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Application of chlorine dioxide for secondary effluent polishing

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Abstract

There are still many difficulties for developing the projects of using treated effluents. In this study, the efficiency of chlorine deoxide in the process of preparing the effluent of Sahebgharanieh Plant of Tehran for reuse purposes has been determind. Major results are as follows: Total COD reductions resulted from effluent treatment by ClO_2 solutions having concentrations equal to 1/4, 1/2 and 1/1 of COD samples at one hour contact time have been about 42%, 49% and 59% respectively. Total suspended solids were also reduced by treatment with ClO_2 solutions having the certain concentrations mentioned, and the reductions were about 37% ,47% and 58% respectively. Besides total and fecal coliforms results indicated that ClO_2 apllied was quite efficient in effluent disinfection. The conclusion is that reasonable reductions would be expected in the amounts of remained major pollutants and so reuse applications for some non-potable purposes may become possible. The acidification of chlorite has been used for ClO_2 generation as it is better suited to small treatment systems.

Key words: *Wastewater treatment, chlorine dioxide, chemical oxidation, secondary effluent*

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Introduction

Chlorine dioxide (ClO_2) which was first used in drinking water treatment is an oxidant increasingly of interest for industrial and wastewater treatment (Eckenfelder and Bowers, 1994). It has become a disinfectant alternative to chlorine and ozone because it offers the prospect of disinfection without the production of trihalomethanes and bromates so it is gaining acceptance as a water treatment promise (Otterholm and Jadesjo, 2000). As an oxidant, ClO_2 is generally considered for reuse strategies, because it is more effective than chlorine in inactivation of most pathogens (Metcalf and Eddy, 2003). Besides, its biocidal properties are not influenced by pH and it is a more powerful oxidant than chlorine (Reynolds and Richards, 1996). However, the findings of Stanford group indicate that ClO_2 is only slightly superior to chlorine as a bactericide but it is a much superior virocide. Compared to ozone which is the strogest oxidant of the common disinfecting agents, ClO_2 has the advantages of easier generation in point of use and a longer life of the preservation (White, 1992).

Interest in ClO_2 for chemical waste treatment is of more recent origin to reduce and eliminate the environmental problems caused by the discharge of waste streams without inadequate treatment (Eckenfelder and Bowers, 1994). In particular, oxidation offers one of the few methods for removing odor, color and various potentially toxic organic substances, often found in wastewaters (Jackman and Powell, 1991). ClO_2 is equally effective in secondary nonnitrified or nitrified effluents for disinfection purposes and the increased disinfection effectiveness seen in filtered versus nonfiltered wastewaters is not accompanied by any significant change in disinfectant demand (WPCF, 1986). In this article, we discuss the usefulness of ClO_2 as a disinfectant and chemical oxidant for secondary effluent polishing. ClO_2 production and so its use for wastewater treatment has not already been performed in Iran.

Materials and Methods

Generating chlorine dioxide

There are several methods available for ClO_2 generation. For this study, direct acid system has been used because it was well studied for most small treatment systems (White, 1992). This method utilizes the reaction of a strong acid with sodium chlorite ($NaClO_2$). The following reaction which is most accepted for H_2SO_4 is:

$10\ ClO_2 + 5\ H_2SO_4 \longrightarrow 8\ ClO_2 + 5\ Na_2\ SO_4 + 2\ HCl + 4\ H_2O$

Figure 1 is a schematic diagram of the manual small generation system arranged for this study. It was also needed to apply a compressed air supply to transfer the generated ClO_2 gas to the final flask. This flask was put in an ice bath to preserve the strength of the prepared stock solution. Both sulfuric and chloridric acids which were used in the preliminary tests, showed favorable results and the concentration of ClO_2 solutions prepared was enough to use in wastwater treatment. The stock solution was then stored in a glass-stoppered dark-colored bottle in a refrigarator.

