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APPLICATION OF CHLORINE DIOXIDE (CLO_2) IN CONTROLLING BIOFILM GROWTH OVER HEAT EXCHANGERS: THEORETICAL & EXPERIMENTAL APPROACH

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Abstract - Biofilm refers to an association of microorganisms in which microbial cells adhere to each other on a living or non-living surface within a self-produced matrix of extracellular polymeric substance. It is a topic of major concern in naval, industrial plants as well as drinking water quality. The penalties and costs associated with impaired heat exchanger operations cause great economic loss. The detrimental effects of Biofouling in heat exchangers are reduced heat transfer capability, reduced fluid flow, increased pressure drop and accelerated corrosion. The disinfection of surfaces containing biofilm is difficult since the bacteria within biofilm develop a protection mechanism that leads to an enhanced resistance against commonly used disinfectants. In order to eliminate biofilm contamination, microorganisms within the biofilm must be destroyed and the biofilm structure itself must be removed from surface. The article focuses on how ClO_2 can be used as a biocide for controlling this bio growth over heat exchangers. Chlorine dioxide offers some unique advantages, due to its selectivity, effectiveness over a wide pH range, and speed of kill. Another important aspect studied here is related to the quantification of chlorine dioxide while it is being used as a biocide. It is essential because of the environ- mental constraints pertaining to maximum permissible concentration that can be released into the environment. A mathematical model was developed in order to quantify the amount of chlorine dioxide required depending upon factors such as extent of biofilm growth, pH of operating environment, etc. The basis of this model was the laboratory trials conducted in this aspect.

Keywords - Biofilms, Heat Exchangers, P. Aeruginosa , Chlorine Dioxide , Lagrange Polynomial

I. INTRODUCTION

A biofilm is any group of microorganisms in which cells stick to each other and often these cells adhere to a surface. These adherent cells are frequently embedded within a self-produced matrix of extracellular polymeric sub-stance (EPS). Microbes form a biofilm in response to many factors, which may include cellular recognition of specific or non-specific attachment sites on a surface, nutritional cues, or in some cases, by exposure of plank - tonic cells to sub-inhibitory concentrations of antibiotics.

Biofilm formation is a common problem of heat exchangers (e.g. cooling towers) and water distribution networks. Rapid bio-corrosion takes place on surfaces that are in contact with water. Specifically, in cooling towers, biofilms form an insulation layer, leading to poor heat transfer. Last but not least, biofilms also form a safe haven for pathogens such as legionella, raising severe health risks. Hence millions of dollars are spent looking up for a solution for this biofouling. Currently, chlorine is the most common disinfectant, used for preventionof biofouling in heat exchangers. But it's use has come under scrutiny, due to the adverse impact its use has on the environment. Recently, ClO_2 has come to be used as a much more efficient and environmental friendly alternate. The aim of this paper is to demonstrate the effectiveness of ClO2 in controlling growth of biofilm in heat exchangers and cooling towers, through laboratory experiments and establish a mathematical modelto predict the amount of chlorine dioxide required for removing a given amount ofbiofilm.

II. EXPERIMENTAL STUDIES

2.1. Properties of Bacteria andCulture:

Necessary conditions for choosing bacteria
1. The first basic condition was that the bacteria should be capable to producebiofilms.
2. The second important condition was that the bacteria should thrive under conditions of high temperature and high pressure. This could replicate theconditions in a heatexchanger.

P. aeruginosa is known to follow these properties thus this bacterium was selected. Although we did not perform experiments at conditions of high temperature and pressure, we did give importance to the fact that these conditions are present in equipment's such as heat exchangers and thus we should select bacteria that has the capability to produce biofilms under these conditions. The strain of the bacteria to be used was PA14. This bacterium is also known to be Gram negative as well as possess good conjugation properties. The growth medium was LB broth / MOPS medium with nitrogen and carbon sources. The growth temperature was 37 ℃ and incubation time was 16 to 24 hours.

