent treatment using electrochemically bleached seawater—oxidative degradation of pollutants

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Abstract

Use of seawater electrolytically enriched with hypochlorite and the in situ generation of hypochlorite on the high seas, stand a good chance for disinfection and decrease of bio and non-biodegradable organics in effluent before discharged into estuaries and deep oceans. Enriched seawater effectively decreased the biological oxygen demand measured over 5 days (BOD) and chemical oxygen demand (COD) levels of semi-treated wastewater. The oxidative degradation of Brilliant Blue, a triaryl industrial dye by hypochlorite and electrolytically enriched seawater are compared at pH 6.5. Both had similar magnitude second-order rate constants ($21 \pm 1\,M^{-1}\,s^{-1}$) and procedure is feasible. Increase in acid concentration enhanced the reaction rate. With 1:1 and 1:100 molar ratios of dye to hypochlorite, the COD $= 140\,mg\,L^{-1}$ of 1.0×10^{-3} M dye reduced to 100 and 30 mg L^{-1} respectively.

Keywords: Seawater; Hypochlorite; Electrochemical generation; Oxidative degradation; Chemical pollutants; Disinfection

1. Introduction

Urbanization has had significant impacts on the human health through hydrology of the environment by controlling, the nature of runoff waters and the delivery of pollutants to rivers, streams, lakes and ocean. The striking feature of the distribution of the world's population is the tendency for urbanization near vast water sources. Since the beginning of the Industrial Revolution, urban development has influenced the flow and storage of water, as well as the quality of available fresh water. Many coastal cities dispose their municipal wastewater to the sea through ocean outfall facilities, either as raw sewage or after preliminary treatment. The environmental impacts of these discharges depend strongly on the discharge location, level of treatment, if any, and on the physical, chemical and biological nature of the water body. Due to poor water quality resulting from highly polluted effluent discharges, many estuaries and sea beaches are health hazards. The impact of wastewater discharges on the marine environment is likely to worsen in the future, due to population growth, urbanization and the increase in water supply connection and sewerage levels. The growth will be most severe in developing countries, while in industrialized countries it might actually decrease as a result of water demand management and the introduction of cleaner production and water saving technologies [1].

Literature survey shows a number of oxidative methods including advanced oxidation processes involving ozone, peroxide, UV radiation and catalysts [2]. Comminellis and Pulgarin have investigated the anodic oxidation of organics on the electrode surface [3]. Rodrigo et al., have reported improved ways to treat wastewater electrochemically, using boron-duped diamond electrodes [4], while Ferro et al., have reported the efficient way generating chlorine using boron-doped diamond electrodes. Haenni et al., have reported the scope for such system in disinfecting pool water have been reported [5,6]. Chlorination through use of gas chlorination or hypochlorination has become the most common type of wastewater and water disinfection [7]. Hypochlorination of water is more economical in water treatment. Hypochlorite is a strong oxidizing agent, biocide, defouling agent and deodorizer. Normally, the hypochlorination is achieved through a chemical feed pump to inject

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a calcium or sodium hypochlorite solution. The generation of hypochlorite using seawater as the chloride source has great scope, as it leads to insitu generation of hypochlorite under verity of situations, where seawater is accessible and abundant. Another dimension the utility of bleached sea water is reported passivity in metals from corrosion through decreased dissolved oxygen levels. The solubility of oxygen in water is dramatically reduces by increased hypochlorite levels.

This manuscript covers the systematic studies showing the effect electrochemically generated hypochlorite using seawater and its scope in oxidation of organics and in disinfection to achieve hygienic, aesthetic and sustainable environment through the improved effluent quality.

2. Experimental

Natural Seawater composition of chloride ion, Cl^- is about 19,5000 ppm or 19.5 g L^{-1} and Na^+ ion is about 10.7 g L^{-1} [8]. Thus seawater with 0.53 mol L^{-1} of chloride ion, works out to be a abundant source of chloride for electrochemical generation of chlorine, and then hypochlorite, through it's disproportionation reaction [9].

