Research Article

Adsorption of SO$_2$ on ZnO Nanowires Using Activated Carbon by Langmuir Adsorption Isotherm

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Sulphur dioxide (SO$_2$) is one of the contaminants present in the environment. They are the by-product of combustion, industrial pollution, generation of electricity, etc. After some reactions in the atmosphere, SO$_2$ changes its form and produces acid rain. The presence of SO$_2$ needs to be detected to combat its effect. Many nanosensors are designed to detect the presence of SO$_2$ in the environment. Zinc oxide (ZnO) nanowire sensor is one of those sensors used for SO$_2$ detection. The size, structure, cost-effectiveness, and unique properties made it a choice for sensing purposes. Activated carbon is another compound that has porous substances that help the adsorbate to settle down on the large surface area of its adsorbent surfaces. Combining the nature of ZnO nanowire and activated carbon, the adsorption of SO$_2$ can be increased. This paper proposes a novel technique involving the activated carbon in the ZnO nanowire sensor to increase its SO$_2$ adsorption capacity and rate. The Langmuir adsorption isotherm is used to find the adsorption efficiency between the solid adsorbent and gaseous adsorbate. MATLAB simulation was carried out for the proposed work in which it is seen that the novel method shows 33.34% efficiency in terms of SO$_2$ adsorption capacity. The response of the proposed sensor shows 23% efficiency over time. The analysis shows that the usage of the activated carbon increases the adsorbent site for SO$_2$ adsorbate to adsorb on the surfaces. According to the adsorption quantity, SO$_2$ level has been obtained in the environment.

1. Introduction

One of the indirect greenhouse gases is sulphur dioxide (SO$_2$). The SO$_2$ contributes less percentage in greenhouse gases, but it has hazardous effects on nature. The sulphates are the by-product of SO$_2$ which leads to acid rain [1]. The derivatives of SO$_2$ when it reacts with the atmosphere are even worse. The provenance of SO$_2$ is mainly combustion fuels, refineries, industrial boilers, electricity generation, diesel engines, metal processing, etc. The Eastern States are mainly affected areas due to this SO$_2$. It causes respiratory illness and leads to some cardiological effects [2]. To reduce the effect of SO$_2$ or combat SO$_2$, the main thing needed is to observe the places where it is present. Wireless sensor networks play a major role in sensing many particulars in unmanned areas.

The nanowire sensors are very tiny with a 1D structure [3]. Many kinds of nanowire sensors like metallic nanowire sensors, metal oxide nanowire sensors, metal nanowire gas sensors, and silicon nanowire gas sensors are evolved. This paper uses a ZnO nanowire gas sensor to detect the presence of SO$_2$ in the atmosphere [4]. For determining the sulphur
dioxide concentration in the exposure chamber, known vol-
umes of the gas-air mixture were taken periodically with the
help of a device known as an aspirator and analyzed. This
suction apparatus is connected to a rotameter to regulate
the gas-air mixture’s suction. The selection of the ZnO
nanowire sensor is due to the solid-gas interaction. Usually,
the nanowire sensors work efficiently at low temperatures.
The characteristics will change when the temperature varies.
The ZnO nanowire sensors are widely used for SO2 detec-
tion. The Langmuir adsorption algorithm isotherms explain
how pressure affects the gaseous adsorbate on the solid
adsorbent [5]. Zhang et al. discuss the various manufactur-
ing techniques of ZnO nanowires, their features, and their
applications. The paper mainly focused on the photocata-
lytic property of ZnO nanowires which helps to protect the
environment [6]. The food aroma detection and identifica-
tion of solvents are discussed by Kohl [7]; the author
discussed the temperature dependent of open reactive
surfaces of the gas sensors. Cui gave the survey of ZnO
nanowires, including their structure, functionality, area of
research, and future applications. The p-type doping of
ZnO nanowires was also provided [8]. Ramgir et al.
presented the survey of recent developments of nanowire-
based sensors and discussed different types of nanowire sen-
sors and the efficiency of the array of nanowire sensors for
future medicinal purposes [9]. The biological and chemical
species are studied using the nanowire sensors which have
the property of ultrasensitive and significant way of using
the nanowire sensors for diverse applications [10]. Zhang
et al. describe the top-down and bottom-up approaches for
detecting chemicals and explain various metal oxide sensors
and their applications. The QSAR model is used to study the
adsorption of SO2 on the ZnO nanowire sensors explained
in paper [11]. Li and Ma elucidate the mechanism of
removal of SO2 using the activated carbon. The tempera-
ture-dependent characteristics were also studied [12].
Dunicz explained that the specific area of adsorption of
charcoal is studied using Langmuir Adsorption isotherm
[13]. Many studies are now available showing the effects of
gaseous and particulate pollutants emitted from power
plants. However, the effects of those pollutants on human
health and animals are less extreme, which does not constit-
tute a direct health hazard. Given the global increase in
atmospheric change (CO2, CO, NO, and acid gases), the
consequences of a massive increase in the use of coal, while
not fully understood, are likely to be disastrous. Novel of this
research work is was aimed at investigating the usage of the
activated carbon on the surface of ZnO nanowire sensors to
reduce the porous dimensions to enhance the absorption
rate of SO2. The solid-gas interaction-based Langmuir algo-
rum is used to estimate its performances.