2.2. Chlorine dioxide as a suitablebiocide:

Traditionally ClO_2 is used as biocide in various industries. However, over the years there was increasing concern over the environmental damage caused due to the usage of chlorine. Thus gradually new biocides such as chlorine dioxide are coming up which apart from having less environmental damage also possess certain advantages.

2.3. Preparation of surface for biofilmformation

The main aim of the project is to form biofilms and then treat it with chlorine dioxide. For this purpose we needed a set of suitable bodies on which the biofilms canbe formed. For this purpose we chose a set of rods made of 'Low carbon steel' and they had to be machined before they can be used for biofilmformation.

Figure 1(a) Initial Stage of rods with rust

Figure 1(b): Final Stage of rods without rust

Figure 1(a) & (b) show two different stages of rod i.e. before machining and after machining.

2.4. Production of ClO_2:

In the experiment procedures a large production rate of chlorine dioxide was not needed, thus instead of a continuous process, a batch process was chosen to produce the chlorine dioxide. ClO_2 was produced by the acidification of sodium chlorite ($NaClO_2$) solution with sulphuric acid(H_2SO_4):

$4NaClO2 + 2H2SO4 ---> 2\ ClO_2 + HCl + HClO3 + 2Na_2SO_4 + H_2O$ [4]

For each set of production of ClO2 of 'ppm' level reac- tants required was found out from 'stoichiometric' calcu- lations. The following amounts were required to produce 40 ppm of ClO_2.

(i) 107.25 mg of sodiumchlorite
(ii) 1 ml of sulphuricacid

2.5. Preparation of bacterialculture

The culture was prepared using 'NB' i.e. nutrient broth. For preparation of culture six flasks having the capacity of 500 mL and three flasks having capacity of 1000 mL were used. The total volume of culture prepared was 3 L(considering the working volume of 50%) . The calculation of the salt was according to the guideline that 13.5 g of the NB should be used for 1000 mL of solution. Each of these flask had to be closed with a cotton plug immediately after preparing the solution. This was followed by autoclaving of the prepared mixtures. For this process steam was used at temperature of 120 ℃. However, in this case inoculation was not done because of the fact that in actual engineering situations very high level of purity is not needed. The total volume of inoculum used was 30 mL for the total culture volume of 3L. Next the culture solution (which contains the inoculum) was 'incubated'at 30 ℃ 'without shaking'. The main reason for putting it without shaking was that we put the rods as along with the solution to allow the growth of biofilm. The culture solu-tion was used immediately. However, f the solutions had to be used later then the cultures could have been stored at 4 ℃. At this temperature the metabolic activity of the bacteria slows down, however when it returns to room temperature the metabolic activity startsagain.

2.6. Biofilmformation

Figure 2: Formation of biofilm on top of solution (reason for turbid nature)

For production of biofilm rods were placed in the solution of just after adding the inoculum to the culture solution. After a period of 24 hours the colour of the solution had changed from 'green' to 'black' , clearly indicating the re- lease of ferrous ions in the solution. Another observation was that the colour of rod had changed also for 'grey' to 'black' indicating the presence of biofilm on it. However, the major amount of biofilm had not adhered to the rod and it had collected on the surface of the solution.

III. DATA COLLECTION & MODEL DEVELOPMENT:

ClO_2 can definitely be used to tackle the problem of biofilm growth. However, the main problem which arises is that how to quantify the amount of ClO_2 required to tackle a particular amount of biofilm growth. For this purpose, a mathematical model was developed using the followingmethodology:

- Selection ofparameters
- Selection of identificationvariable
- Generation ofdata
- Algorithm of themodel
- Environmentalconcerns
- Someresults

3.1. Selection ofParameters:

The system consists of various parameters including:

- Initial biofilmconcentration
- Amount of ClO_2 to beused
- pH of operatingfluid
- Residence time ofoperation

All the above mentioned quantities are the ‘variables of the process’ . Among them the ‘amount of chlorine dioxide’ is the 'output variable' and the rest are 'input variable'. The model would take the inputs and thus generate the required outputs .The output variable means the unknown values and the input variable means all those values which are known.

