Removal of Sulphur Dioxide by Ferric Oxide In Packed Bed And Analyze Break Through Curves And Mass Transfer Zone

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Abstract

Adsorption is regarded to be the practicable separation method for purification or bulk separation in newly developed material production process. In the present study Metal Oxides were used in the removal of Sulphur Dioxide (SO_2) by adsorption. The adsorbent used was Ferric Oxide (Fe_2O_3) and it was prepared by thermal decomposition process. Amount of Sulphur Dioxide gas produced was analyzed titrimetically. The adsorbent (Fe_2O_3) produced was analyzed for purity and characterized using X-ray diffraction and Atomic Absorption Spectroscopy to determine the properties. Adsorption of sulphur dioxide (SO_2) onto the ferric oxide in a packed bed under various operating conditions was studied. Breakthrough curves for SO_2 under various adsorption conditions were obtained and some characteristic parameters such as breakthrough time $T_{0.05}$ exhaustion time $T_{0.95}$ length of mass transfer zone L_{MTZ} and adsorption rate constant K were derived from these breakthrough curves.

Key words: adorbate, adsorbent, adsorption process, sulphur dioxide removal

1. INTRODUCTION

Sulphur dioxide is a gas with a nasty, pungent sulfur smell. It is soluble in water, and has potent antimicrobial properties. Huge quantities of poisonous Sulphur Dioxide (SO_2) gasses are formed by the combustion of fuels such as coal, oil and natural gas in power plants, factories and homes. As a consequence, SO_2 is a major pollutant and its removal from combustion gases is of great importance. The need to control SO_2, emission from fossil fuel power plants has lead to the development of commercially proven adsorption technologies, best known method being selective catalytic reduction adsorption. This high surface area typically results in a higher adsorption capacity which is usually defined as the pounds of adsorbate that can be adsorbed per pound of adsorbent. Here we have selected Ferric Oxide as an adsorbent. It is a polar type adsorbent. The ferric oxide cost is lesser than the other adsorbents. Kent S et al (2008) studied Adsorption. The journal Adsorption provides authoritative information on adsorption and allied fields to scientists, engineers, and technologies. Coverage includes fundamental and practical aspects of adsorption.Wei Shao et al (2009) studied Adsorption of CO_2 and N_2 on synthesized NaY zeolite at high temperatures, NaY zeolite particles with a high surface area of 723 m^2/g were synthesized by a hydrothermal method. It was found that the adsorption isotherm of CO_2 on the synthesized zeolite is higher than that on other porous media reported in the literature Shakhapure et al (2005) studied uses of a-Fe_2O_3 and fly ash as solid adsorbents. Solid adsorbents have shown great promise for control of particulate and non-particulate matter and as gas sensing devices in recent times. These studies are characterized by employing solid state and solution studies. Kaixi et al (1985) studied influence of water vapor on the adsorption of SO_2 on activated carbon fiber (ACF). The Activated carbon materials have been used commercially to remove SO_2 from coal combustion flue gases. Recent studies have showed that ACF may have potential in that application due to their adsorption capacity.T A Steriotis et al (1997) studied A novel experimental technique for the measurement of the single-phase gas relative permeability of porous solids. A novel design of a single-phase item of equipment, capable of providing satisfactory relative permeability data at low relative equilibrium pressures, was presented. T. T. Suchecki et al (2004) studied fly ash Zeolites as Sulfur Dioxide adsorbents. Air protection technologies generate massive amounts of solid wastes, including fly ash (FA). Zeolites synthesis from FA seems to be an effective method for FA utilization. In addition, Fly Ash Zeolites (FAZs) could be used for sulfur dioxide (SO_2) adsorption.

2. MATERIALS AND METHODS

Ferrous sulphate, Sodium Carbonate, Sodium Sulfite, Hydrogen Peroxide, Sodium Hydroxide, Hydrochloric acid and Methyl Red used in this study are obtained from SRL (Mumbai). The experiments were conducted in three parts Preparation of adsorbent, Preparation of adsorbate and Analysis of adsorbate.

2.1Preparation of Adsorbate

The experimental procedure performed for adsorbate preparation based on a weighed quantity of Sodium Sulfite salt was taken in one conical flask. The conical flask mouth was closed with rubber cork, which has two openings in it. Through one of the opening, diluted Hydrochloric acid introduced into the conical flask and the other opening is fitted with a tube and leads into another flask, which contains Hydrogen Peroxide solution (6%). The Hydrochloric acid reacts with Sodium Sulfite and the produces Sulfur Dioxide gas. The produced SO_2 gas was sent to another conical flask through a tube. Hydrogen Peroxide (H_2O_2) solution absorbs the Sulphur Dioxide gas at 79^{o}C and thus solution is converted to sulphuric acid. The produced sulphuric acid content was sent to Sulphur Dioxide gas analysis section.

