

# Measurement of Interfacial Area in A Bubble Column Reactor by Chemical Method

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**Abstract:-** The interfacial area is an important parameter needed in the calculations for design and operation of gas-liquid reactors. An experimentally convenient method of determining this parameter is indirect evaluation from the absorption rates of a suitable model reaction. The most suitable model reaction is the oxidation of sodium sulphite solution catalyzed by the cobalt sulphate. In the present study, interfacial area between the gas and liquid phase was determined for a vertical bubble column reactor (BCR) having 50 cm in height and 4 cm (i.d.) in diameter by varying pH of the absorbent solution, absorption time, concentration of cobalt sulphate (catalyst) and concentration of sodium sulphite (absorbent). In this study, the initial & final concentration of the sodium sulphite during absorption was determined by using standard iodometric method. The results showed that the average value of interfacial area for a vertical BCR was found in the range of 25 to 30 cm<sup>2</sup>.

**Keywords:** Bubble column reactor (BCR); interfacial area; sodium sulphite; absorption; rate of absorption.

## 1. INTRODUCTION

From the last few decades, enough emphasis is giving to effect of simultaneous chemical reaction on the rate of gas absorption. This is due to the increasing number of industrial applications in which gas absorption rate is appreciably affected by a simultaneous chemical reaction. Gas-liquid bubble columns are extensively used in the chemical industry. It is well known that bubble column reactors have a wide range of applications such as absorption, coal gasification, catalytic slurry reactions, and bioreactions etc<sup>1</sup>. These are preferred because of simplicity of operation, low operating costs and ease with which liquid residence time can be varied. In its simplest form, bubble column reactor (BCR) is a vertical cylinder, in which the gas enters at the bottom through a gas distributor are brought into contact and react with the liquid phase having a component dissolved or suspended in it. The liquid phase may be supplied in batch form (or) it may move with (or) against the flow of the gas phase. Interfacial area is one of the most important parameters for gas-liquid reactor design. Interfacial area is a necessary parameter in determining reactor output, particularly in the region, in which absorption is accompanied by fast chemical reaction. In general, gas-liquid interfacial area is a function of the unit's geometric size, operating parameters, and the physical and chemical properties of the specific substances constituting the system.

In general, experimentally convenient method for determining interfacial area in bubble columns can be divided into two groups - physical and chemical. Physical methods are characterized by the processes based on  $d_s$  (Sauter mean bubble diameter) determination & based on bubble size distribution. Most physical methods are optical in nature and can be used to determine the interfacial area directly. Optical methods are based on the direct measurement of the reflection, refraction, or diffraction, of monochromatic light on the actual bubble surface. The light flux reflected, refracted or penetrating through the gas-liquid interface is measured. Physical method gives local values of interfacial area and whereas, the mean interfacial area over a part or whole reactor volume could be assessed by using chemical method. Interfacial areas determined from the physical and chemical methods may differ significantly<sup>2-4</sup>. The significant advantages of the chemical method are: economy for large-scale equipment, lack of toxicity, fire safety, etc.

One of the few reactions suitable for estimation of interfacial area in gas-liquid systems is oxidation of aqueous sodium sulphite solutions in the presence of cobalt sulphate as a catalyst. This reaction is often been used for determination of the interfacial area between gas and liquid in various absorption devices like mechanically agitated contactors, packed columns and bubble columns, and also for evaluating the performance of aerobic fermentors. The rate of reaction of sulphite to sulphate is used as a measure of the efficiency of oxygen transfer to the liquid phase in all the situations.

### 1.1. THEORY

In the present study, experimental results were interpreted in terms of relations derived from the theory of absorption accompanied by a (m, n)-order reaction (Here m and n are the orders with respect to oxygen and sulphite, respectively). The experimental conditions were chosen so as to carry out measurements in the region where the oxygen absorption rate is a

function of the kinetic parameters of the reaction only, and is independent of the kinematics of the liquid flow in the equipment. In principle, this may be achieved in two situations:

1. If the rate of the accompanying reaction is so slow and the interfacial transport of oxygen reacts until it reaches the bulk of the liquid phase, and
2. When the reaction is fast enough for all absorbed oxygen to react in the bulk of the liquid film near the interface.

The strong catalytic effect of the catalysts in use practically precludes the first approach. Hence, in the present study, experiments were carried out according to the second proposition, where the absorbed oxygen reacts in the bulk of the liquid film (fast-reaction regime). If the reaction between gas (oxygen) and liquid (sodium sulphite solution) are fast and irreversible, in comparison with mass transfer, then the absorption rate is given by the relation



and the kinetics of the reaction is as follows:

$$r_A = k_{m,n} C_A^m C_B^n \quad \text{----- (2)}$$

From the absorption-reaction theory, absorption rate can be expressed as

$$\text{Absorption rate per unit area, } R_a = C_A^* (2D_A k_{m,n} C_A^{m-1} C_B^n / (m+1))^{0.5} \quad \text{----- (3)}$$

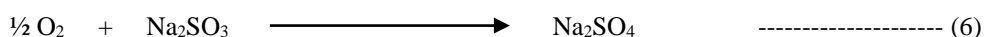
If B is not much more depleted at the interfacial area than in the bulk, then the reaction is of the pseudo-m<sup>th</sup> order. Then,

$$k_m = k_{m,n} C_{B0}^n \quad \text{----- (4)}$$

and it follows from equation (1) that

$$R_a = C_A^* (2D_A k_m C_A^{m-1} / (m+1))^{0.5} \quad \text{----- (5)}$$

In this study, Oxygen reacts with sodium sulphite to give sulphate according to equation as follows:



