CHAPTER IV
HUMORS AND HUMOURS
3.0 METHODS AND MATERIALS

The methods adopted generally for the removal or for controlling sulphur dioxide are by condensation, oxidation, dry absorption or adsorption with or without chemical reaction.

In the present study, adsorption method is selected. Adsorption methods are adopted for non-combustible gases and these should be present in lower concentrations. Sulphur dioxide is a non-supporter in the combustion process and by adopting adsorption techniques of $SO_2$ can be can easily control it.

Adsorption is a surface phenomenon. The process of accumulation of the gas or solute of the interface is termed as adsorption. The gases or solutes, which gets adsorbed, are termed as adsorbate and liquid or the solid, which has adsorbed them, is termed as adsorbent.

Adsorption is of two types
- Physical adsorption or vanderwaals adsorption.
- Chemical adsorption.

In physical adsorption, the adsorption forces are vanderwaals forces or intermolecular forces. Physical adsorption is always reversible. In chemical adsorption, the adsorption forces are chemical in nature and are irreversible. In chemisorption, the adsorptive molecules are capable of moving on the surface of the adsorbent, and in localized adsorption the adsorptive molecules are incapable of moving along the surface. For the adsorptive molecules to move on the adsorbent surface, they must apparently overcome definite potential barriers. As the temperature rises localized physical adsorption becomes non-localized owing to the growth in the kinetic energy of the molecules and their ability to overcome the potential barrier.
3.1 SELECTION OF ADSORBENTS

The most challenging task for the adsorption process is to select and find out the effective adsorbent for sulphur dioxide removal. There are a number of patent catalytic units for the removal of sulphur dioxide, and a special reference is to automobile exhaust. It is very probable that adsorption occurs on all the surfaces. For example, a layer of water molecules almost invariably covers glass but the effects are not evident unless the adsorbing material is porous and has very large surface area for a given mass. For this reason, various forms of charcoal have been extensively used in adsorption studies. In recent years silica gel has also been employed for the experimental work as well as in industrial practices.

The substances initially selected are

- Sawdust
- Brick powder
- Powdered Concrete
- Gypsum
- Marble Chips
- Iron ore
- Bauxite
- Dolomite
- Manganese Oxide
- Alum Sludge
- Alumina
3.1.1 SAWDUST

Sawdust is a waste and cheap material obtained from sawing operation of timber and furniture manufacturing units. Though it was used as fuel earlier, with the availability of other fuels, it is left as a waste material. To some extent it is used in compressed boards and panel boards. It is a well-known fact that plants\textsuperscript{1-2}, the origin of sawdust, adsorb sulphur dioxide from the atmosphere. Sawdust being porous and mainly composed of cellulose is selected. Activated carbons\textsuperscript{3-10} are used as adsorbents and they are produced by

- Mixing vegetable matter with inorganic substances such as calcium carbonate for carbonizing and leaching away the inorganic substances.
- Mixing organic matter such as sawdust with porous substances such as pumice stone followed by heating and carbonization.
- Carbonizing wood and sawdust.

Taking the above factors into consideration sawdust is selected for the studies as one of the adsorbents.

3.1.2 BRICK POWDER

Fuller earths are natural clays and they are chiefly Magnesium Aluminium Silicates in the form of minerals Attapulgite and Montmorillonite\textsuperscript{11-14}. When clay is heated and dried during this operation it develops structure. Activated clays\textsuperscript{15-24} and fuller earths are useful in decolorizing, neutralizing, drying petroleum and transformer products like lubricating oils, transformer oils such as kerosene and gasoline as well as vegetable and animal oils. Bricks are soaked in water for 24hrs to increase its weight to almost one and a half times. This reveals the fact that bricks have a large number of pores. Taking this into account Brick powder is selected in this study of adsorption process. Bricks are also obtained from clay by heating and drying process. It develops a capacity to adsorb gases.
3.1.3 POWDERED CEMENT CONCRETE

Concrete powder\textsuperscript{24} is a mixture of silica, stones and cement in the ratio 1:2:4. Cement consists 2.5\% of MgO, 62\% of CaO, 22\% of SiO\textsubscript{2}, 7.2\% Al\textsubscript{2}O\textsubscript{3}, 2.5\% of Fe\textsubscript{2}O\textsubscript{3} and SO\textsubscript{3}, 1\% of K\textsubscript{2}O.

Whenever modifications of buildings and structures are undertaken solid waste such as dismantled concrete cement consists of calcium and cement is obtained. As this mixture consists of Al, Mg, Fe, Ca it is considered for the study of removal of SO\textsubscript{2}.