2.2 Preparation of Adsorbent

Ferrous sulphate stock solution (0.9M) was prepared by dissolving a weighed quantity of the Ferrous Sulphate in distilled water. An aliquot of the stock was diluted and hot (70oC) Sodium Carbonate (0.50 M) solution was added as a thin stream with constant stirring until the pH reaches 9.5. The precipitated Ferrous Carbonate was filtered and washed with warm distilled water to remove the excess alkali and Sodium Sulphate. The wet precipitate was transferred to a silica crucible and calcined using a muffle furnace. Three different heating rates viz., 2, 5 and 10^{o}C per min were used up to a temperature of 500^{o}C. In each case, the calcined iron oxide powder was washed thoroughly with hot water and dried at 110^{o}C for 6 h. This experimental procedure performed for adsorbent preparation in Fig 2.

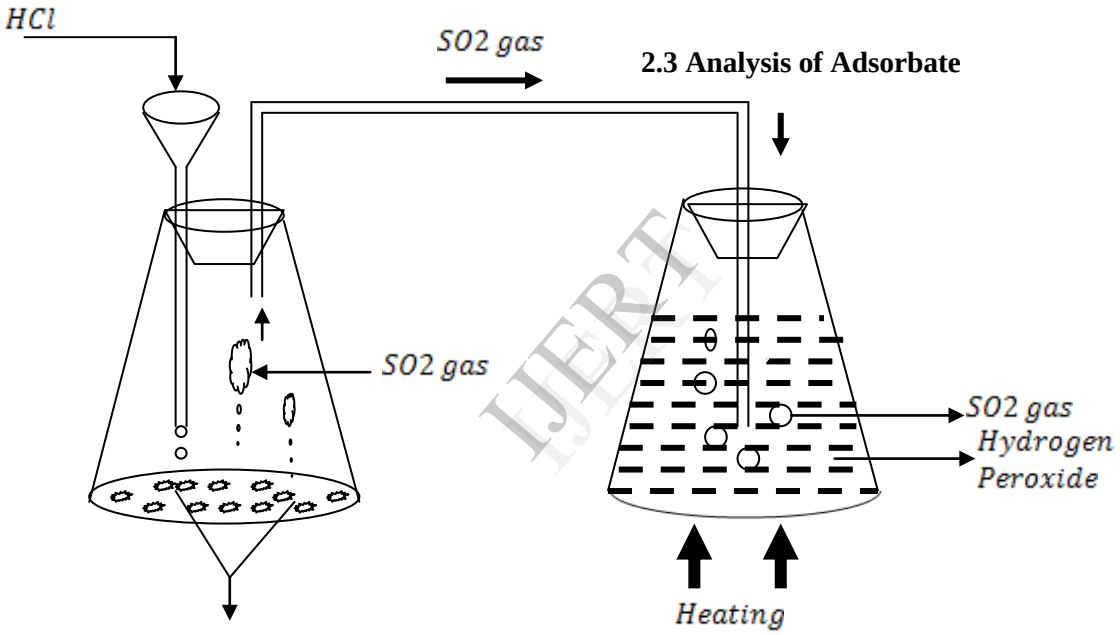

Fig. 1: Preparation of Adsorbate

2.3 Analysis of Adsorbate

The produced Sulphur Dioxide gas was determined by using acid-base titration. Sodium Hydroxide solution (0.5N) was prepared by known quantity of Sodium Hydroxide pellets, which was added into 100 ml distilled water. Methyl red indicator solution was added into the produced Sulphuric acid which is colorless solution becomes light pink color. The pink color solution was titrated with Sodium Hydroxide solution. The produced Sulphuric acid acts as an acid and Sodium Hydroxide solution acts as a base. The end point of titration was disappearance of pink color. From this titration we came to know the normality of produced Sulphuric acid

$$\text{Normality of produced } H_2SO_4 = \frac{NaOH\ Volume\ consumed \times Normality\ of\ NaoH}{Volume\ of\ H_2SO_4\ Solution} \quad (1)$$

The quantity of produced Sulphur Dioxide gas was calculated from the normality. The sequence of calculation to find out the quantity of Sulphur Dioxide presented in the solution is given below.