Then, the rate of absorption per unit area was given as

$$R_a = C_{O_2}^* (2D_{O_2} k_2 C_{O_2}^* / (2+1))^{0.5} \quad \text{----- (7)}$$

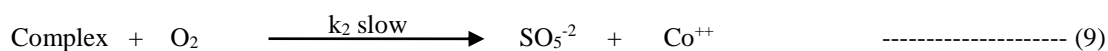
Where,

$C_{O_2}^*$  = Interfacial oxygen concentration, gmole/lit

$D_{O_2}$  = Diffusivity of oxygen in sodium sulphite solution, cm<sup>2</sup>/sec

### 1.1.1. REACTION MECHANISM

For the reaction of sulphite ion with cobaltous ion as a catalyst, a mechanism could be followed as below



In the present study, the formation of a cobalt complex in solutions of sodium sulphite was found from ultra-violet spectra. Since the concentration of the complex is small in this study, the steady state assumption can be applied. Then,

$$\frac{d(\text{complex})}{dt} = 0 \quad \text{----- (11)}$$

$$k_1 [\text{Co}^{++}] [\text{SO}_3^{-2}] - k_{-1} [\text{complex}] - k_2 [\text{complex}] [\text{O}_2] = 0 \quad \text{----- (12)}$$

If  $[\text{Co}^{++}]_0$  is the initial concentration of cobalt sulphate, it follows that

$$[\text{Co}^{++}] = [\text{Co}^{++}]_0 - [\text{complex}] \quad \text{----- (13)}$$

and therefore

$$[\text{complex}] = \{k_1 [\text{Co}^{++}]_0 [\text{SO}_3^{--}]\} / \{k_1 [\text{SO}_3^{--}] + k_{-1} + k_2 [\text{O}_2]\} \quad \text{----- (14)}$$

This leads to the expression for the rate of reaction of oxygen

$$- [d(\text{O}_2)] / dt = \{k_1 k_2 [\text{Co}^{++}]_0 [\text{SO}_3^{--}] [\text{O}_2]\} / \{k_1 [\text{SO}_3^{--}] + k_{-1} + k_2 [\text{O}_2]\} \quad \text{----- (15)}$$

where  $[\text{Co}^{++}]_0$  is the initial cobaltous concentration. If the reverse reaction of reaction 1 is fast (i.e., equation 8) & but reaction 2 (i.e., equation 9) is slow, then the reverse reaction establishes a concentration of complex very near the equilibrium concentration. Subsequently, the slow reaction 2 (i.e., equation 9) having little effect on the equilibrium. Consequently,  $k_2 [\text{O}_2] \ll k_{-1} \sim k_1 [\text{SO}_3^{--}]$  and the rate equation (rate of absorption per unit volume,  $R_v$ ) becomes

$$\text{Rate of absorption per unit volume, } R_v = - [d(\text{O}_2)/dt] = \{k_1 k_2 [\text{Co}^{++}]_0 [\text{SO}_3^{--}] [\text{O}_2]\} / \{k_1 [\text{SO}_3^{--}] + k_{-1}\} \quad \text{---- (16)}$$

Interfacial area can be expressed in terms of  $R_a$  (Rate of absorption unit area) and  $R_v$  (Rate of absorption per unit volume) as follows:

$$\text{Interfacial area} = a = R_v / R_a \quad \text{----- (17)}$$

## 2. MATERIALS AND METHOD

In the present study, sodium sulphite solution (absorbent) was prepared by dissolving the required quantity of sodium sulphite (AR Grade) in distilled water as per the requirement of the experimental studies. A known quantity of the catalyst (cobalt sulphate) was added to confer the required catalyst concentration in the sodium sulphite solution. The pH of the solution was adjusted in accordance with the respective scheme of experimental studies in range of 7.5 to 9 by the addition of dilute sulphuric acid. In this study, initially, gas (air) from the air compressor at a fixed & stable feed rate was passed through the moisture trapper (in which silica gel as an adsorbent) followed by pressure gauge & orifice meter, and finally to the bottom of the single stage perspex bubble column reactor. The aspect ratio (L/D) of the BCR was 10. The number of perforations of BCR were 21 with 1.5 mm in hole diameter & 3 mm of space between the holes. In all the experiments, 400 ml of solution was taken into the column. The solution was allowed to absorb the oxygen from the inlet gas. The final gas outlet (after absorption) was connected to a bent tube dipped in a beaker of water acting as bubbler and it also facilitates the column being maintained at a pressure very close to the atmospheric pressure. After absorption, the samples from the top, middle, and bottom portions of the bubble column were collected. The samples before and after absorption were analysed for unoxidised sulphite ion concentration in the solution using standard iodometric method<sup>5,6</sup>. This procedure was repeated for different time of absorption, pH, concentration of catalyst and the concentration of absorbent. The detailed process flow diagram followed in the present study was clearly shown in the Figure 1 below.