For the control experiments, hypochlorite was generated by bubbling chlorine gas through cold solution of 5% sodium hydroxide. The Baird and Tatlock Electrolytic Analysis apparatus was used for electrochemical generation of hypochlorite from seawater. The equipment consists of a single compact unit containing its own low voltage direct current supply unit capable of giving an output of 0–10 A at up to 12 V. Optimum and cost effective conditions for the generation of hypochlorite from sea water were covered vessel with volume 200 ml water; electrolysis duration 45 min; temperature 20 °C; pH 6.74. Under these conditions $(12.2 \pm 0.3) \times 10^{-2}$ M of hypochlorite was obtained [9]. Arsenite method was used for the determination of the hypochlorite concentration in the sample [7,10].

The electrolysis chemistry is as follows:

$$\text{Anode} : 2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

$$\text{Cathode} : 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

$$\text{Overall} : 2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$$

and

$$Cl_2(g) + H_2O(l) \rightarrow 2H + (aq) + OCl^-(aq) + Cl^-(aq)$$

2.1. Bacterial sensitivity, BOD and COD tests

These tests constitute a simple and reliable technique especially applicable to routine bacteriological work. It consists of concentrating disks with known concentrations of hypochlorite, placing them on plates of a culture medium containing a bacterium and after incubation, determining the degree of sensitivity by measuring the easily visible areas of inhibition of growth produced by the diffusion of hypochlorite from the disks into the surrounding medium. biological oxygen demand measured over 5 days (BOD), chemical oxygen demand (COD), total dissolved and total suspended solids were determined using standard procedures [9].

2.2. Kinetics

The kinetics of the reaction is studied using the HITECH SF-61 DX2 Micro volume double mixing stopped flow apparatus with thermostat control and software for data capture and analysis. The reaction kinetics was monitored at (25.0 ± 0.1) °C.

3. Results and discussion

3.1. Bacterial sensitivity

The bacterial sensitivity test using the medium nutrient agar coated on petri dishes and the bacterium, *Escherichia coli* (*E. coli*) showed that the hypochlorite solution generated using seawater sample is good anti bacterial and equally efficient as the commercial bleach samples under comparable conditions in the bacterial growth inhibition, after the 24 h incubation [9].

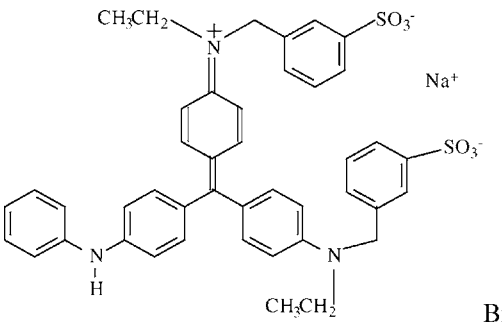
3.2. BOD_5 and COD

The effect of the seawater sample containing hypochlorite on the BOD levels of wastewater is investigated by adding varying amounts of seawater to fixed volumes of wastewater. Wastewater samples were collected from the sewage treatment works after the primary treatment, but prior to the secondary treatment. The BOD level for the untreated samples (200 ml) was reduced from 1.3 mg L^{-1} to 0.1 mg L^{-1} upon treatment with seawater sample (6 ml). The reduction of BOD levels is expected based on the diminished bacterial oxidation of organics mater due the anti bacterial action of hypochlorite. Sample from waste water works after secondary treatment had almost zero BOD levels, which had no effect due to addition of bleached seawater [9]. The chemical oxygen demand of primarily treated Sample (100 ml) was reduced from 440 mg L^{-1} to 160 mg L^{-1} upon mixing with 50 ml to 40 mg L^{-1} with 100 ml of the bleached seawater sample. Obviously, the powerful oxidizing capacity of hypochlorite decreases the COD levels [9].