3.1.4 GYPSUM

It was found that many thermal power plants are using CaCO\textsubscript{3} for removing oxides of sulphur from their flue gases. The familiar reaction of calcium and sulphur dioxide produces waste material in the form of sulphate of calcium otherwise called gypsum. Gypsum is used for preparation of cement and Plaster of Paris in limited quantities. The reaction is not totally complete in scrubbing operations and it is found that this waste gypsum still contains the capacity to remove SO\textsubscript{2} to some extent. To evaluate the use of such waste materials experiments are conducted to access the extent of adsorption on this waste gypsum\textsuperscript{26-29}.

3.1.5 MARBLE CHIPS

Marble is extensively used in building construction for flooring and decorative purpose, and while preparing marble slab and other patterns, waste materials in the form of chips are left. Marble is one of the ores of calcium and it is chemically called as calcium carbonate. Many ecologists, art lovers' environmental engineers\textsuperscript{30-36} and members of parliament have expressed grave concern about the adverse and improper
location of the refinery near Taj Mahal and its environs. The 17th century Taj Mahal developed yellow spots at various places on its translucent white surface. Taj Mahal made of marble is affected by SO$_2$, emitted by the refineries surrounding Taj Mahal. So in the present study an attempt is made to use marble chips$^{37-47}$ as an adsorbent for controlling SO$_2$.

### 3.1.6 IRON ORE

Many metal oxides and oxide mixtures are used as adsorbents for the removal of SO$_2$ in flue gases. Due to its chemical nature Hematite ore is selected for the removal of SO$_2$. Hematite ore consists of ferric oxide and it is apparently black in color. For the present study ferric oxide ore which is dark red in luster is selected as an adsorbent. Fe$_2$O$_3$ is used as adsorbent and catalyst in many studies$^{48-50}$.

A natural degradation material widely used in construction is rusted iron, which is chemically known as ferric oxide. Rusted iron has a capacity to react with SO$_2$ compounds. However rusted Iron oxide materials are considered as waste materials, however lean iron ores from which metal extraction is not economical can be used for controlling SO$_2$. It is also one of the reasons for selecting hematite ore as experimental material for adsorption purposes.

### 3.1.7 BAUXITE

Bauxite is widely used mineral ore available as earthy deposits in rock consisting of one or more hydrated Aluminium oxide species. Hydrated alumina is generally used for decolorizing petroleum products or drying various types of gases. Because of reaction of trivalent aluminium (low-grade) Bauxite ore$^{51-53}$ is used in the experiments for exploratory study.
The other hydrated aluminium oxide minerals are Gibbsite, Boehmite and Diaspore. Both Boehmite and Diaspore are monohydrate and have the same chemical compositions, but Diaspore is harder and has a higher specific gravity than Boehmite. Gibbsite is aluminium trihydrate mineral. Regarding chemical properties, purity to the extent of 98% to 99.99% is available. Physical properties vary widely according to the mine source, granulations (include: 50mm by downlumps) crushed coarse sizes (-3mesh, -8mesh, -12mesh) and ground powder sizes (-100mesh, -200mesh and -325mesh technical constants).

3.1.8 DOLOMITE

A mineral which naturally occurs contains Calcium along with Magnesium is Dolomite. Dolomite is available in our country in the Udaipur region. It has many uses as source for magnesium or for making use in various other materials of insulation. Dolomite$^{54-60}$ is also used for removal of SO$_2$. It is included for completeness and comparison of studies envisaged.

3.1.9 MANGANESE OXIDE

Manganese oxide is amphoteric in nature and forms salts of tetravalent manganese. It is a good oxidizing agent and it can easily take an atom of oxygen. Due to oxidizing nature of Manganese oxide and reducing nature of SO$_2$, a reaction takes place between them. With the similarities between iron and manganese, it is also selected as adsorbent$^{61}$. Iron and manganese are transition metals and both are amphoteric in nature. Manganese oxide is widely available as Pyrulsite ore in India and it is economical to use. It can be used in the fixed bed as well as in continuous and semi continuous operations.
It is black insoluble powder and it is a good conductor of heat and electricity. The commercially available Manganese oxide contains 60-68% of Manganese and traces of Fe₂O₃.

3.1.10 ALUMINA

Alumina and Alumina oxide in nature is present as corundum, bauxite, rubies; sapphires are its pure forms. Alumina is the purest form of Aluminium oxide. This material is selected as adsorbent for study as reaction between alumina and SO₂ is observed in many processes.

3.1.11 ALUM SLUDGE

Salts of Alumina have been found significantly effective in the removal of SO₂. The reactions of Alumina salts depend on the type of anions. Hydrated alumina has been used as decolorizing agent for petroleum products as well as drying agents.