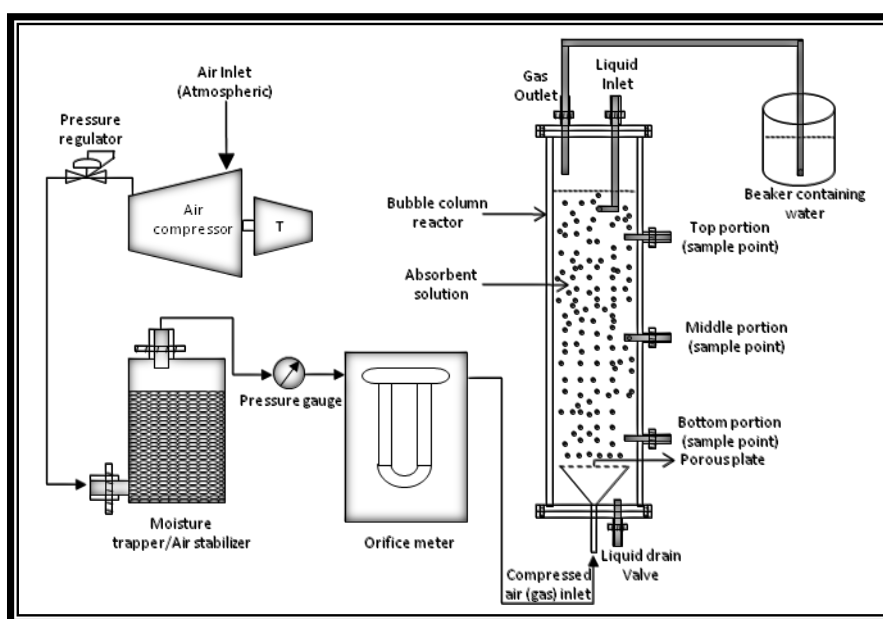


Fig. 1: Process flow diagram

### 3. RESULTS AND DISCUSSION

The knowledge of the interfacial area, “a” is important parameter needed in the calculations for design and operation of gas-liquid reactors. Though physical methods namely, light scattering, light reflection, and photographic techniques etc. were well established for estimation of “a” but due to inherent disadvantages namely requirement of highly sensitive and costly equipments, enormous work & time for estimation, etc. makes physical methods incompetent. So, an experimentally convenient method of determining this parameter is indirect evaluation from the absorption rates of a suitable model reaction. With regard to the various requirements put on such reaction, the choice becomes rather limited. The most suitable and common model reaction is the oxidation of sodium sulphite solutions catalyzed by the cobalt sulphate. The major reasons for selecting this system in preference to the other systems are (i) Chemicals used in the study were easily available and cheap; (ii) The analytical method (iodometric titration), for determination of absorption rate based on decrease of sulphite concentration during the experiment is simple and sufficiently accurate; (iii) Gas phase resistance is low enough, so we can use air instead of pure oxygen. Therefore, the system is attractive for use in apparatuses of technical size; (iv) It is not necessary to remove large quantity of the heat evolved by the reaction to maintain the isothermal conditions; (v) The changes in oxygen concentration of the gas phase, in absorption devices, are lower in the case of diluted oxygen absorption. Consequently, the error in the estimation of an average driving force for the absorption process is not so large; (vi) The choice of a proper concentration of cobalt catalyst and pH value of the solution, makes it possible to change the rate constant of the reaction over a wide range, so that the system can be used for the determination of both aeration efficiency of absorption equipment and the determination of the interfacial area of gas dispersion by the chemical method, etc.

In the present study, a batch bubble column reactor, into which air at a fixed flow rate was sent into the vertical column, was used for the determination of interfacial area between the gas and liquid phases. The initial concentration of the sodium sulphite and final concentration of sodium sulphite after absorption were determined by using iodometric method. In the present study, a series of experiments were conducted for the measurement of interfacial area in selected ranges at: different pH of the solutions, different times of absorption, different concentrations of cobalt sulphate (catalyst) and different concentrations of sodium sulphite (reactant). In all the cases, the samples were collected from 3 different portions (top, middle and bottom).

#### 3.1. Effect of pH of the absorbent (sodium sulphite) Solution

Initially, the experiments were conducted for pH below 7.5 of absorbent solution (sodium sulphite). It was observed that large amounts of sulphuric acid is needed to lower the pH further and therefore influence of impurities in the sulphite solution becomes considerable. On the other hand, from the literature reports at pH>9 of sodium sulphite solution, low catalyst concentration is preferred and this causes precipitation. So, both cases were not suitable for the present studies. Therefore, the optimum range of the pH of the solution to be taken for the present studies was fixed in the range of 7.5 to 9. So, the influence of pH of the solution on the absorption rate in the present study was studied in the range  $7.5 < \text{pH} < 9$ . From the results, it was found that absorption rate dependence upon the pH of solution was very steep. This dependence was linear in the region of pH values from 7.5 to 9 and was shown clearly in Fig. 2 and 4. The absorption rates increases with increasing in the pH of the solution and also the interfacial area goes on decreases with increasing the height of the column. The results also shows that the absorption rates linearly increases with increasing in the pH of the solution and it was clearly shown in the Fig. 2, 3, 4 and 5. On comparing the results at sodium sulphite concentration = 0.4 M (Fig. 2 & 4) and 0.5 M (Fig. 4 & 5), absorption rates and interfacial areas were higher in 0.4 M case. On an average, the interfacial area of the BCR based on the pH studies is taken to be  $24$  to  $27 \text{ cm}^{-1}$  at bottom portion,  $23$  to  $26 \text{ cm}^{-1}$  at middle portion and  $22$  to  $25 \text{ cm}^{-1}$  at top portion.