Volume of H_2SO_4 present in the solution (V_1, ml) = Normality of solution * Volume of solution

Weight of H_2SO_4 present in the solution (W_1, g) = V1 * Specific gravity of solution

$$SO_2 \text{ present in the acid} = \frac{Molecular\ Weight\ of\ SO_2 \times W1}{Molecular\ weight\ of\ H_2SO_4} \quad (2)$$

2.4 X-Ray Diffraction.

X-rays were produced whenever high-speed electrons collide with a metal target. A source of electrons accelerates from hot filament which acts as cathode and copper as anode. The anode was a water-cooled block of Cu containing desired target metal. Unknown substances were identified by powdered diffraction. It has done by comparing diffraction data against a database maintained by the International Centre for Diffraction Data (ICDD). The following conditions were maintained and results are obtained.

2.5 Adsorption process.

The constant diluted Hydrochloric acid was sent to reactor, this contains Sodium Bisulphite by PERISTALTIC pump. During addition of Hydrochloric acid into the Sodium bisulphate, it produces sulphur dioxide gas and produced gas sent to the adsorption column, which contains Ferric Oxide (Fe_2O_3).Small quantity of SO_2 gas was adsorbed by the Ferric Oxide. Remaining quantity of SO_2 gas sent to absorption section, which contains 6% of H_2O_2 solution. It absorbs the SO_2 gas and converts to Sulphuric acid. From acid-base titration we come to know, how much quantity of SO_2 gas adsorbed by Fe_2O_3. Three different SO_2 gas flow rate sent to absorber and analyzed. The set up shown in fig.2.

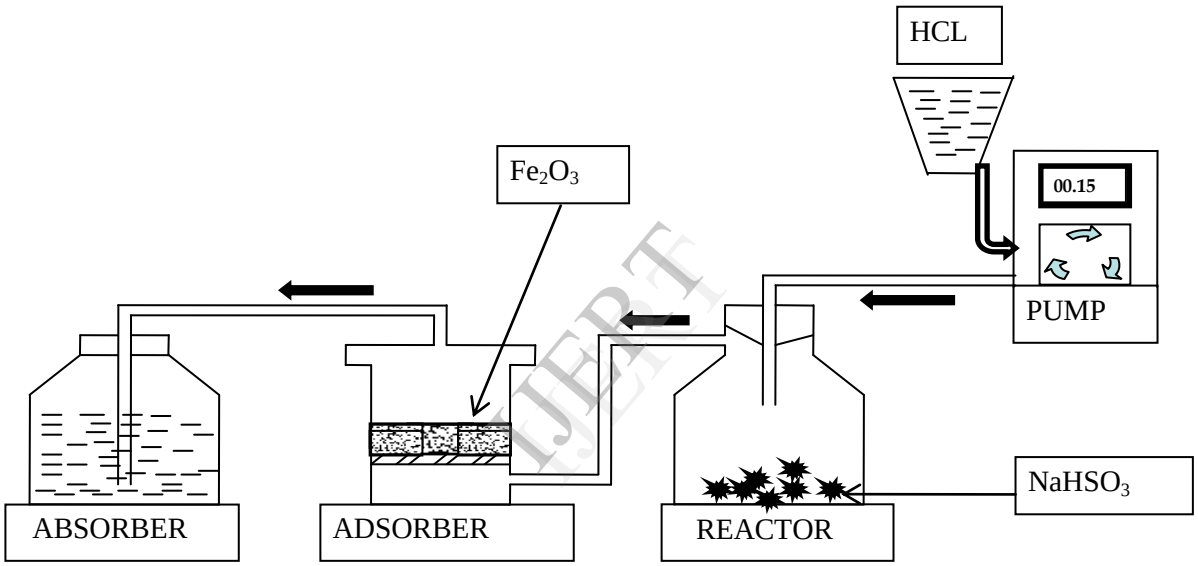

Figure. 2: Sulphur Dioxide Adsorption Process

2.6 Characteristic Parameters Derived from Breakthrough Curves

The concentration wave moves through the bed, most of the mass transfer is occurring in a fairly small region. This mass transfer zone moves down the bed until it "breaks through" and breakthrough time is defined as the time when the outlet concentration is five percentage of the inlet concentration. Exhaustion time is defined as the time when the outlet concentration is ninety-five percentage of the inlet concentration. A packed bed displays a gradient in adsorbate concentration from zero to equilibrium is called the mass transfer zone (MTZ). As the saturated part of the bed increases, the MTZ travels downstream and eventually exits the bed. [4] The length of the MTZ (L_{MTZ}) may be estimated as follows

$$L_{MTZ} = \frac{(T_{0.95} - T_{0.05}) \times L}{(T_{0.95} + T_{0.05})/2} \quad (3)$$