2. Materials and Methods

2.1. ZnO Nanowires. The unidimensional property of
nanowires yields interest for many electrical, optical, electro-
chemical, and mechanical applications. Among the different
nanowires, ZnO nanowire has unique properties that show
remarkable performance in various applications [14]. The
important feature of ZnO nanowire is its exciton binding
energy which is high, and the surface to volume ratio is also
large. The quantum confinement effects of ZnO nanowires
makes the transport of photons, electrons, and carriers.
The ZnO-based nanowires are the richest among the other
nanostructures because of their structures and properties
[15]. There are two main structures of ZnO nanowires:
hexagonal wurtzite and cubic zinc blende. The wurtzite
structure of the ZnO nanowire is more stable at ambient
temperatures. The ratio of planes approximates the unity
that forms the hexagonal structure, making its faster growth
in three different directions and helps in adjusting the area
of the facets in the same three directions. The ratio c/a =
1.633 which equals unity, thus forming HCP structures.
The structure of ZnO nanowires is studied using scanning
electron microscopy, X-ray diffraction patterns, and trans-
mision electron microscopy. The studies show that ZnO
nanowire is a single crystal structure with the <001> growth
direction; it grows vertically on the substrate with 100 nm
diameter. The negative field effect only enhances the proper-
ties of nanowires, and the diffraction pattern suggests that
they are single crystals [16].

There are two methods employed for the synthesis. Figure 1 shows different methods for synthesis. The first
method is vapor phase synthesis (VPS). The vapor species
are produced in the closed chamber by evaporation, gaseous
reduction, and chemical reaction at very high temperatures
500°C to 1500°C. The different types of vapor phase synthe-
sis are vapor liquid solid growth (VLS), chemical vapor
deposition (CVD), metal-organic chemical vapor deposition
(MOCVD), physical vapor deposition (PVD), molecular
beam epitaxy (MBE), pulsed laser deposition (PLD), metal-
organic vapor phase epitaxy (MOVPE) [17]. The MOCVD
and VLS have widely used techniques for synthesis.