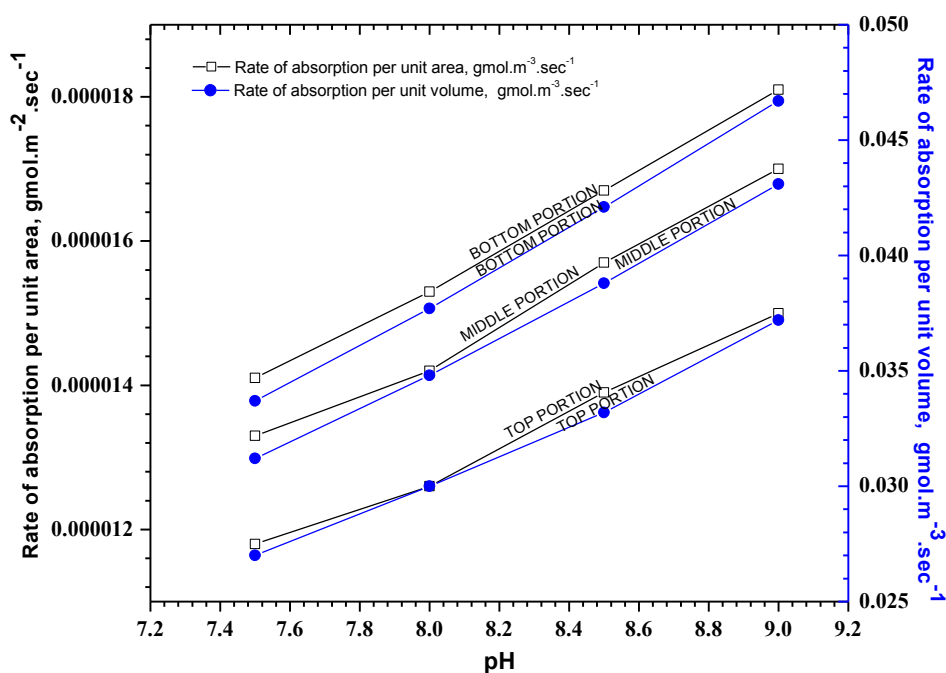


Fig. 2: Profile of pH Vs. Rate of absorption per unit area and Rate of absorption per unit volume