By and large the use of aluminium sulphate is maximum in water treatment. Each milligram of aluminium sulphate reacts with approximately half a milligram of alkalinity in water producing Aluminium hydroxide flocks settle down in clariflock flakes. The sludge may be in wet or dried form. It is disposas as a solid waste material. Aluminium hydroxide flocks gather considerable amount of clay silt and many other suspended particulate materials and is becoming a problem for waste management. Since the properties of hydrated alumina include the reaction with SO₂, dried sludge material is used in the adsorption studies.
3.1.12 MAGNESIUM CARBONATE

One of the materials that have been tried for SO₂ adsorption experiments is MgCO₃ which is used as coagulant in certain processes. Mg(OH)₂ has been active in removing turbidity. The selection of the compound is mainly exploratory. Magnesium silicate is used as adsorbent for many gases and vapours.

3.2 APPARATUS AND INSTRUMENTS AND REAGANTS USED

3.2.1 APPARATUS

Mettler (Zurich) single balance is used for weighing SO₂ gas cylinder of 5lit capacity is used for the present studies.

N₂ cylinder is used to maintain the inert atmosphere.

SO₂ analyzer designed by spectrochem. Private limited is used to estimate the concentration of the gas.

3.2.2 REAGENTS

3.2.2.1 ABSORBING REAGENT (Sodium Chloro Mercurate Solution)

27.2gms Mercuric Chloride and 11.7gms of NaCl is dissolved in one liter of distilled water and stored at room temperature for two months.

3.2.2.2 PARA ROSALINE HYDROCHLORIDE (Acid Bleached) STOCK SOLUTION

0.5gms of Para Rosaline dissolved in 100ml distilled water and filtered after keeping for two days. The filtrate solution is stable for three months.
3.2.2.3 WORKING SOLUTION

6ml concentrated Hydrochloric acid is added to 4ml stock solution (Para Rosaline Hydrochloride) and diluted to 100ml-distilled water. This solution will be pale yellow with a greenish tinge. It can be stored for a week or even for about 3 weeks if refrigerated and this solution is used as coloring agent during analysis.

3.2.2.4 STANDARD SOLUTION FOR SO₂

Solution of sodium Meta bisulphate is used for preparing the standard solution of SO₂.

3.3 ANALYSIS OF SO₂

SO₂ concentrations are determined by West-Gaeke method. SO₂ is trapped in a solution of Mercuric chloride and NaCl. The solution is then reacted with Formaldehyde and Para Rosaline Hydrochloride. A violet-red dye is formed and its absorbance is measured. A calibration curve is plotted with the absorbances on Y-axis and SO₂ concentrations on X-axis.

The standard solution of 260 micrograms Sodium Meta Bisulphate solutions was prepared. The solution is diluted to get required concentrations. 10ml absorbing solution, 1ml Para Rosaline solution, 1ml Formaldehyde and 1ml of Sodium Meta Bisulphate solution of different concentrations are added. The solutions are mixed well and after 15min, the absorbances were measured in 1cm cell. The calibration graph is obtained by plotting absorbance values against concentrations of SO₂.
3.4 DESCRIPTION OF EXPERIMENTAL SETUP

The test gas mixtures were produced from a cylinder of 100% SO₂ (span gas equipment Pvt. Ltd) and diluted to require concentration using nitrogen gas. The flow of the carrier gas and SO₂ are adjusted by valves of Gas Dilution System (fig 3.1). Based on the data obtained, the SO₂ content of the gas stream is determined using West-Gaeke method.

N₂ and SO₂ gas cylinders are connected to the dilution system by operating the pressure regulating valve PRV₁ for N₂ gas and pressure regulating valve PRV₂ for SO₂. The inlet pressure gauge ₁₂ connected to PRV₂ for SO₂ gases and similarly ₁₁ is connected to PRV₁ for N₂ gas outlet pressures of the gases entering into the mixing chamber can be determined by using the gauges ₀₁ and ₀₂ respectively. V₁ and V₂ valves are used to get different concentrations of N₂ gases. V₃ and V₄ are used to get different concentrations of SO₂ gases. The two gases gets mixed up into a chamber and this mixture of these gases enters into another chamber and the pressures of these can be controlled using V₅, V₆, V₇, V₈ valves the flow rate of these mixtures of these gases is maintained as 60cc per minute. High sensitivity and good results are obtained with low flow rate. To get the effective results this flow rate is fixed. By opening V₉ valve the mixture of these gases enters into the catalytic tube which having an adsorbent in it. The gas from catalytic tube is pumped with a pump into the detection cell, which consists of Para Rosaline hydrochloric reagent. The concentration of gas is determined by using SO₂ analyzer, which is based on West-Gaeke method.
fig 2: simplified schematic diagram of the test jig

1 = inlet pressure gauge, PRV = Pressure regulating valve.