The VLS method is a cheaper and easy process for
manufacturing large wafers. Another type is solution phase
synthesis, which comprises three techniques: hydrothermal,
emulsion, and ethanol-based. The solution-based
synthesis uses organic and inorganic substrates using the
a aqueous solution or organic solution for the growth pro-
cesses [18]. It is quite simple, cost-effective, and easy to
manipulate. There is also one type of growth called pat-
terned growth, where arrays of nanowires are grown to meet
optical properties for lasers. The properties of ZnO nano-
wires are spontaneous emission, stimulated emission,
electrical properties, piezoelectric properties, dilute magnetic
properties, etc. The ZnO nanowires are n-type material
because of four oxygen connected to two zinc ions intesti-
nally [19]. The FET is designed using ZnO nanowires where
the back gate is present. The n-type and p-type shows differ-
ent responses and characteristics for the same inputs [20].
The applications of ZnO nanowires are gas sensors, biosensors, UV detectors, UV laser, light-emitting diodes,
dye-sensitized solar cells, nanogenerator, field emission
device, field effect transistors, photocatalysis, photodetectors,
ferromagnetism, electricity generator, etc.
bottom-up. In the ZnO nanowire sensor, the silicon substrate is formed on the surface, which adsorbs the chemicals gases present in the environment. The adsorption rate of the ZnO nanowire sensor based on the redox reactions induced by the charge transfer process is made. The selectivity and sensitivity of the ZnO nanowire sensor are very high so that it will particularly adsorb the chosen gases from the environment for which it is designed. The main reason for high sensitivity is gas diffusion at porous and shell layers, which leads to electron depletion [21]. The ZnO nanowire sensor obtained using the thermal vaporization method yields more efficiency and faster recovery. The array of ZnO nanowire sensors helps to detect H2S in the environment. The ZnO nanowire sensor act as FET with the back gate electrode. The back gate electrode by applied voltage increases the sensitivity of the sensors [22]. The sensitivity of the ZnO nanowire sensor is directly proportional to the electric potential applied to the back gate. The full refreshment of the ZnO used in a FET varies from 20 to 60 nm. The amount of charge transfer examines the ZnO surfaces and SO2 interaction. Depending on the charge value and its direction, the function of the sensing material will be described [23]. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) define the interaction amount for different concentrations of SO2 exposed. By studying the Fermi energy level, the energy barrier is reduced by applying the back gate voltage, which helps the sensor adsorb more SO2 on the surface [24].

2.3. Activated Carbon. Activated carbon is tiny and low-volume porous materials of powdered or granular form. The pyrolysis and chemical treatments are the way to produce activated carbon using coal, coconut shells, bamboo, organic materials, etc. With its low-volume pores, the activated carbon increases the substrate’s surface area, which helps the adsorbate interact at the porous site created [25]. The pore diameters of the activated carbon show heterogeneity, which creates different sites for adsorbate to settle down. Usually, the activated carbon is used to remove unwanted materials. The physical compounds which are interacting the number of carbonaceous impurities present, specific chemicals present, and the physical and chemical properties of the activated carbon decide the efficiency and capacity of adsorption of the organic molecules [26]. Dunicz explained the surface area calculation of the activated carbon using Langmuir adsorption isotherm. The interaction between the activated carbon and chemicals is usually \Pi-\Pi interactions due to van der Waal forces or hydrogen bonding [13]. The environmental factors like pH, temperature, the concentration of adsorbate, physical size, ionic concentrations, pore blockage, and diffusion of small compound particles decide the efficiency of adsorption rate of the activated carbon. The activated carbon can be used as a substrate over the metal oxide surface to adsorb the chemical gases present [27].

3. Experimental Procedure

The experiment involves the activated carbon in the ZnO nanowires, which can be used as a sensor for detecting SO2. To adsorb more SO2, more compound sites are required. The interstation of SO2 with the surface requires
more molecules for bonding. With the help of bonding, more charge transfers have occurred, which helps detect the \( \text{SO}_2 \) presence in the environment. In the case of selecting only the \( \text{SO}_2 \), there are more charge transfers, which helps avoid other gaseous substances present in the environment and select the \( \text{SO}_2 \) alone [28]. Both \( \text{ZnO} \) nanowires and activated carbon have a large surface area from the literature survey. So here, the paper proposes the new method of introducing the activated carbon in the \( \text{ZnO} \) nanowire substrate to detect \( \text{SO}_2 \). Few researchers described the usage of the activated carbon for the removal of \( \text{SO}_2 \). By utilizing the property of a large surface area of the activated carbon, the paper proposes the detection of \( \text{SO}_2 \) in this work [29]. The low-volume pores of the activated carbon form adsorption sites for the \( \text{SO}_2 \) adsorbate to settle down on the substrates. The heterogeneity of the activated carbon helps the substrate of \( \text{ZnO} \) nanowire to produce more cation and anions. In this way, the band excitation occurs by moving electrons from the valence band to the conduction band. The following reaction will take place as shown in equation (1). The photocatalytic equation shows the formation of electrons and holes that will react with the oxygen molecules [30].

\[
\text{AC} - \text{ZnO}^{hv} \rightarrow e^- + h^+ \quad (1)
\]