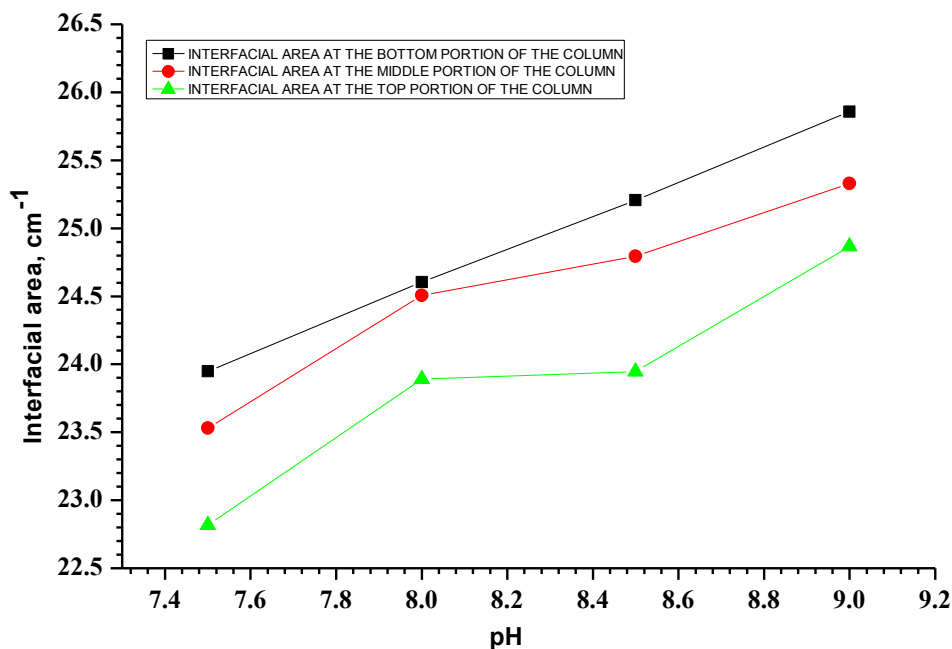


Fig. 3: Profile of pH Vs. Interfacial area

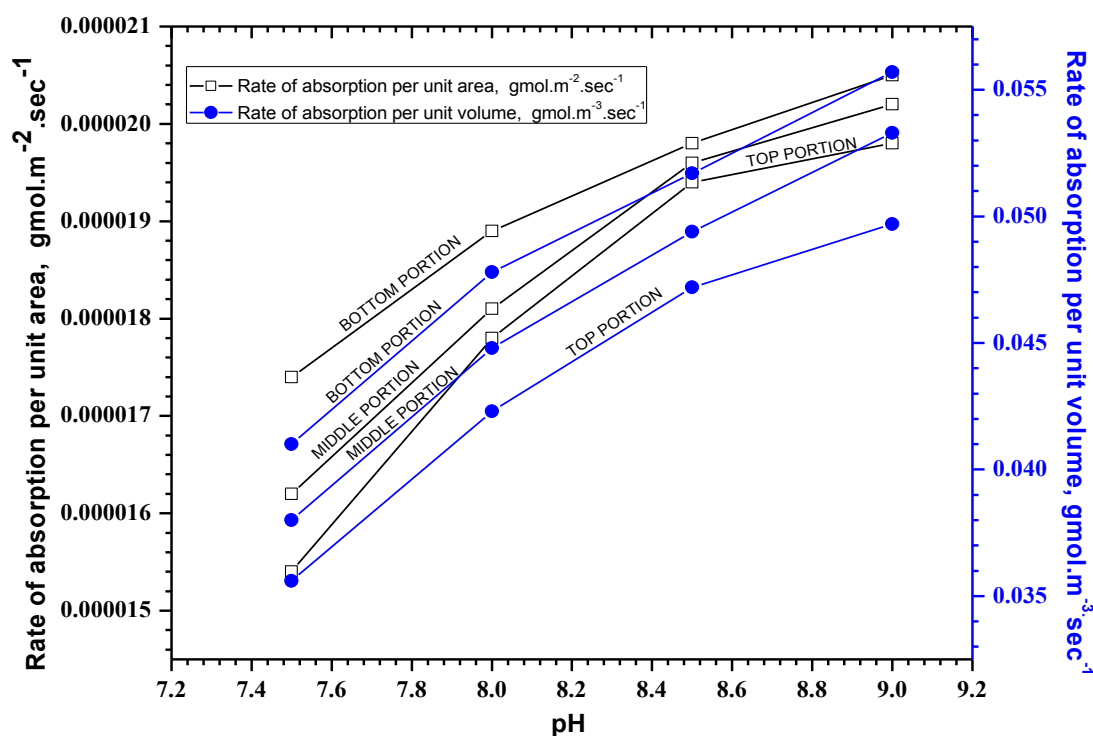


Fig. 4: Profile of pH Vs. Rate of absorption per unit area & Rate of absorption per unit volume

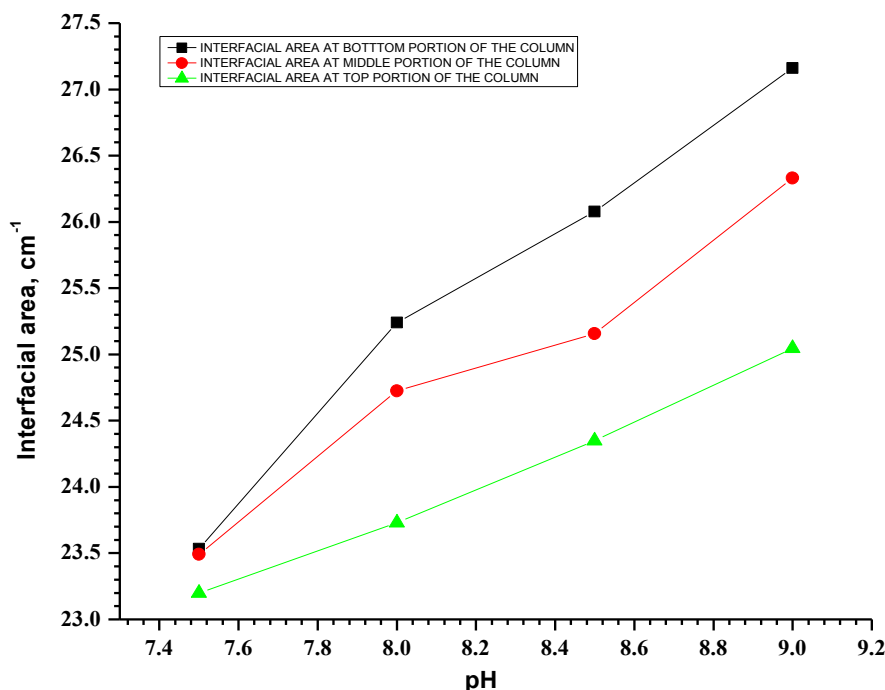


Fig. 5: Profile of pH Vs. Interfacial area

### 3.2. Effect of time of absorption

In present study, it was observed that absorption rate of oxygen was influenced by the time of absorption for 5, 7, 10 and 12 min. at different concentrations of sodium sulphite (0.4M & 0.5M), concentration of cobalt sulphate =  $5 \times 10^{-5}$  M, pH = 8 and  $T = 30^\circ\text{C}$ . The experimental results show that the absorption rates increases as the time of absorption increases and it is clearly shown in Fig. 6 and 8. The results also prove that the absorption rates were found to be higher in the case 0.4M of

concentration of sodium sulphite. The maximum values of absorption rates and interfacial area were found at 0.4M concentration of sodium sulphite and time of absorption is 12 min. The average interfacial area at bottom portion, middle portion and top portion by this study was found to be 24 to 26  $\text{cm}^{-1}$ .

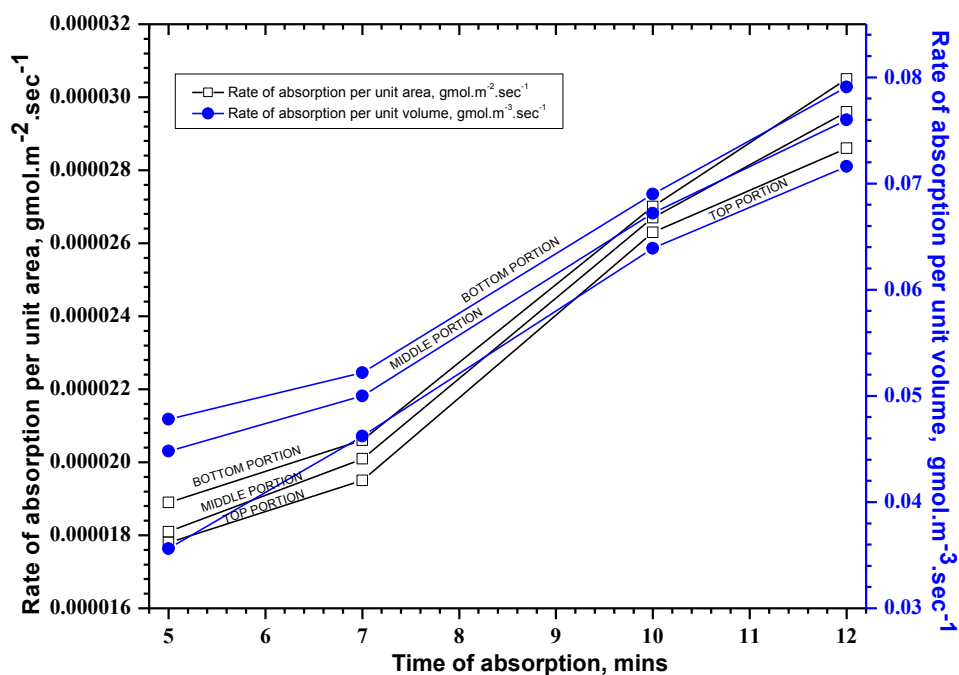


Fig. 6: Profile of Time of absorption Vs. Rate of absorption per unit area & Rate of absorption per unit volume