3.3. Oxidative degradation of organics

Further, the oxidative degradation kinetics of the organics normally present in the effluent is investigated in detail. The reaction of a selected representative dye, Brilliant Blue

which is used in textile and food industries, with hypochlorite is studied under controlled conditions and using the bleached seawater.



Brilliant Blue

Brilliant Blue is a triarylmethane type of dye (disodium α-(4-(*N*-ethyl-3-sulfonatobenzylamino) phenyl)-α-(4-*N*-ethyl-3-sulfonatobenzylamino, cyclohexa-2,5-dienylidene) toluene-2-sulfonate). Brilliant Blue is water soluble with λ_{MAX} at 555 nm and absorption coefficient, $\varepsilon = 2.15 \times 10^4\,dm^3\,mol^{-1}\,cm^{-1}$. Hence the kinetics was monitored at 555 nm.

All the kinetic runs were conducted with excess hypochlorite and low dye concentrations. Under such conditions experiments followed pseudo first-order kinetics, indicating reaction order with respect to the dye is one. Further the pseudo first-order rate constant, k' increased proportionally with the increase in the initial concentration of hypochlorite suggesting that reaction has first-order dependence on the concentration of the oxidant and total order is two.

All experiments were repeated with seawater containing electrochemically generated hypochlorite. Fig. 1 illustrates the kinetic profiles of depletion of Brilliant Blue in presence of seawater containing different initial amounts of hypochlorite. The reaction of dye both with control hypochlorite solution and enriched seawater too had second-order and one each with respect to both the dye and hypochlorite. Table 1 summarizes the pseudo first-order constants from the experiments, and the estimated half reaction times and second-order rate constants for both the control and seawater enriched experiments.

Further, the $\ln k'$ versus ln [hypochlorite] for the control and seawater experiments gave straight lines with ($y = 1.1572x + 4.0049$, $R^2 = 0.9954$) and ($y = 1.0891x + 4.0049$, $R^2 = 0.9885$) respectively. A perusal of the slopes shows that under both the situations, the reactions have first-order dependence on hypochlorite concentration. The second-order rate constants of the two sets of experiments are of similar magnitude and most importantly the reactions are fast. This conclusively confirms the scope of hypochlorite enriched seawater in treatment of wastewaters and industrial effluent.

At very high pH, where bulk of the hypochlorite is in the hypochlorite form and with very low concentration of HOCl, reaction is very slow suggesting the rate constant for the reaction between OCl^- and the dye is small.

As all the experiments were done at pH 6.5, the effect of acid on the reaction between Brilliant Blue and hypochlorite is further investigated with added acid under both control and seawater enriched with hypochlorite conditions and results were similar. The kinetic data obtained with seawater conditions is summarized in Table 2. With the increase in the concentration of added acid the pseudo first-order rate constant increased. To understand the reaction dynamics, a close look at the chemistry of hypochlorite is essential. HOCl with $pK_a = 7.4$ is a week acid and it's dissociation constant is 4×10^{-8} indicating that even very low concentration of acid shifts the equilibrium towards formation of HOCl [11]. The