When the \( \text{ZnO} \) adsorbs the \( \text{SO}_2 \), the following reaction will take place:

\[
2\text{ZnO} + 2\text{SO}_2 \rightarrow 2\text{ZnS} + 3\text{O}_2 \quad (2)
\]

Therefore, 3 oxygen molecules formed will react with electrons produced during the \( \text{AC} - \text{ZnO} \) reaction which is explained in

\[
e^- + 3\text{O}_2 \rightarrow 3\text{O}_2^- \quad (3)
\]

The 3 oxygen ions help the electrons to move from valence band to conduction band, thus by increasing the conductivity which directly improves the selectivity property of the \( \text{ZnO} \) nanowire sensor.

The Langmuir adsorption isotherm is used to calculate the capacity of the proposed work. The reason for choosing this isotherm is that it manipulates solid-gas interactions. The isotherm is considering that the adsorbates are gaseous, which get adsorbed to the adsorbent sites of the solid state. The following assumptions are made in the Langmuir adsorption isotherms:

(I) The immobile state of adsorbate should get adsorbed

(II) The energy is equivalent in all sites of adsorbent

(III) The site should have the ability to hold at least one molecule

(IV) The surface of the adsorbent must be homogeneous

(V) The interaction of molecules on the adsorbent’s adjacent sites should be either zero or ideal

The Langmuir adsorption isotherms formula is given in [14, 17]

\[
\theta = \frac{K_{eq}^A p^A}{1 + K_{eq}^A p^A}, \quad (4)
\]

where \( \theta \) is the fractional occupancy of adsorbent sites, \( K_{eq}^A \) is the equilibrium constant, and \( p^A \) is the adsorbate’s partial pressure.

Another equation described by Langmuir is given in

\[
\theta = \frac{V}{V_m}, \quad (5)
\]
where $V_m$ is the volume of adsorbate in an immobile gaseous state and $V$ is the volume of homogeneous adsorbent sites where the adsorbates get occupied.

The adsorption of the acid by the activated carbon can be described using Langmuir isotherm [13] as shown in

$$\frac{C}{X} = a + bc,$$

(6)

where $C$ is the concentration of SO$_2$ adsorbed on the adsorbent sites, $X$ is the number of moles adsorbed on the 1 gram of adsorbent, and $a$ and $b$ are the constants.

In equation (6), the value of $a$ will tends to be very small if the adsorbate concentration increases, so the value is omitted.

$$\frac{C}{X} = bc,$$

(7)

By taking reciprocal of equation (7), we get

$$X_{\text{max}} = \frac{1}{b}.$$ 

(8)

Equation (8) shows the maximum amount of adsorbate adsorbed on the 1 gram of adsorbent. Therefore, the specific surface area of the adsorbent can be calculated by

$$S = \frac{1}{b} \times N \times 21 \times 10^{-20} \text{ meters}^2,$$

(9)

where $S$ is the specific surface area in meters$^2$ and $N$ is the Avogadro number.

Using equation (9), the adsorbent sites’ capacity is calculated for adsorption. The value of $b$ is obtained if the value of $S$ is known already. The value of $X_{\text{max}}$ helps to calculate the amount of adsorbate adsorbed on the various adsorbent sites.

4. Results and Discussions

The experiment for the proposed work is done using MATLAB 2021B software. Table 1 shows the user data for simulation. The ZnO nanowire of size 100 nm is considered. The nominal temperature at 165°C in the simulation is carried out. The assumptions according to the Langmuir adsorption isotherm are made.

Figure 2 shows the plot of the time vs. adsorption capacity of SO$_2$ on the ZnO nanowire sensor involving activated carbon. The simulation is taken for both normal ZnO nanowire sensor and activated carbon in ZnO nanowire sensor. With the increase in time, it is seen that the adsorption capacity of adsorbate on the adsorbent increases. Due to the addition of the activated carbon in ZnO nanowires, the adsorption rate increases over time. It is seen that the adsorption rate is gradually increasing until an hour. After an hour, the adsorption of SO$_2$ reaches the saturation point, and it shows a little slope. So it proves that it takes an hour
for the adsorbent to start to adsorb the SO₂ adsorbate on the surfaces. From the graphical analysis, the adsorption rate of the proposed work at an hour is 33.34% efficient compared to the existing ZnO nanowire sensor.

