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MODIFIED NERNST MODEL FOR ON-LINE CONTROL OF THE CHEMICAL OXIDATION DECOLORING PROCESS

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ABSTRACT

A modified Nernst equation was used to describe the decoloring reaction using the Oxidation-reduction potential (ORP) as an on-line monitoring and control parameter of the chemical reaction. In the modified equation, an "S" term is defined to indicate the oxidative potential (or decoloring potential) of dyes being studied. The laboratory study utilizes sodium hypochlorite (NaOCl) to reduce the color of wastewater spiked with textile dyes. Five dyes were used in preparing the wastewater samples : methyl red (MR), methyl violet (MV), methyl blue (MB), malachite green (MG) and methyl orange (MO). The color was measured by use of an automatic ADMI (American Dye Manufacturer Institute) measurement system in which a visible spectrophotometer was connected to a personal computer and the samples were scanned from 400 nm to 700 nm with a 10 nm interval each step. During the batch decoloring studies, several factors including ADMI, ORP, temperature and pH were continuously monitored with the computer. In this study, the potential of the decoloring compound of the dyes studies are in the following order : MG>MV>MO>MR>MB, with numeric ratios of 2.08 : 1.78 : 1.78 : 1.28 : 1.00, respectively. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd.

KEYWORDS

Decoloring; dye; decoloring coefficient; Nernst model; Oxidation-Reduction Potential (ORP).

INTRODUCTION

Many industries discharge effluent containing visible colors thus causing many environmental pollution problems to some extent. Normally, organic matter in the effluent can be removed by use of secondary biological treatment processes, but the color and its causing substances must be reduced using physicochemical methods (Weeter *et al.* 1977). Although the color may be aesthetically unacceptable, it has been considered harmless to environment and is traditionary not removed from the final effluent discharge of many industries. In the foreseeable future, however, more stringent color limitations will be imposed on industrial effluent discharges in the U. S. and some Asian countries. Thus, removing color from wastewater effluent will become an important objective in wastewater treatment.

Among the many physicochemical methods such as activated carbon adsorption, oxidation, coagulation, etc. proposed for removing color from wastewaters (Kreye, 1974; Shelly, 1976), chemical oxidation is considered to be the most cost-effective alternative. According to the oxidation mechanism proposed by Perkin *et al.* (1980), the oxidants applied destroy the bond dye stuff thus reducing the color. The oxidants which can be used for decoloring purposes include: ozone, chlorine and sodium hypochlorite.

The treatment cost of all chemical oxidation methods depends primarily on the consumption of chemicals. Generally speaking, more chemical addition will result in a better effluent quality but the treatment cost increases. Thus, the most cost-effective operation of the chemical oxidation process is to control the chemical dosage in such a way that the dosage of chemical applied is stoichiometry sufficient to reduce the effluent color to an acceptable level. This control strategy requires that progress of the chemical oxidation process must be closely monitored and controlled. In the past, it was almost impossible to assemble a device to achieve a dosage control mechanism. With the advent of less expensive and more powerful personal computers, it is feasible to implement an on-line color measurement and feed-back control to automatically control the degree of the oxidation process.

On-line color measurement

The studies that are described in this paper are based on the on-line monitoring of the parameters relevant to the color removal. Thus, on-line measurement of color is of great importance for monitoring and controlling the chemical oxidation process. Several methods have been developed for measuring color in water samples. In the "Standard Methods" (APHA, 1992), the color of a sample is compared to a series of dilutions of a standard Pt-Co solution. This method has been traditionally used for measuring the color in drinking water and the results are expressed in unit or equivalent concentration of the Pt-Co solution. But it is not suitable for on-line measurement of the color in wastewater.

The American Dye Manufacturers Institute has developed the ADMI method based on Nikerson's chromatic formula for a more scientific measurement of the color in textile wastewaters (Allen *et al.*, 1973). Both laboratory procedures and data calculations of this method are considered very tedious, so it has not been applied to field practice except in laboratory studies. Using a personal computer, the ADMI method has been automated (Chang *et al.*, 1992) so that the measurement can be quickly obtained and the complicated calculations can be performed by use of a computer program. Hence on-line monitoring of the sample color is made possible using the automated ADMI method. The visibility value of 15 cm corresponds to an ADMI value of 567 units.