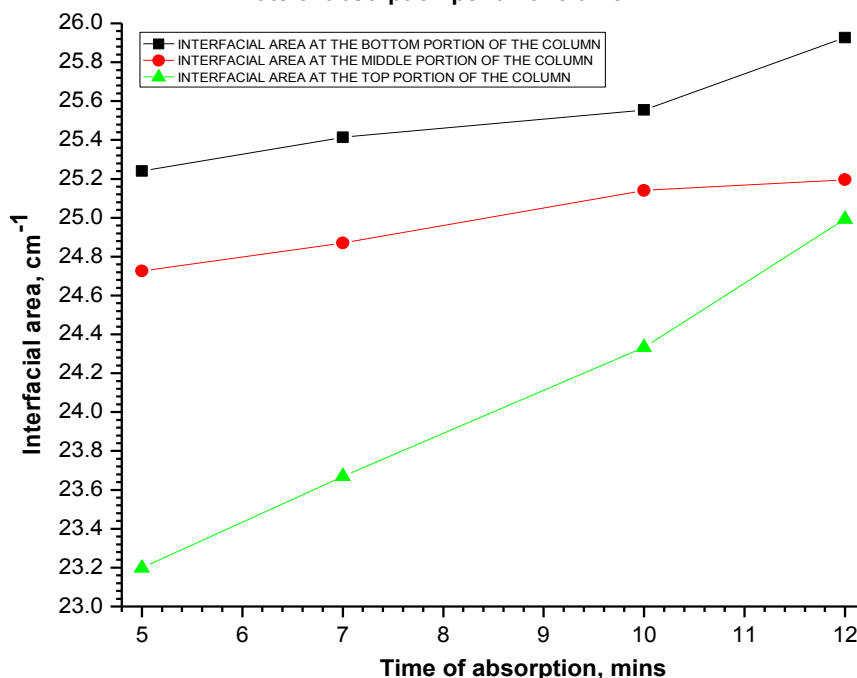


Fig. 7: Profile of Time of absorption Vs. Interfacial area

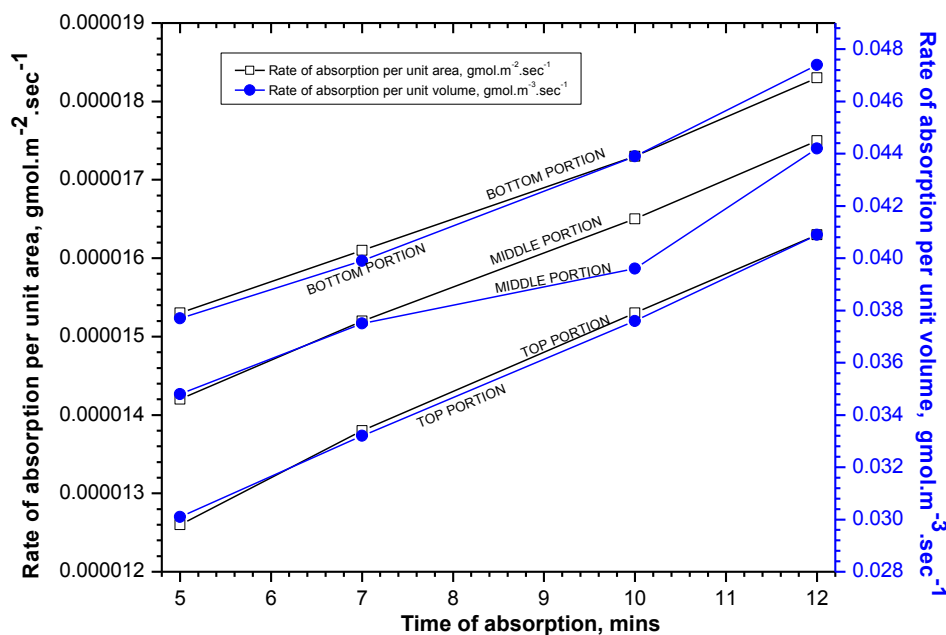


Fig. 8: Profile of Time of absorption Vs. Rate of absorption per unit area & Rate of absorption per unit volume