Where,

L is the length of the packed bed (cm), and $T_{0.05}$ and $T_{0.95}$ are the breakthrough and exhaustion time (min) respectively, which are normally defined as the times when the outlet concentrations are 5% and 95% of the inlet concentration respectively. For gas-phase adsorption in the packed bed, the breakthrough time can be expressed using the following semi-empiricalequation[4]

$$T_{0.05} = \frac{\rho_b \times W \times L}{C_0 \times U} - \frac{\rho \times W \times \ln(C_0 - C_{0.05})/C_{0.05}}{C_0 \times K} \quad (4)$$

Where
ρ_b is the bulk density of the packed bed (g/cm^3), W is the adsorption capacity, which is amount of gas adsorbed per mass of adsorbent (g/g),U is the gas superficial velocity (cm/min);C_0 is the inlet concentration(g/cm^3); C0.05 is the outlet concentration at breakthrough (g/cm^3); and K is the adsorption rate constant min^{-1}. Accordingly, $T_{0.05}$ plots versus bed length L should give a straight line. The parameters K and W can be obtained from the values of slope and intercept respectively.

3. RESULTS

3.1 Density of Adsorbent

5ml quantity of distilled water was taken in 10 ml measuring jar. 1 gm of produced adsorbent added into the measuring jar. Increased volume of water was measured and density is calculated by the following formula.

$$\text{Density} = \frac{\textit{Quantity of Mass Taken}}{\textit{Increased Volume}} \quad (5)$$

Density of Fe_2O_3 was 5 g/cc. This value was more or less same compare to theoretical value of Ferric Oxide.

3.2 AAS Analysis

Total iron content present in the produced adsorbent was found by using Atomic Absorption Spectroscopy (AAS). Standard solutions were prepared by known quantity of Ferric Oxide added into one liter of distilled water. Samples were taken from the standard solution. Unknown solution was prepared in the same way as prepared of standard solutions. The unknown concentration solution was determined by the following graph (Fig 4). The graph plotted between concentration and absorbance. AAS gives unknown solution absorbance. The unknown solution concentration was found from linearized equation

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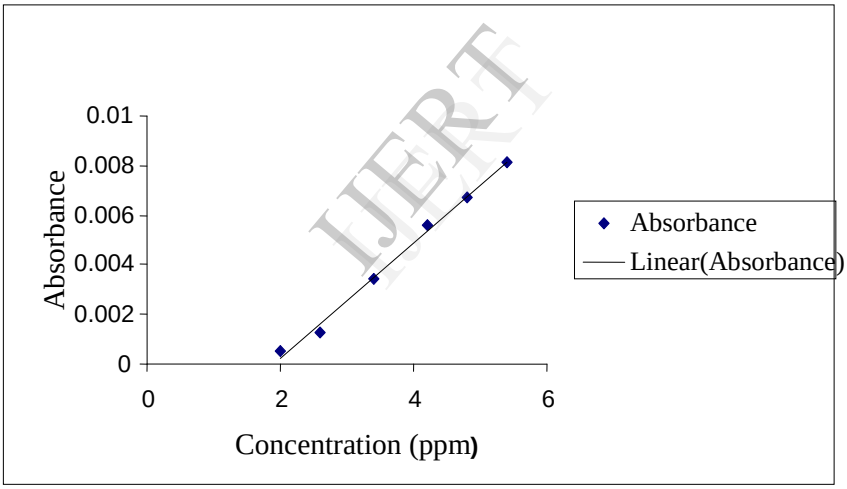

Fig. 3: AAS Analysis

Fig.3 shows linear line. The unknown solution concentration was found by the linearized equation. Total iron present in the given sample was calculated from the concentration. Total iron content percentage was 67.3.

3.3 XRD Analysis

Ferric Oxide was analyzed by X-Ray Diffraction analysis. The graph (Fig.4) plotted between position of Fe_2O_3 atoms and intensity of Fe_2O_3 crystals. The purity of Ferric Oxide was calculated by using the graph data. The purity of Fe_2O_3 was 95.97 %. The d-space and relative intensity of Fe_2O_3 were 2.5192 and 100. The d-space and relative intensity of Ferric Oxide crystals was measured by the following equation.

$$n\lambda = 2d\sin\theta \quad (6)$$

Where
λ = wave length of X-ray (STD value =1.54), d = d-space, θ = position (Degree)
n = 1.