On-line measurement of color is carried out by pumping the liquid with an Eyela MP-3 micro-tube pump into a 1-cm quartz cell that is placed inside a Hitachi U-2000 Spectrophotometer. The range of scanning wavelengths is set from 400 nm to 700 nm with a 10-nm interval. Thus a total of 31 sets of data can be obtained for each color measurement . The signal is transmitted to a personal computer for recording and processing the measured ADMI data. With appropriate arrangements, the computerized monitoring system can be used as a feed-back control to adjust the chemical dosing of oxidant as needed for achieving the desired level of color removal.

The oxidation/reduction potential (ORP)

The oxidation process is known to be caused by electron transfer from the oxidant to the substances being oxidized. The Nernst Equation can be used to relate the Oxidation/Reduction Potential (ORP) of the system to the concentration ratio of the substance being oxidized and the oxidant by (Weber, 1972) :

$$E=E^0 + (RT/nF) \ln ([Oxid]/[Red]) \qquad (1)$$

R = gas constant
T = the absolute temperature
n = the number of electrochemical gram equivalent per gram mole exchanged during the redox reaction
F = Faraday's constant

E = the electrode potential of chemical reactions
E^0 = the standard electrode potential
[Oxid] = the molar concentration of oxidant
[Red] = the molar concentration of substance being oxidized

According to the Nernst Equation, the system Oxidation-Reduction Potential (ORP or E) is indicative of the ratio of the oxidant to the substance that is being oxidized. Thus, the degree of the oxidation/reduction reaction can be monitored by measuring the system ORP value (or E value). Using the ORP measurement has been shown to be applicable to monitoring both chemical and biological reactions. Charpentier *et al.* (1989) used the ORP measurement as a control parameter to optimize the aeration of a pilot-scale plant. They reported a correlation between the ORP value of the aeration tank content and its effluent TKN and NO_3^-. In addition to biological systems, the ORP measurement is also applicable for the chemical oxidation/reduction wastewater process. It has been applied for controlling the breakpoint chlorination for removal of cyanide, treatment of chromium sludge, removal of ammonia nitrogen (Eilbeck, 1984) and treatment of metal finishing wastewater. Chang *et al.* (1994) applied the ORP measurement to simulate the decoloring mechanism of secondary textile effluent and obtained satisfactory results.

The ORP measurement of the dye waste that is being decolored with addition of chemical oxidant can be used as an on-line monitoring of the progress of the chemical reactions and as a control parameter of the oxidant dosage application. Variations of the system ORP and its relationship to other system parameters under different experimental conditions are being studied with the ultimate goal of applying the ORP technique as an on-line monitoring and control of the dye decoloring process. In this paper, the control is based on a proposed modified Nernst equation to relate the ORP measurement to the dosage requirement as well as degree of difficulty (or easiness) of decoloring a wastewater containing selected textile dyes.

EXPERIMENTAL PROCEDURES

Five synthetic basic dyes purchased from Merck Inc: methyl red (MR), malachite green (MG), methyl violet (MV), methylene blue (MB) and methyl orange (MO) were used in this study. The solutions were prepared with an initial concentration of 10 mg/l in aliquot of 2 litres to be used in batch oxidation studies. The experimental apparatus is shown schematically in Fig.1.

The initial solution pH was adjusted to 5, 8 and 10 by addition of NaOH or H_2SO_4, without the use of buffer solution. The reactor was submerged in a water bath to have its temperature controlled constant at 20°C. The ORP and pH signals were sent to a personal computer which was linked to a Schott Titronic T200 automatic titrator. Addition of sodium hypochlorite was controlled by the automatic titrater at a rate of 0.024 mg/l until a pre-selected dose, which calculated based on the ORP value was reached. During the reaction period, 5ml of samples were collected every 2-5 seconds for analyses.