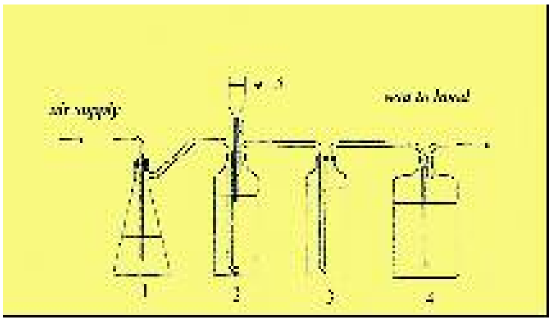

Figure 1: Manual feed equipment arrangment for generating ClO_2

1. *aspirator flask*
2. *gas generating bottle (reaction vessel)*
3. *collecting bottle containing $NaClO_2$ solution (1g/l)*
4. *collecting bottle containing water for gas absorbsion*
5. *separatory funnel containing 10% H_2SO_4*

Methods of ClO_2 control

As it was already mentioned, ClO_2 gas produced in direct acid system was absorbed in enough distilled water. The ClO_2 concentration thus, prepared can be determined by iodometric method as outlined in Standard Methods (APHA, 1995). However, yield determination can be done only when laboratory apparatus for determination of chlorite and chlorate ions are available, because for calculating ClO_2 yield by the following equation (Aieta and Hernandez, 1984), the concentrations of these ions should have to be known :

$$\mathbf{ClO_2\ yield} = \frac{[ClO_2]}{[ClO_2] + [ClO_2^-] + 0.808\,[ClO_3^-]} \times 100$$

Wastewater sample and characteristics

The samples were collected from Sahebgharanieh Treatment Plant in Tehran. This Plant which is located in north part of Tehran is an extended aeration system having 2 aeration basins. The wastewater is treated with an average flow of 25 m^3h^{-1}. Characteristics of secondary effluent samples before and after treatment by ClO_2 solutions, were determined according to the procedures outlined in the Standard Methods. The tests were confined to the determination of total COD, soluble COD, total suspended solids (TSS), total and fecal coliforms which all are considered to be the most important pollutants remained in the secondary effluents of conventional plants which do not practice disinfection. The period of this experimental study was performed in Tehran from January 2000 to July 2001. In this period, the Sahebgharanieh Plant was often unabled to produce effluent with BOD and TSS of less than 20 mgl^{-1}.

Results

Figure 2 shows the results of secondary effluent treatment in total COD reduction by ClO_2 in different contact times. In Figure 3, the efficiencies of COD removal by ClO_2 in different pHs could be considered in one hour contact time and results of total and dissolved COD reduction by various amounts of ClO_2 solution can be seen in Figure 4. Although the disinfection effect of ClO_2 is a well known phenomena, the efficiency of the treatment in reduction of both total and fecal coliforms was determined. The results of this treatment in 60 minutes contact time with various concentrations of ClO_2 solutions are in Table 1. Finaly, Figure 5 shows the results of TSS removal by various amounts of ClO_2 solutions in one hour contact time.

Table 1: Reduction of total and fecal coliforms by ClO_2 treatment of effluent samples

mg/l ClO_2 applied *	Contact time (min.)	Total coliforms (MPN/100ml)	Fecal coliforms (MPN/100ml)
0	0	100	90
C/4	60	<2	<2
C/2	60	2	<2
C	60	<2	<2
0	0	80	50
C/4	60	2	<2
C/2	60	<2	<2
C	60	<2	<2

*C=COD concentration of the effluent sample

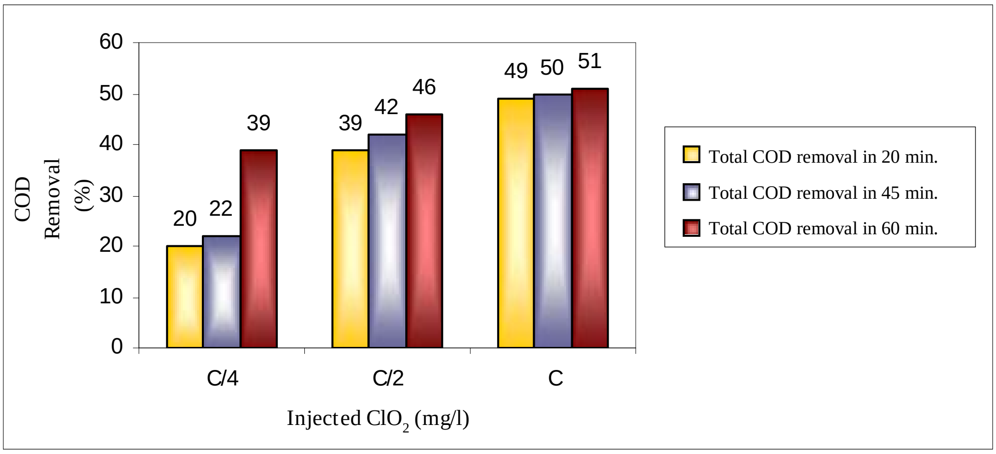

Figure 2: Total COD removal as a function of injected ClO_2 in different contact times
(C= influent COD concentration)