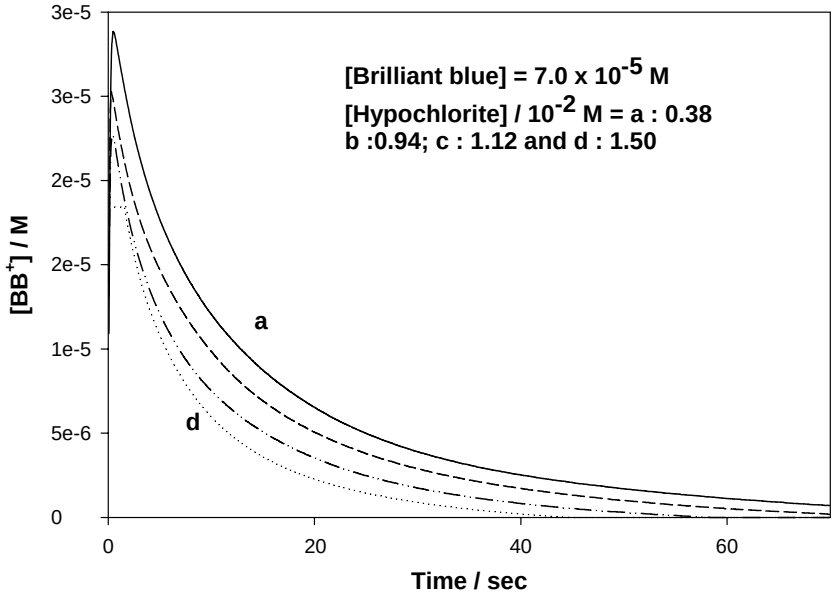


Fig. 1. Effect of Electrolyzed seawater on the depletion rate of Brilliant Blue–absorbance vs. time plots.

Table 1
Rate coefficients for the reaction between Brilliant Blue and (i) hypochlorite (control), and (ii) electrolytically bleached seawater

Hypochlorite (control)[a]				Seawater enriched with hypochlorite[a]			
OCL^- (10^{-3} M)	k' (10^{-2} s^{-1})	$t_{1/2}$ (s)	k (M^{-1} s^{-1})	OCl^- (10^{-3} M)	k' (10^{-2} s^{-1})	$t_{1/2}$ (s)	k (M^{-1} s^{-1})
1.17	2.23	31.0	19.09	3.75	7.90	8.8	21.07
2.34	5.13	13.5	21.94	7.50	15.95	4.3	21.27
3.51	7.39	9.4	21.06	9.38	19.29	3.6	20.58
4.68	10.73	6.5	22.94	11.25	24.11	2.9	21.43
5.85	13.13	5.3	22.44	15.0	33.45	2.1	22.30
Mean $k = 21.49 \pm 0.64$				Mean $k = 21.34 \pm 0.52$			

$[BB^+] = 7.5 \times 10^{-5}$ M, pH = 6.5 and temperature = 25 °C.
[a] Total hypochlorite concentration = $[OCl^-] + [HOCl]$.

preliminary experiments showed that at very high pH, above 9, when bulk of the hypochlorite is in the hypochlorite form and with very low concentration of HOCl, the reaction was very slow suggesting the rate constant for the reaction between OCl^- and the dye is small. At pH 7.4, the concentrations of hypochlorite and hypochlorous acid will be equal. With the increase in acid concentration, the HOCl concentration increases and at pH 6.5, the percentage of hypochlorous acid in the mixture reaches about 71%, suggesting the major pathway for the reaction is through of oxidation by HOCl (Table 1).

With initial concentration of hypochlorite 1.5×10^{-3} M (Table 2) to achieve pH 6.5, in the control experiment the added acid concentration is about 1.68×10^4 M and the resultant hypochlorous acid concentration is 1.166×10^4 M in both cases.

Table 2 summarizes the added initial acid and the compiled hypochlorous acid concentrations and the corresponding pseudo first order rate constants (k') obtained. The plot of the $\ln k'$ versus $\ln$ [HOCl] concentration gave a good straight line with $R^2 = 0.987$, suggesting the first-order dependence of the reaction rate on the acid concentration. The calculated second order rate constants for the over all second-order rate constants are also summarized in Table 2.

To investigate the impact of the oxidation of Brilliant Blue using hypochlorite, the BOD and COD for the reaction mixture was determined in duplicate experiments. The BOD values were very low with significant changes, for prior to and after reaction of dye with the bleached seawater. 1.0×10^3 M Brilliant Blue (1 ml) had initial COD of 140 mg L^{-1} and upon addition bleached seawater in the 1:1 and 1:100 molar ratios, the COD reduced to 100 and 30 mg L^{-1} respectively. Even with 1:100 molar ratio, the residual COD shows that the dye is oxidized, but not completely mineralized. The total oxidizable carbon (TOC) could not be determined.