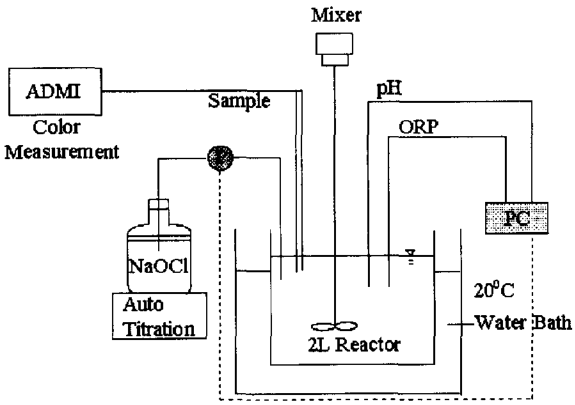

Figure 1. Automatic NaOCl titrator and monitor system of decoloring apparatus.

RESULTS AND DISCUSSION

Figure 2 shows typical variations of the pH, ORP and color of the dye solution undergoing decoloring oxidation studies with sodium hypochlorite. Since the chemical dosage is applied at a constant rate, the concentration of NaOCl in the reactor is linearly proportional to time. The plots indicate that during the initial reaction period, all the measured parameters show rapid changes. An increase of the sample pH and ORP was observed while the measured color was noted to drop drastically. After this initial active reaction period, all the measured parameters level off and vary slowly until the end of the test period. This initial vigorous oxidation may be caused by the reaction of free chlorine. The residue color substance reacts with the remaining combined chlorine after the initial reaction period and the reaction rate is greatly reduced.

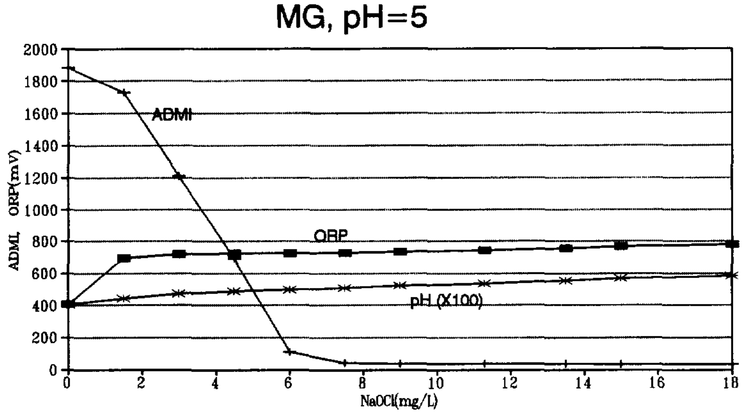

Figure 2. Variations of pH, ADMI, ORP of the dye stuff sample with various dosages of NaOCl.

Models for process control

ORP vs. pH and NaOCl. A typical relationship between ORP vs. pH and NaOCl can be obtained using multiple regression:

$$ORP = a + b\, pH + c \ln[NaOCl] \tag{2}$$

a = intercept.
b = the characteristic parameter of pH.
c = the characteristic parameter of oxidant.

In this equation, the value of "b" relates to the solution pH that is closely related to the chemical oxidation process. If the value of b is negative, a lower pH will cause a relatively higher ORP value. Since higher ORP values are favourable to the oxidation reaction, a negative "b" value in equation (2) causes a lower solution pH and is desirable for promoting the chemical reaction. The model with a negative "b" value is similar to that proposed by Charpentier *et al.* (1989). The coefficient "c" concerns the influence of [NaOCl] on the resulting ORP value. A positive "c" value implies higher ORP values vs. dosage of NaOCl that is favourable for the reaction to occur. The regressional results for all the dyes used in this study are shown in Table 1. During the initial reaction stage, the wastewater containing MG shows a drop in ORP generating a negative c value. With addition of sodium hypochlorite a positive c value is obtained throughout the entire reaction. Based on this model and results shown in Table 1, a lower pH value result in higher redox potential and better decoloring results.