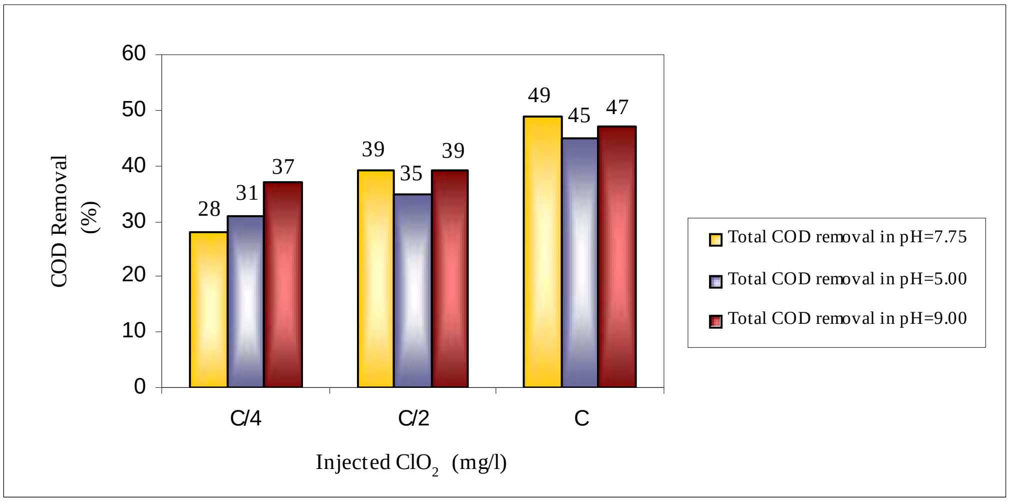

Figure 3: Total COD removal as a function of injected ClO_2
in various pH_s of treatment

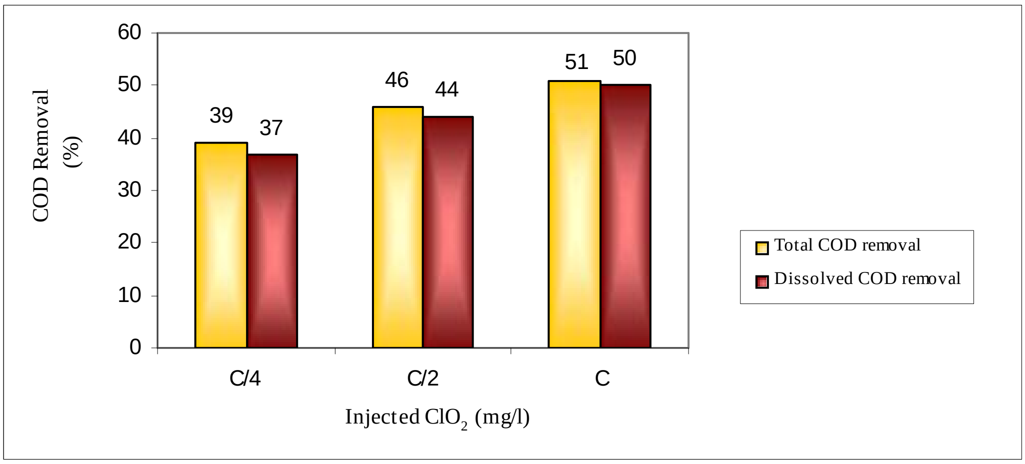

Figure 4: Total and dissolved COD removal as a function of injected ClO_2 in one hour contact time
(C = influent COD concentration)

Discussion and Conclusion

Most small scale ClO_2 generators in industrialized countries use sodium chlorite as the base chemical and sulfuric acid as the chlorite activator (White, 1992). This was the reason of choosing direct acid system for this study. However, some difficulties were experienced and according to the results, the concentrations of ClO_2 solutions prepared in the 4 tests were 200, 250, 270 and 400 mgl^{-1}, whereas it could be at least 250 mgl^{-1} (APHA, 1995). The conclusion is that even if there is only a slight deviation in operating conditions of synthesis, the quality of final solution would be affected. This matter should be considered in all treatment plants that would utilize this method for wastewater polishing. The yield could not be reported for ClO_2 generator, because the apparatus needed for determination of the probable chlorite and chlorate produced was not available.