Relative intensity = Height of peak value*100/Highest value of peak height

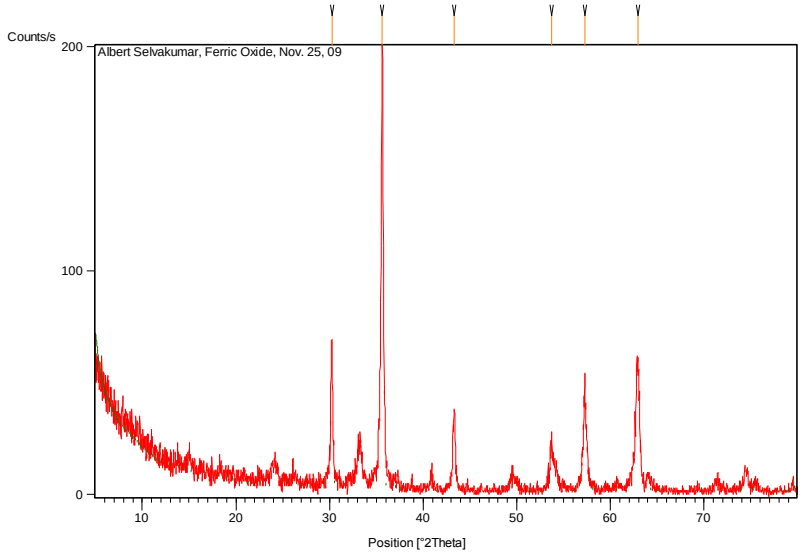

Fig. 4: XRD Analysis

3.4 Acid-Base Reaction Analysis For Fe_2o_3

Preparation

Fig.5 shows the acid base reaction analysis. Required quantity of Sodium Carbonate solution to form Ferrous Carbonate was found by this analysis. Ferrous Sulphate Heptahydrate solution acts as an acid and Sodium Carbonate solution acts as a base. The solution mixture pH was measured for each 10 ml of Sodium Carbonate solution added. It makes use of the neutralization reaction that occurs between acids and bases and the knowledge of how acids and bases would react if their formulas were known. However, if a strong base was used to titrate with a weak acid, the pH at the equivalence point will not be 7. There was a lag in reaching the equivalence point, as some of the weak acid was converted to its conjugate base. We saw the resultant lag that precedes the equivalence point, called the buffering region. In the buffering region, it took a large amount of NaOH to produce a small change in the pH of the receiving solution. That point was equivalence point.

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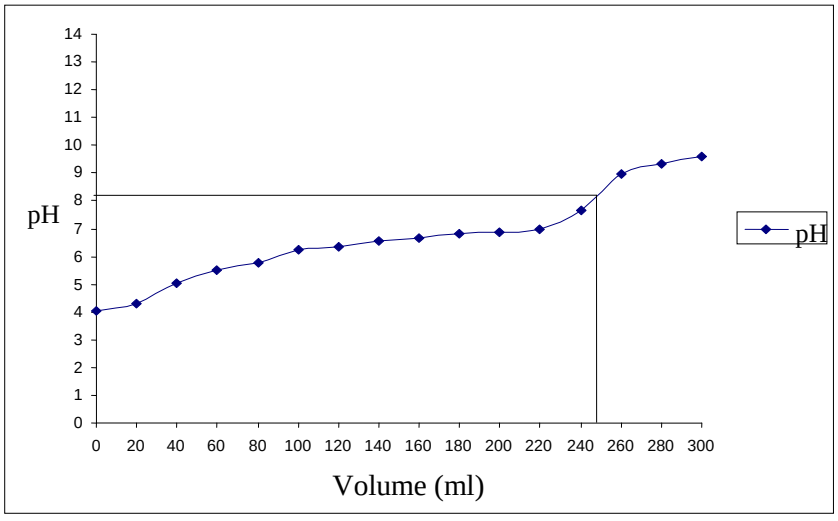

Fig.5: Acid-Base Analysis

3.5 Reaction Time Analysis For So_2 Preparation

The main reaction for the Sulphur Dioxide production is given below.

$$Na_2SO_3\ (s) + 2\ HCl\ (l) \rightarrow SO_2\ (g) + H_2O\ (l) + 2NaCl\ (l) \qquad \text{---------- (7)}$$

Fig.6 shows the quantity of produced Sulphur Dioxide production with respect to time. The experiments carried out for 10, 15, 30, 45 & 60 minutes. The graph plotted between quantity of Sulphur Dioxide produced and time taken for batch wise process. After 15 minutes it gave constant quantity of Sulphur Dioxide gas. It tells reaction was completed between 10 and 15 minutes. The produced quantity of Sulphur Dioxide was calculated by using acid-base titration. The exact reaction time was found and is explained in section 3.6.