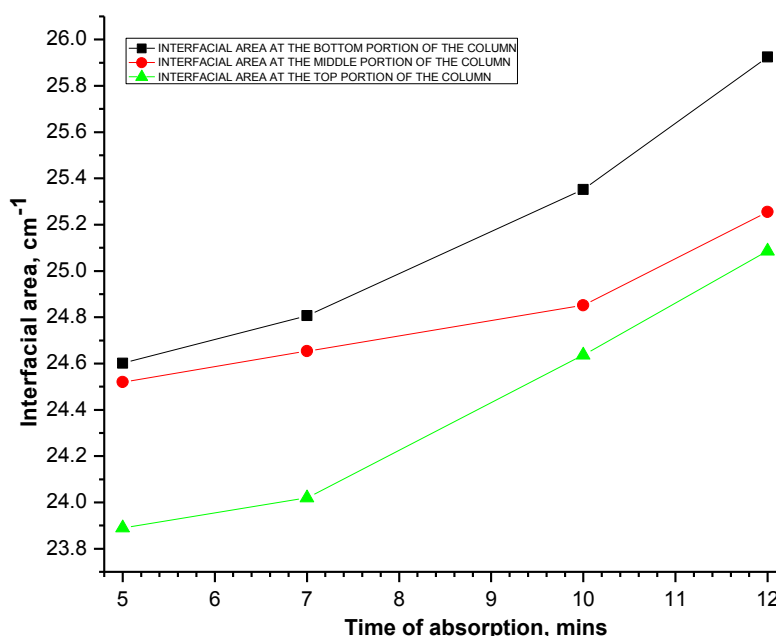


Fig. 9: Profile of Time of absorption Vs. Interfacial area

### 3.3. Effect of concentration of catalyst (cobalt sulphate)

Initially, the experiments were conducted at high cobalt sulphate concentrations ( $> 10^{-4}$  M). It was found that at high cobalt sulphate concentration, a brown colour precipitate is formed and that a black oily film floated on the top of the solution. On the other hand, at lower concentrations ( $< 10^{-6}$  M), it was observed that the solution becomes turbid and green coloured during oxidation. So, the influence of cobalt sulphate concentration (catalyst) on the rate of absorption in the present study was restricted in the selected range of  $10^{-6}$  to  $10^{-4}$  M, at specific values of sodium sulphite concentration, keeping the pH and the temperature of the solution constant (at  $C_{Na_2SO_3} = 0.4$  M, pH = 8 and Temperature =  $30^\circ\text{C}$ ). The results show that the absorption



rates goes on increasing with increasing concentration of cobalt sulphate and it was clearly in Fig. 10 and 11. The maximum values of absorption rates and interfacial area were found at  $4 \times 10^{-4}$  M concentration of cobalt sulphate. From the study of effect of cobalt sulphate, the average interfacial area is taken to be  $30 \text{ cm}^{-1}$ .

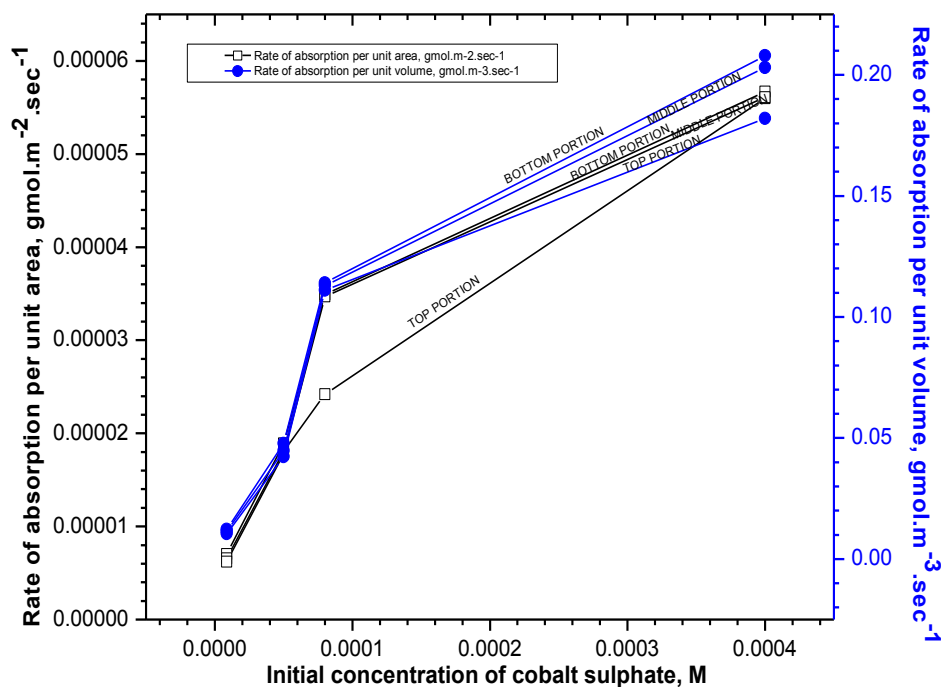


Fig. 10: Profile of initial concentration of cobalt sulphate Vs. Rate of absorption per unit area & Rate of absorption per unit volume

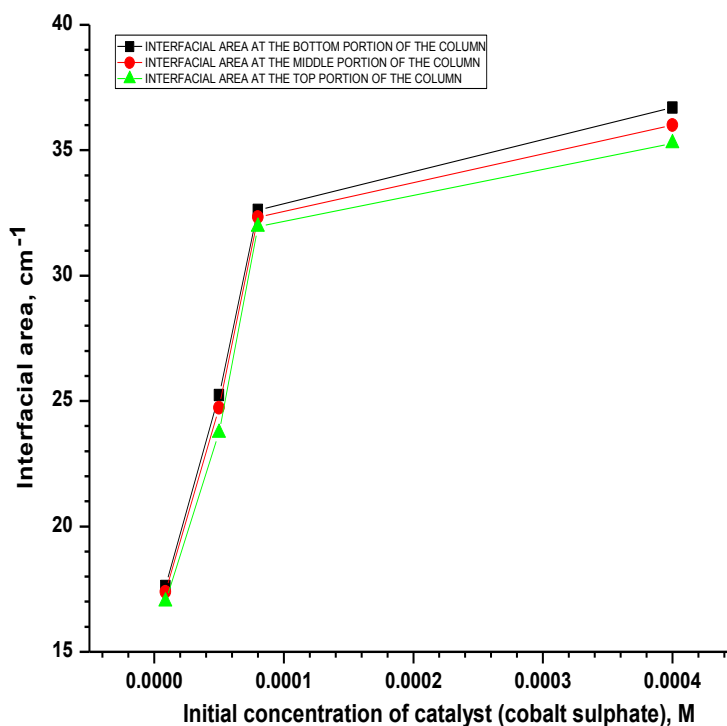


Fig. 11: Profile of initial concentration of catalyst (cobalt sulphate) Vs. Interfacial area