In the study of oxidation power of ClO_2 for effluent polishing, 3 contact times of 20, 45 and 60 minutes were chosen. Also, three concentrations of ClO_2 solutions were used which were as high as the total, half and one forth of the COD concentration of effluent sample under treatment. The best results were belong to the highest amounts of both contact time and ClO_2 concentration i.e., more than 60% removal in COD was achieved by 60 minutes contact to about 30 mgl^{-1} ClO_2. However, for reducing the remained COD of secondary effluent to less than 20 mgl^{-1}, less ClO_2 concentrations and/or contact times were quite sufficient, for example, 15 mgl^{-1} ClO_2 in 1 hour contact time or 30 mgl^{-1} in 45 minutes. But, reducing the contact time to less than 45 minutes is not recommended. According to Figure 4, it could be concluded that most of the considered reductions in COD are belong to dissolved fraction of this parameter.

The changes of pH in common range of 5 to 9 have not appreciable effect on the efficiency of organics removal by ClO_2. It seems similar to the accepted fact of independence of disinfecting power of ClO_2 to pH changes.

Disinfection power of ClO_2 is a well known phenomena and results of our study also indicate that complying with the standard of less than 2 total and fecal coliforms in 100 ml of effluent would be easily achieved by ClO_2 treatment. Besides, organic and microbiological pollutants, TSS (often specified as turbidity) reduction is also recommended for all reuse applications of secondary effluents. ClO_2 treatment seems to be successful in complying with this standard too, for the reason that the reduction of about 60% of remained TSS is possible in 1 hour contact to ClO_2 in concentration equal to the amount of COD of treated effluent.

Assessment of advanced treatment of secondary effluent by ClO_2 shows the considerable effect of this gas in reducing the remained pollutants of these effluents. Moreover ClO_2 has been shown to be effective disinfectant for bacterial indicators at Sahebgharanieh Treatment Plant. Safe production of ClO_2 is possible by direct acid system and required amounts for effluent polishing would be reduced by modifying the performance of treatment plants to have a typic effluent (20/20 or less for BOD and TSS) at all times and even further by upgrading them to produce effluents with new standard of 10/10 for example by employing a filtration step prior to ClO_2 injection. ClO_2 treatment seems to be an acceptable treatment technology to ensure good effluent quality for reuse applications such as agricultural and landscape irrigation and even for all the other urban non-potable applications, when it is employed for filtered effluents. One final but important point for ClO_2 treatment concerns the required time. Because the data on ClO_2 in the references are limited, it is recommended to perform site specific testing to establish appropriate dosage ranges. However, the contact time for ClO_2 oxidation should be longer than 20 minutes.

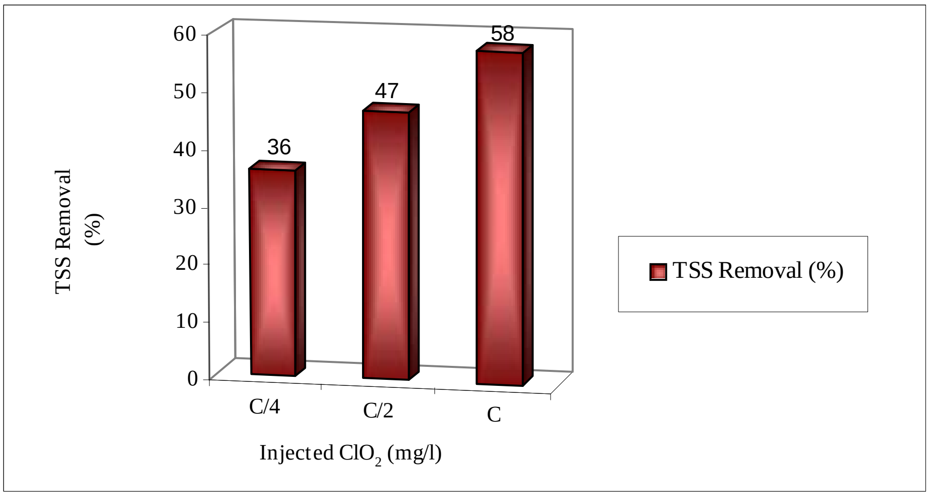

Figure 5: TSS removal as a function of injected ClO_2 in contact time of 1 hour
(C = influent COD concentration)

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