Decoloring Model. The Nernst equation will be used to generalize the oxidation reaction for on-line monitoring and control of the decoloring process. If the ORP value of the wastewater sample prior to addition of NaOCl is taken as the initial electrochemical potential value (E^o) then the term "E" in the Nernst equation represents the ORP value of the sample after addition of chemical oxidant. The ADMI value of the sample after the oxidation reaction is used to indicate the concentration of the dye stuff in its reduced form,

[Red], and the sodium hypochlorite concentration represents the oxidant form, [Oxid], in the equation. Hence, the Nernst equation can be modified to:

$$ORP_0 - ORP = -(RT/nF)\ \ln(ADMI_t/NaOCl) \tag{3}$$

ORP= sample ORP value before addition of NaOCl.
ORP_0= sample ORP value after addition of NaOCl.
$ADMI_t$= sample color after addition of NaOCl.
NaOCl= concentration of NaOCl , mg/l.

The term RT/nF in the above equation is a constant for consistent conditions under which the oxidation study is performed. Thus, the above equation can be re-written in the following form:

$$ORP - ORP_0 = S\ \ln(ADMI_t/NaOCl) \quad \text{and } S = RT/nF \tag{4}$$

The S value represents the dye oxidation potential, i.e., a higher S value represents a faster rate at which the dyestuff is oxidized by oxidant. The modified Nernst equatioen in this paper is similar to that shown the previous work (Chang *et al.*, 1994), in which the term $ADMI_0$ is used as the oxidant part of the Nernst equation. In this paper, the oxidant part is replaced by [NaOCl] to provide a better approach for simulating the overall reaction.

Table 1. Calibrated equations parameters relating ORP, S, and P to other parameters for different dyes

Dye		ORP Model Parameter				S Model Parameter				P Model Parameter			
	pH	a	b	c	r^2	a'	b'	c'	r^2	a''	b''	c''	r^2
Red (MR)	5	1161	-64	71	0.909	-11	13.6	15.7	0.980	3.1	0.28	-1.97	0.994
	8	1413	-96	86	0.996	239	-23	25	0.978	59	-6.3	-0.21	0.985
	10	-6633	707	16	0.831	-1292	129	201	0.78	75	-6.7	-1.21	0.993
Green (MG)	5	315	81	-17	0.971	-482	110	-13	0.96	-10	2.8	-4.5	0.935
	8	752	-22	97	0.983	-527	75	18	0.98	-3.5	1.1	-2.7	0.926
	10	1757	-140	125	0.995	680	-64	20	0.99	25	-7	-2.2	0.948
Violet (MV)	5	683	21	28	0.992	-437	101	-7	0.94	20	-2.8	-1.5	0.960
	8	1916	-168	74	0.878	-478	67	9.4	0.98	-	12.7	-2.7	0.921
	10	12134	-1198	46	0.723	3458	-349	12.9	0.65	54	-6	-1.4	0.972
Orange (MO)	5	-29	141	81	0.886	-395	88	-2.13	0.96	6	-0.11	-2.57	0.953
	8	5447	-568	147	0.961	-59	10	11	0.99	9.5	-0.35	-1.6	0.956
	10	-116	1199	291	0.829	-1841	185	4.36	0.79	21.7	-1.4	-1.1	0.999
Blue (MB)	5	1174	-67	60	0.993	45	2.6	11	0.99	8.8	-0.26	-0.99	0.999
	8	3673	-373	152	0.982	203	-20.9	16.8	0.99	7.9	-0.05	-1.02	1.000
	10	1753	-140	125	0.995	680	-64	20	0.99	2.6	0.48	-1	0.999