3.2. Selection of identification variable:

Identification variable basically means a variable to identify the biofilm growth/decay. Many methods can be applied to measure the biofilm concentration and track it’s changes. However, a method was needed which gives a quick estimate of the changes in biofilm growth. Thus 'Optical Density (OD) ' was chosen as the identification variable.

3.3. Generation of Data:

Following procedure was followed in the generation of data:

1. Using sodium hypochlorite and concentrated sulphuric acid prepare ClO_2 solution of a particular concentration.
2. Take already prepared biofilm solution and bring this solution to the desired pH values of7,8,9,10,11.
3. Measure the OD of the biofilm solution.
4. Take a specified amount of biofilm solution (0.5 mL) of any one pH value (say 7) and add a specific amount of prepared ClO_2 solution to it. (0.5mL)
5. After the selected residence time measure the final OD of thesolution.
6. Perform the same steps for all the pHvalues.

3.4. Algorithm of the Model:

3.4.1. Calibration: The following chart was used to convert the values of OD to concentration inmg/L

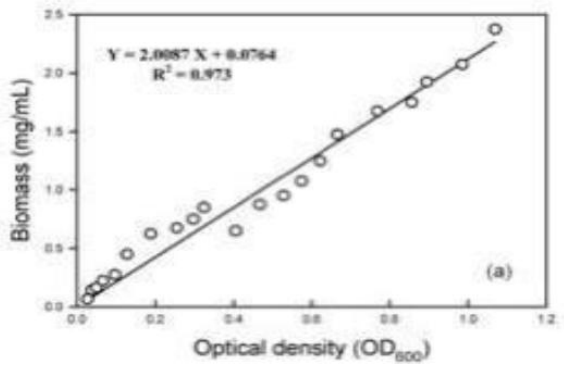

Figure 3: Calibration chart for converting OD values into biomass concentration in mg/L. [3]

All the experimental results were in the form of optical density. We used this chart to convert the values of optical density obtained experimentally to mg/L.

3.4.2. Calculations:-

From this calibration chart we get , The initial weight of biofilm = $W_i = C_i \times V$ is calculated from the calibration chart given in Fig.6

OD_i = Initial optical density of the solution
C_i = Initial concentration of biofilm (mg/L) = $f(OD_i)$
V = volume of the biofilm solution

After adding chlorine dioxide the final weight of biofilm
= $W_f = C_f \times V$, where
OD_f = Final optical density of the solution

C_f= Final concentration of biofilm (mg/L) = $f(OD_f)$
V = volume of the biofilm solution

Therefore $X = W_i - W_f$ = decrease in weight of biofilm

Let 'C' be the concentration of ClO_2 solution prepared and 'V_c' be the volume of ClO_2 added.
Therefore Y = Mass of ClO_2 consumed = $C \times V_c$

3.4.3.Tabulation of Data:- In this model tabulation of

data plays a major role in visualising the inputs and outputs. At each pH value (say 7) we have the data corresponding to the amount of biofilm to be decreased and amount of ClO_2 required. Thus it can be visualisedas follows:-

X = Mass of biofilm to be decreased	Y = Mass of chlorine dioxide required
X1	Y1
X2	Y2
X3	Y3
X4	Y4

Table I: Tabulation of data at a particular pH say pH =7

3.4.5. InterpolatingPolynomial:-

The technique of 'Lagrangian Polynomial' was usedto develop relation between 'X' and 'Y' at all pH values at which the experiments wereperformed:-
Thus at pH = pH1 , Y1 = f(X)
pH = pH2 , Y2 = f(X) and so on.