V = Needle valve, F = Flow meter
3.5 EXPERIMENTAL PROCEDURE FOR REMOVAL OF SO$_2$ FROM AQUEOUS SOLUTION OF SO$_2$

An aqueous solution of 100ml of SO$_2$ from various concentrations (ranging 26-260mg/m$^3$) is taken in 100ml stopper bottle and 1gm of adsorbent is added to the solution. Batch adsorption experiments are carried out at room temperatures. A contact time of 60min is maintained. The sulphur dioxide analyzer is used to determine the initial and final concentrations of aqueous solutions of sulphur dioxide. The experiments are conducted with Sawdust, Brick Powder, Powdered Concrete, Gypsum, Marble Chips, low grade Iron Ore and waste Alum Sludge from water works, Dolomite, Magnesium Carbonate, Manganese Oxide, Bauxite and Alumina.

3.6 EXPERIMENTS ON ADSORPTION OF SO$_2$

The experiments on the adsorption of SO$_2$ gas were studied with respect to

- Contact time between adsorbate and adsorbent
- Particle size of the adsorbent
- Inlet SO$_2$ gas concentration
- Adsorbent dosage
- Adsorption isotherm
- Adsorption kinetics
- Calculation of entropy, enthalpy and free energy of the system

3.7 CONTACT TIME BETWEEN ADSORBATE AND ADSORBENT

Contact time between the adsorbent and adsorbate plays a vital role in designing a system. To study the effect of contact time following experimental procedure is adopted.
3.7.1 EXPERIMENTAL PROCEDURE

$\text{SO}_2$ gas mixed with $\text{N}_2$ gas is made to pass through adsorbent, which are taken in a catalytic tube, and batch adsorption experiments are carried out at room temperature. The initial and final concentrations were determined. The amount of the gas adsorbed at different time intervals were determined. The experiments were performed with the particle size 710mic, 500mic and 250mic to bring the correlation between surface area and adsorption phenomena. The experiments were performed by using marble chips, magnesium carbonate, dolomite, gypsum, magnesium carbonate, manganese oxide, and Alum sludge as adsorbents.

3.8. EFFECT OF INLET $\text{SO}_2$ CONCENTRATION

The mechanism of the adsorption is certainly dependent on the available surface area but it is dependent on the concentration. The experiments were performed for particle size 710mic, 500mic and 250mic.

3.8.1 EXPERIMENTAL PROCEDURE

Various concentrations of $\text{SO}_2$ gas mixed with $\text{N}_2$ gas is made to pass through the catalytic tube, which is maintained as constant temperature, and it is filled with the adsorbent. A flow rate 60ml/min is maintained. A constant contact time is maintained which is determined by contact time experiments. The experiments were performed for different concentrations with a constant amount of the adsorbent and with the particles of different sizes. The initial and final concentrations were determined by using West-Gaeke method\textsuperscript{76}. These experiments were performed with different substances.
3.9 EFFECT OF ADSORBENT DOSAGE

To study the effect of adsorbent dosage, a mixture of N₂ and SO₂ gas is made to pass through a catalytic tube, which is made to pass through the different amounts of adsorbent. A fixed flow rate 60ml/min constant temperature is maintained. This experiment is performed for different concentrations and for different substances.

3.10 EFFECT OF TEMPERATURE

The most experiment of adsorption experiment is the measurement of the relationship between the amount of the adsorbent and the concentration of the gas. Such measurements are usually made at constant temperature and constant pressures and the results are presented as adsorption isotherms. The quantity of the gas adsorbed by the given adsorbent depends on the temperature as well as pressure or concentration of the gas.

3.10.1 FREUNDILICH ADSORPTION ISOTHERM

He gave an empirical relationship between amount of the adsorbent and concentration at particular temperature

\[ \frac{X}{m} = Kc^{1/n} \]

\[ \log \frac{x}{m} = \log k + 1/n \log c \]

1/n gives the slope of the curve and log k gives the intercept.

3.11. CALCULATIONS OF THERMODYNAMIC PARAMETERS

Thermodynamic parameters were calculated from variations of the thermodynamic equilibrium constants Kc with the temperature. Kc values are
calculated by the method given by Khan and Singh\textsuperscript{7b,7c} by plotting $\log x/m/c_0$ versus $x/m$ and extrapolating to zero $x/m$. The standard free energy and entropy change and enthalpy change are calculated using the equation

$$\Delta G^0 = -RT \log K_c$$

$$\log K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}$$
calculated by the method given by Khan and Singh\textsuperscript{76-77} by plotting $\log x/m/c_e$ verses $x/m$ and extrapolating to zero $x/m$. The standard free energy and entropy change and enthalpy change are calculated using the equation

$$
\Delta G^0 = -RT \log K_c
$$

$$
\log K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
$$