Langmuir adsorption isotherm graph is shown in Figure 3. To calculate the solid-gas interaction between the adsorbate SO₂ and the adsorbents of ZnO nanowire using activated carbon, the plot of pressure vs. fractional occupancy on the adsorbent site is done. The graph obtained is similar to the ideal Langmuir adsorption isotherm. Still, some deviations are present. But it shows some of the ideality when compared with it. The values used for simulating this plot are given in Table 1. The ratio of $V/V_m$ reaches almost unity at the end of the process. It means that SO₂ adsorbates occupied all the adsorbent sites. In ratio, the numerator will always be unity but the denominator value will vary from zero to 1. The adsorbate will take some time to get adsorbed on the adsorbent. The adsorbate gradually will get increased, and it reaches the saturation point. From this graph, the proof for SO₂ adsorption capacity which gradually increases with time is also proved.

As the power plants use coal of high ash content, large amount of ash in either form causes severe disposal problems and environmental concern. Their surface disposal causes choking of natural drainage, and the trace elements released from this produce toxicity to animals, plants, and human beings. The bottom ash collected below the combustion unit is discharges from the nearby channel, tailing ponds, or dumpsites. When air-polluting substances leave their site of origin to enter the atmosphere as emissions, they are exposed to many influences before reaching the site, where they take effect as emissions. Sulphur dioxide may drift along with the wind for hundreds of kilometers away from the emission sources. However, large amounts of sulphur dioxide usually get deposited in the areas closer to the sources.

Figure 4 shows the plot of concentration vs. response measured. This calculation is necessary to study the characteristics of the ZnO nanowire sensor response to the SO₂ adsorption. Depending on the concentration of the SO₂ range, the response of the proposed sensor also increases. When the concentration of SO₂ in the environment increases, the response of the sensor detection rate also increases. From the plot, it is clear that the proposed work shows a high response rate compared to existing work. At 5 ppm concentration, the proposed work shows 23% efficiency compared to the normal ZnO nanowire sensor. The response of the sensor mainly depends on the adsorbate present. But at the low amount of adsorbate concentration, even the sensor’s response is little good.

The adsorbate and adsorbent concentrations complete each other so that the SO₂ absorbency increases gradually with time. Figure 5 shows the plot of time vs. $C/C_0$. The analysis is carried out to find the concentration gradient with an increase in time. There are gradual increases, which shows that the adsorbate gradually settles in the adsorbent sites regarding time. Once the $C/C_0$ reaches unity, the plot shows the saturation level which is also an interpretation of Langmuir adsorption isotherm.

The particulate matters are biologically active and may have direct toxic effects on themselves, indirect toxic effects through interactions with other pollutants, and chronic effects through cell transformation or regular alternation in cell function. The chemically inert soot emitted by insufficient coal and fuel oil combustion is less dangerous for plants, the particulates from industrial process (>10 pm) promptly to other parts of the body.

5. Conclusions

The various simulation paradigms are used to study the proposed work of usage of the activated carbon in the ZnO
nanowire sensor. The adsorption capacity of the sensor increased by 33.34%. The sensor’s response to the SO₂ adsorbate increases to about 23%. The novel method follows the isotherm of Langmuir adsorption isotherm. The more adsorbent sites adsorb more SO₂ in the environment, increasing the charge transfer on the surface of the ZnO nanowire sensor. The selectivity of SO₂ compounds from the environment mainly depends on their concentration. The chemical reactions due to adsorption decrease the energy gap and increase the conduction of the ZnO nanowire sensor. When there is more conduction, there increases the electron transfer, which indirectly increases the sensor’s signal strength. The increase in the signal strength helps to detect SO₂. The future work of this paper can be improvised by increasing the efficiency of the sensor to detect SO₂ even at lower concentrations in the environment. The carbonaceous impurities of the activated carbon will degrade the sensor’s performance. The impurities will react with the oxygen groups in the ZnO nanowire surface. The array of the proposed work will also be used to enhance the selectivity of the SO₂, and the sensitivity to the low concentration rate of SO₂ improved.

Data Availability

The data used to support the findings of this study are included within the article. Should further data or information be required, these are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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