The Lagrange interpolating polynomial is the polynomial P(X) of 'degree <=(n-1)' that passes through the 'n' points (x_1 , y_1 =f(x_1)) , (x_2, y_2 = f(x_2)) ,...., (x_n, y_n = f(xn)), and is given by:

$$p(x) = L_1(x)y_1 + L_2(x)y_2 + L_3(x)y_3 + \dots L_N(x)y_N$$

$$L_k(x) = \frac{(x-x_1)(x-x_2)\dots(x-x_{k-1})(x-x_{k+1})\dots(x-x_N)}{(x_k-x_1)(x_k-x_2)\dots(x_k-x_{k-1})(x_k-x_{k+1})\dots(x_k-x_N)}$$

[5]

3.5. Final Calculation:-

X = Amount of biofilm to be decreased from an equipment say a heat exchanger.

pH = pH of the operating liquid in the heat exchanger

The value required is how much chlorine dioxide will be required to remove this given amount of biofilm.
Following series of steps will be performed by the model (code in some kind of programming language):

1. Find two pH values (pH1 and pH2) at which the experiments were performed such that pH1 < pH < pH2.
2. Using the value of X the model will calculatethe values Y1 and Y2 , from the generated interpolating polynomials.

Y1 = f1(X) and Y2 = f2(X)

3. Y= amount of chlorine dioxiderequired

Y = (pH - pH1)/(pH2-pH1) * (Y2 - Y1) + Y1
The above expression is obtained using the concept of linear interpolation with the two values of pH (pH1 and pH2) and the two values of amount of chlorine dioxide (Y1 and Y2) at corresponding pH values.

3.6 Environmental Concerns:

Although ClO_2 has some advantages over chlorine in terms of environmental constraints , still there are limits to the exit concentration which can be flowing. In most of the cases this concentration this limit is 200 ppm. The code developed also asks for this limit and hence accordingly varies the volume of chlorine dioxide which would berequired.

IV. RESULTS

Following are some of the graphs showing how the values of 'Amount of biofilm' vary with values of 'Amount of chlorine dioxiderequired'.

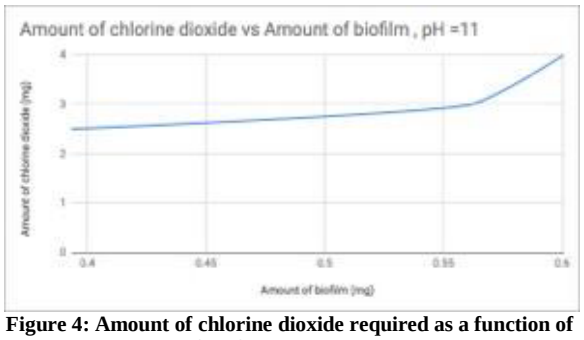

Figure 4: Amount of chlorine dioxide required as a function of amount of biofilm to be removed, pH 11

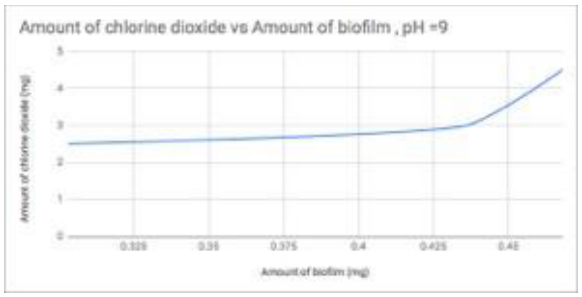

Figure 5: Amount of chlorine dioxide required as a function of amount of biofilm to be removed, pH 9.

V. CONCLUSION

Following conclusions can be drawn on the basis of results from experiments and model:-

- Clearly if the amount of biofilm to be removed increases the amount of chlorine dioxide required is alsoincreasing.
- At both the pH values we see that there is a sudden jump observed in the graph. It is expected that as the biofilm amount keeps on increasing, more sudden jumps can beencountered.
- In the model Lagrange Polynomial has been used as the interpolatingpolynomial.Different interpolating polynomials can be used, depending upon the accuracy with which the model predicts the chlorine dioxide required.
- In the final step of calculation linear interpolation is used whenever pH values other than the standard ones are encountered. This can again be replaced by other techniques in other situations like the experimenter is already aware that the pH of the solution is in close proximity to a

particular standard pH value used in the model.

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