To estimate scope of the bleached seawater in oxidizing the wastewater containing other dyes, the kinetics of number of dyes which are normally used in the textile and other industries or as stains with hypochlorite are studied in presence of hypochlorite and bleached seawater from the unpublished data and from the literature are compiled and summarized in Table 3.

Table 3 summarizes the second-order rate constants for the reaction of hypochlorite at pH 6.5 for variety of dyes. The magnitude of the rate coefficients clearly demonstrate that most of the dyes are easily oxidized by the hypochlorie enriched seawater. Ru(III) is observed to catalyze the oxidation by hypochlorite, hence studies are in progress to explore suitable heterogeneous catalyst to enhance the efficiency of oxidation by hypochlorite under seawater pH conditions.

Ocean outfalls can work efficiently and may be a satisfactory solution to effluent management. Under the right conditions, properly treated effluent discharged into deep ocean water with strong currents will have little or no environmental impacts.

Table 2
Effect of acid on the reaction between Brilliant Blue and seawater enriched with hypochlorite

$[H^+]$ (10^{-4} M)	[HOCl] (10^{-3} M)	k (10^{-2} s^{-1})	k (M^{-1} s^{-1})[a]
0	1.066	3.20	30.02
1.0	1.166	3.45	29.59
2.0	1.266	3.71	29.31
3.0	1.366	4.03	29.51
4.0	1.464	4.49	30.66
5.0	1.499	4.62	30.82
Mean = 29.99 ± 0.63			

$[BB^+] = 7.5 \times 10^{-5}$ M, hypochlorite 1.5×10^{-3} M, initial pH = 6.5 and temperature = 25 °C.
[a] $k = k'/[HOCl]$.

Table 3
Second-order rate coefficients for different dyes with hypochlorite

Name of dye	Category of dye	k (M^{-1} s^{-1})
Brilliant Blue[a]	Triaryl dye	21.5 ± 0.6
Indigocarmine [12][b]	Indigo dye	18.0 ± 0.1
Amaranth [13][a]	Azo dye	26.2 ± 0.5
Safranine-O [13][a]	Phenazine dye	48.4 ± 1.1
Methylene Violet [14][b]	Phenazine dye	22.1 ± 0.5
Meldola's Blue [15][b]	Phenoxazine dye	2.1 ± 0.3
Brilliant Cresyl Blue [15][b]	Phenoxazine dye	21.2 ± 0.3
Nile Blue [15][b]	Phenoxazine dye	1020 ± 120

Temperature: 25 °C, pH = 6.5.
[a] Both controlled and enriched seawater experiments.
[b] Controlled runs only.

4. Conclusions

The bleached seawater can effectively oxidize the aromatic dye, Brilliant Blue in short duration, but the residual COD values after oxidation indicate that complete mineralization does not occur for the studies conditions. The effluent treatment using the hypochlorite enriched seawater has potential to decrease the levels of toxins, bacteria, BOD, COD and organics to the acceptable levels before discharged into deep oceans, rivers or estuaries, to afford aesthetic, hygienic and sustainable environment and safe seas for future generations.

In addition to the effluent treatment, the electrolytic generation of hypochlorite in high seas has great scope in the disinfection, deodourising and defouling the deep sea platforms, ship decks and the oceanariams. The use of efficient catalysts and improved electrolyzing systems such as boronduped diamond electrodes could further enhance the economic and effective use of bleached sea water in treatment of wastewaters.

The solubility of oxygen in water is dramatically reduces by increased hypochlorite levels. Thus, bleached seawater also provides an additional advantage as anti-corrosion agent towards metals in the installations exposed to seawater.

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