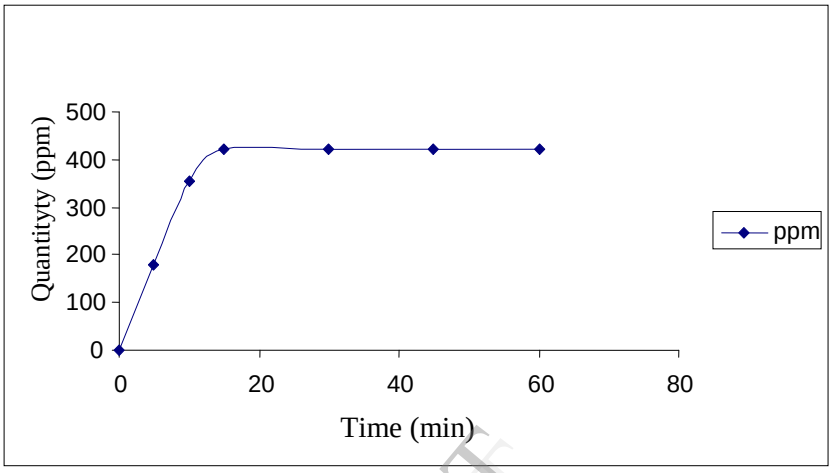

Fig. 6: Reaction Time Analysis

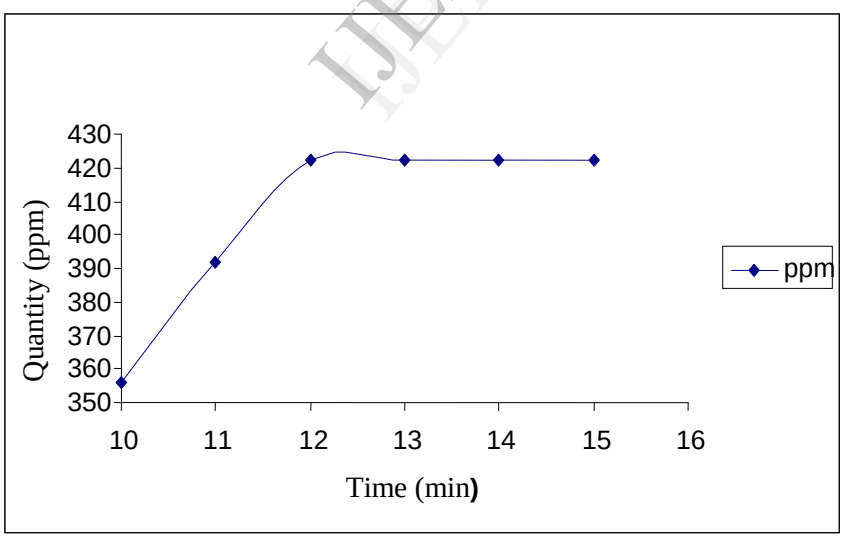

Fig. 7: Exact Complete Reaction Time Analysis

3.6 Exact complete reaction time for SO_2 production

The reaction of Sodium Sulfite with Hydrochloric acid was performed to produce Sulphur Dioxide gas various reaction times 11 to at 12 minutes and the produced Sulphur Dioxide quantity was 422 ppm. During adsorption, the 15 minutes with incremental of 1 minute. This was done to assess the exact reaction time and also calculates the amount of SO_2 produced for a period of time. The graph (Fig.7) plotted between Sulphur Dioxide gas and time. From 12 minutes it gives constant quantity. So the reaction completes amount of SO_2 gas at the inlet was calculated based on the above finding.