### 3.4. Effect of concentration of absorbent solution (sodium sulphite)

The influence of sodium sulphite concentration on the rate of absorption in the present study was studied in the range of 0.1 to 0.8 M, at specific values of catalyst concentration, keeping the pH & temperature of the solution constant (at  $C_{CoSO_4} = 5 \times 10^{-5}$  M, pH = 8 and Temperature =  $30^{\circ}\text{C}$ ). Variation in the concentration of sodium sulphite solution has a marked effect on the absorption rates. Results show that the absorption rates increases with increasing the concentration of sodium sulphite solution from 0.1 to 0.4 M and then decreases with increasing the concentration of sodium sulphite solution up to 0.8 M and it was clearly shown in Fig. 12 and 13. The maximum values of interfacial area and absorption rates were obtained at 0.4 M concentration of sodium sulphite. On an average, the interfacial area, based on the effect of concentration of sodium sulphite study is taken to be 22 to 25  $\text{cm}^{-1}$  at bottom portion, 21 to 24  $\text{cm}^{-1}$  at middle portion and 21 to 23  $\text{cm}^{-1}$  at top portion.

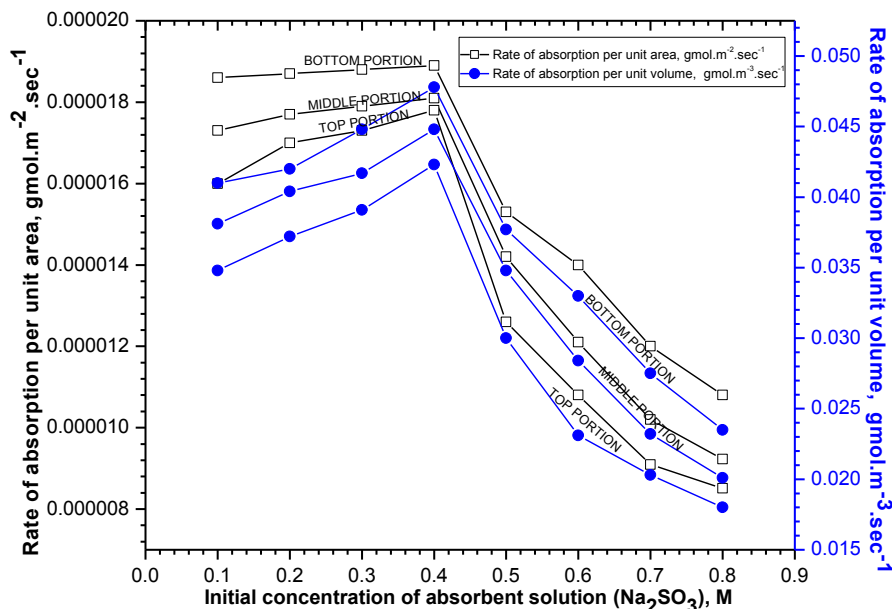


Fig. 12: Profile of initial concentration of absorbent solution ( $\text{Na}_2\text{SO}_3$ ) Vs. Rate of absorption per unit area & Rate of absorption unit volume

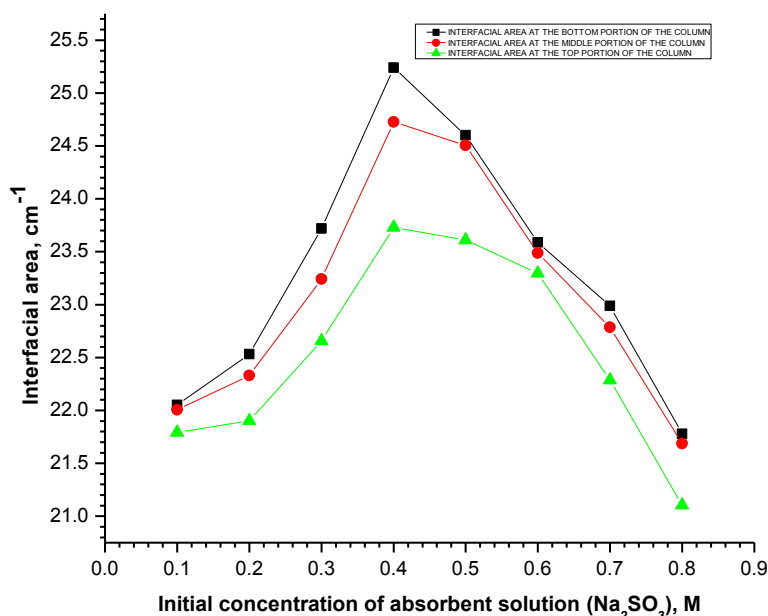


Fig. 13: Profile of initial concentration of absorbent solution ( $\text{Na}_2\text{SO}_3$ ) Vs. Interfacial area

#### 4. CONCLUSIONS

From this study, it was found that the average value of interfacial area is 25 to 30 cm<sup>-1</sup>. It was found that the effect of pH of the solution, time of absorption, concentration of sodium sulphite and concentration of catalyst plays a vital role on interfacial area. The average deviation in the calculation of interfacial area by this sulphite oxidation method in the present study was about 15% and which is in agreement with the literature<sup>7</sup>. Based on this study, it can be mentioned that the effects of the various parameters are indicative of the trends. The present study is evident that the chemical method (though indirect method), can be used for the determination of the interfacial area of investigative type equipments within the observed uncertainties.

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