The relationship between S vs. pH and NaOCl is shown as:

$$S = a' + b'\ pH + c'\ \ln[NaOCl] \tag{5}$$

The S value in the above equation can be calibrated using the results obtained in laboratory studies for the five dyes (shown in Table 1), and the calculated S values of the five dyestuffs under the various controlled pH conditions are tabulated in Table 2. For the lower pH (=5) case, all dyes show higher S values than those at pH values of 8 and 10. The pH value is observed to affect MG dye the most. The results show that under pH = 10, 8 and 5, the S values for MG are 18.13, 10.5 and -1 respectively. For MB, the pH has least effect among all the standard dyes. Under pH = 10, 8 and 5, the S values of MB are 1.39, 0.8 and 1 respectively. In the low pH range, hydrogen ions combine with the hydroxide ion of dyes thus enhancing the decoloring reaction. In pH=5 case, the dye decolor coefficients (S) for the various dyes are: MG(145), MV(126), MO(126), MR(91) and MB(71). If the S value of MB is assumed to be unit, the dye decoloring capabilities (or S value) for other dyes are shown to be in the following order: MG> MV> MO> MR> MB and with the numerical ratio of 2.04: 1.78: 1.78: 1.28: 1.00.

Table 2. The S values of 5 dyes under various pH conditions

pH	Red(MR)			Violet (MV)			Blue (MB)			Green (MG)			Orange (MO)		
	5	8	10	5	8	10	5	8	10	5	8	10	5	8	10
S Value	91	41	9.4	126	39	19	71	41	51	145	84	-8	126	39	19
S Ratio	9.86	4.36	1	6.63	2.05	1	1.39	0.8	1	18.13	10.5	-1	6.63	2.05	1

Note:*when pH=10, S value is assumed to be 1.0, and S values of pH=5 and 8 are compared to pH=10.

Values of the parameters ORP, ORP_0 and S are related to the dosage of NaOCl. These three parameters can be combined into a single parameter P:

$$P=(ORP-ORP_o)/S, \quad (6)$$

$$P=\ln(ADMI_t/NaOCl), \text{ or}$$
$$ADMI_t=(NaOCl)e^P \quad (7)$$

Since the parameter P is a function of the solution pH and the NaOCl dosage applied, the ADMI value of the treated sample can be related to the oxidant dosage and solution pH as:

$$P = a'' + b'' pH + c'' \ln[NaOCl] \quad (8)$$

Values of a, b and c in this equation are calibrated using the data obtained with the five basic dyes. The results are also shown in Table 1. Laboratory studies to verify the validity of the proposed model equations have been carried out. Using the dye spiked sample, dosages of NaOCl for reducing the color to different pre-selected ADMI values and the expected corresponding ORP values can be calculated using the proposed model equations. These predicted values are then compared to the values actually obtained with laboratory oxidation studies. Additionally, the measured ADMI and ORP values show a high degree of repeatability indicating that the on-line method based on the proposed model equation is a reliable tool for monitoring and control of the decoloring oxidation process .

The proposed model may have several other potential applications for the design and control of the chemical oxidation process to reduce the color from industrial dyestuff effluent. If the ADMI and ORP of a wastewater, the solution pH at which the reaction is intended, and the effluent ADMI value limitation are known, then dosage of NaOCl can be calculated. Once the applied chemical dosage is known, the sample ORP value can be determined and used for on-line monitoring and control of the oxidation process. Further, the time required to complete the oxidation reaction can be calculated. Thus, for a given flow rate, the reactor dimensions can be estimated.

CONCLUSIONS

1. The oxidation decoloring reaction results are modeled using a modified Nernst equation to relate the oxidant dosage requirement for reducing the dye color to a pre-selected ADMI value to the working solution pH, the initial NaOCl concentration, the initial ORP and the final ORP of the dye solution being treated.

2. In the proposed model, a parameter "S" which relates to pH and ORP is used to indicate that the oxidation (decoloring) potential of these dyes are in the following descending order: MG> MV> MO> MR> MB and with the ratio of 2.04: 1.78: 1.78: 1.28: 1.00.

3. For field applications, the proposed model equations can be used to predict the dosage requirement, the end-point of the oxidation reaction and the color removal efficiency of the oxidation process.

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