3.7 Breakthrough Curves For SO_2 Adsorption process on Fe_2O_3

Breakthrough curves of 103.6, 89.54, 78.6 ppm SO_2 adsorption with a 1, 2, 3cm long packed bed and a gas superficial velocity of 0.25, 0.26, 0.22 cm/s for ferric oxide prepared from ferrous sulphate heptahydrateare were shown in Fig.8, 9 and 10. It could be seen that the breakthrough time increased as the adsorbent quantity increased. This phenomenon involved three parameters: the intraparticle diffusion rate, the external surface per unit particle volume and the porosity of the bed. As the quantity increased, both the gas film resistance and the interior diffusion path increased, resulting in a slow mass transfer. However, finer particles would cause a larger pressure drop through the packed bed as the packing density of the bed increased. The characteristic parameters, including breakthrough time, exhaustion time and length of the mass transfer zone (MTZ), derived from the breakthrough curves for various length of bed. The breakthrough time increased and the exhaustion time also increased with increasing quantity of ferric oxide, resulting in longer mass transfer zones. In general, the smaller the particle, the faster is the diffusion and thus, the shorter and sharper would be the mass transfer zone as well as a higher adsorption capacity at breakthrough

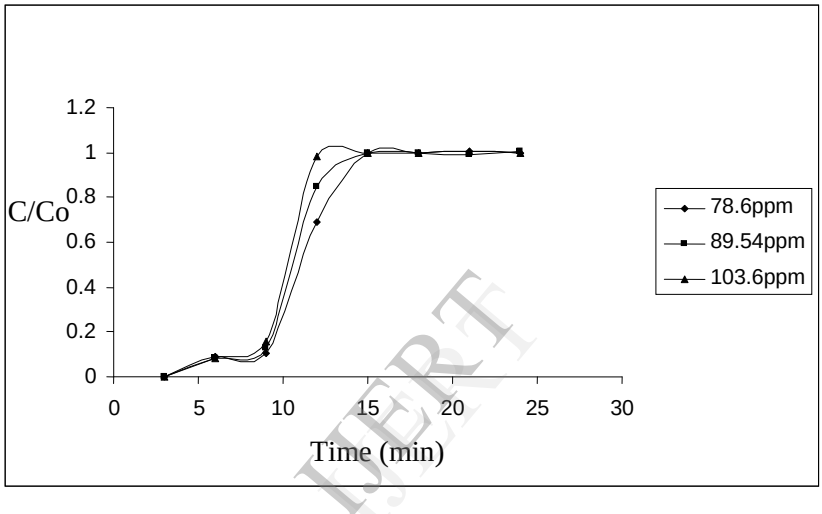

Fig. 8: Breakthrough curves for various concentration of SO_2 gas at 1cm long packed bed adsorption column

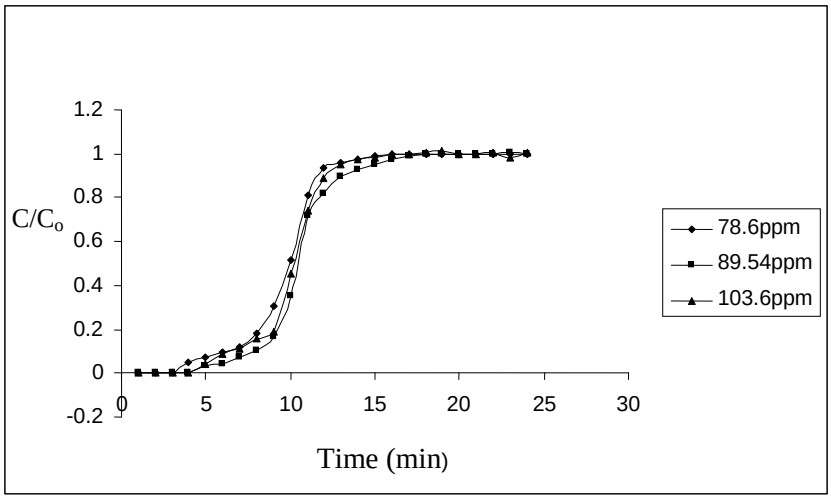

Fig. 9: Breakthrough curves for various concentration of SO_2 gas at 2cm long packed bed adsorption column

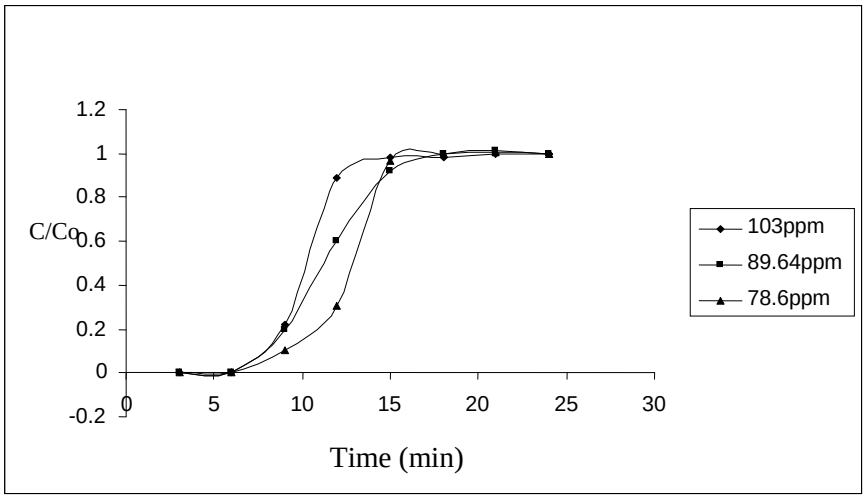

Fig. 10: Breakthrough curves for various concentration of SO_2 gas at 3cm long packed bed adsorption column

Table.1: Effects of Bed length on the adsorption characteristic parameters

Bed Length (cm)	**Inlet SO_2 Concentration (ppm)**	**Breakthrough Time (min)**	**Exhaustion Time (min)**	**L_{MTZ} (cm)**
1	78.6	4	12	0.333333
2	78.6	5	13	0.790698
3	78.6	7	14	1.540541

The breakthrough time versus bed length for the packed bed operating at various SO_2 superficial velocities are shown in Fig.11. The slope of the fitted lines decreased with increasing SO_2 superficial velocity. The superficial velocity was proportional to the gas volumetric flow rate as the column cross-sectional area was constant in all the experimental runs. A smaller gradient implied a lesser amount of SO_2 adsorbed at breakthrough. This was as expected because the contact time between SO_2 gas and the adsorbents in the packed bed decreased with increasing superficial velocity, thereby reducing the amount of gas treated and adsorbed at breakthrough

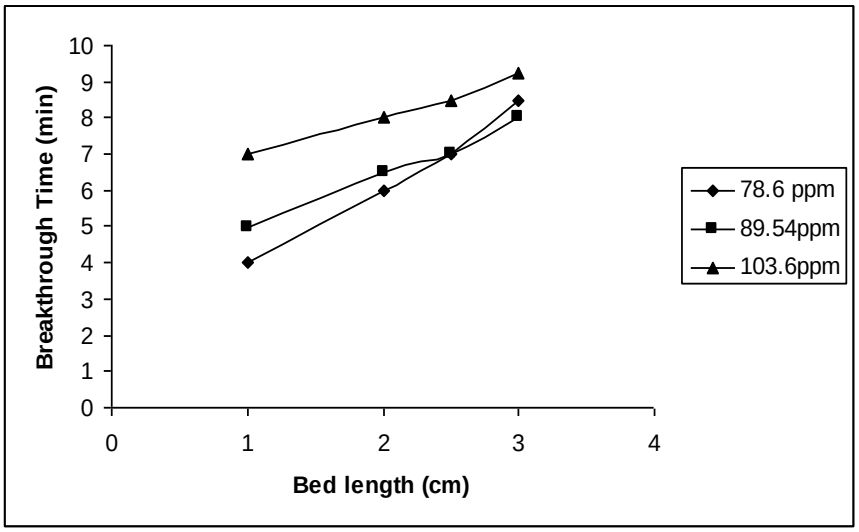

Fig. 11: Breakthrough time versus bed length for the packed bed operating at various superficial velocities.

CONCLUSIONS

Thermal decomposition process was one of the easiest method for production of adsorbent (Ferric Oxide). The cost of production of Ferric Oxide by thermal decomposition process was lower than other process. Maintaining the parameters was very simple for production of adsorbent. The thermal decomposition process easily achieved the theoretical quantity of adsorbent. The properties of adsorbent d-space, purity of adsorbent and relative intensity were found by and XRD. The total iron content presented in the adsorbent was found by AAS.Sulphur dioxide adsorbate was prepared by using Sodium Sulfite and dilutes Hydrochloricacid. An analytical method for Sulphur dioxide gas was simple. Acid-base titration was one of the easiest analytical method. It took less time to find normality of produced Sulphuric acid. Basic calculations were used to determine the Sulphur Dioxide content presented in produced Sulphuric acid. From the dynamic adsorption tests for SO_2 gas, the following conclusions can be drawn. Adsorbent quantity significantly affected the shape of the breakthrough curve. Larger quantity resulted in an earlier breakthrough and a longer mass transfer zone. SO_2 concentration had significant influences on dynamic adsorption in a packed bed. SO_2 superficial velocity was a critical factor to determine breakthrough time, exhaustion time, length of MTZ and adsorption rate constant.

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