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Adsorption of Nitrogen Dioxide (NO_2) for Different Gas Concentrations, Temperatures and Relative Humidities by using Activated Carbon Filter: An Experimental Study

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***Abstract*—** *Noxious gases can be reduced through activated carbon; nevertheless, this process is very complex due to the changing parameters. Nitrogen dioxides take place in the so-called reactive gases. The nitrogen dioxide concentration existing in the environment can be harmful, in particular for asthmatics and it also has the potential to bring about other serious diseases. For instance, interior diseases are often caused by nitrogen oxide gases. Through this study, we have observed the nitrogen dioxide adsorption on the active carbon for varying air temperatures, gas concentrations and air relative humidities. In this context, it has been examined the effect of all three parameters. While conducting this project, we have used parameters between 1ppm and 30ppm (for NO_2 concentration), 23°C and 33°C (for air temperature), 30% and 90% (for air relative humidity). In order to understand this process, breakthrough curves of NO_2evaluated from experiments have been used in the present study. Results show that the humidity has not a remarkable effect on the adsorption of NO_2; however, increasing relative humidity causes to a decrease in the capacity of the activated carbon for NO_2 adsorption. Additionally, NO_2 adsorption is exothermic, therefore it increases the air temperature.*

***Keywords*— adsorption of NO_2, filtration, activated carbon, air pollution, NO_2.**

I. INTRODUCTION

Our environment is polluted by many different noxious gases owing to the production of -among others- the corrosive exhaust gases NO_X, $NO+NO_2$. These gases have been created through power plants and burning of coals and so on. There are two gases inside NOx: one of them is Nitrogen monoxide (NO) and the other one is Nitrogen Dioxide (NO_2). Besides, N_2 gas is also arisen out of the break-up of NOx gas. This process necessitates a quite high temperature. Nitrogen dioxide (NO2) is a corrosive, irritant gas that harms the mucous membrane tissue in the all upper respiratory tract and also irritates the eyes. The indirect effect of NO_2 on human health is its quality as a precursor chemical to fine dust. Constant increased fine dust pollution leads to cardiovascular diseases and illnesses in the respiratory tract and shortens the expectancy of life.

Nitrogen oxides are generated as a result of combustion processes -either man-made or naturally- occurring from gasiform nitrogen and oxygen supplied by combustion air. But also, chemically bonded nitrogen in self-combustible things such as coal, oil, garbage is transformed into its oxides with oxygen from the combustion air. Table 1 justifies that almost all the Nitrogen Oxide (NO) originates from human-driven events like the burning of coal, the usage of gasoline and oil in various forms such as transportation, industries, households, agricultural activities and so on. It follows that the better the combustion it is, the higher the temperature and formation of NO_X it is. In catalytically non-affected combustion processes, NO develops as a main product with a percentage of between 90-95% of NO_X [1].

Table.1: Nitrogen oxide emissions according to the sectors (for EEA member countries) [2]

Sources of NO_x	Proportion
Road transport	42%
Energy production and distribution	20%
Energy use in industry	13%
Commercial institutional and households	14%
Non-Road Transport	7%

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Industrial processes	2%
Agriculture	2%

NO_2 amount around the world poses a great danger to human health and environment. According to a study about NO_2 and other waste gases' effect on human health by Chaloulakou et al. (2008), it is ascertained that the regions where the NO_2 rates diminished in Athens, a 2.6% decrease in the people going to hospital has been observed in these regions [3]. Al-Ahmadi et al. (2013) have shown in their studies that the ratio of NO_2 has a triggering effect on cancer [4]. Moreover, Murphy et al. (1964) have seen that NO_2 gas has nonrecoverable damages on animals along with serious harms to human health [5].

It is important to remove the reasons behind the NO_2 production so as to eliminate these damages. However, current technological developments and modern lives of people preclude from the usage of technological devices producing NO_2. For this reason, minimising the emission of NO_2 and set its ratios back to the levels that does not influence humanity has a vital role in terms of human health and environment since the production processes of NO_2 is impossible to eliminate.

The reduction of NO_2 gas in the available systems is provided with adsorbed filtration systems. The adsorption term denotes to the cleaning of air from NO_2 and other gases with various elements like activated carbon (The adsorption term will be explained briefly). Several studies and experiments have been conducted with regard to the adsorption of NO_X gases in different variations. Before addressing such processes, a more general explanation of adsorption has to be made. Adsorption means the accretion of fluid substances on a solid surface. The components adsorbed are called adsorptive in a free and flexible state while in a bounded state the components are called adsorbents. The solid matter functioning as adjuvant is called adsorbent. In the physical adsorption the bound of the adsorbing molecules are carried out by electrostatic attractive forces, the so-called van [6]. Because of the small range of those forces, the absorbents and adsorptive components enter a loose bond which can be dispensed easily. Adsorption is a thermic separating process. It is mainly used for separating specific gas components that are only contained in a very small amount [7].

Zhang et al. (2008) analysed the adsorption behaviour of NO_2 on activated carbon with different temperatures. Additionally, they also examined the ranges of activated carbon particles and as a result, it was seen that the adsorption of NO_2 includes the reduction of NO_2 to NO actuated via the carbon surface oxidation [8]. Dantaset al. (2009) presented the adsorption behaviours of Carbon dioxide (CO_2) on activated carbon and activated carbon enriched with nitrogen. In this study, adsorption behaviour in a fixed-bed column was analysed. In another study, the experimental parameters were selected between 301K and 428K and total pressure was 1.01 bar. The result showed different adsorption characters. The nitrogen-enriched activated carbon presented lower bed surface than the original activated carbon [9].Bazan et al. (2016) studied on the elimination of NO_2 with carbonaceous adsorbents acquired with supercritical extraction of marigold residue. Also, the results of this study showed that a right carbon and activation process is important in the adsorbents together with inorganic pollutants [10].

Gao et al. (2011) researched the adsorption of NO_2 on activated carbon by adjusting low temperature. The experiment temperature was determined as 50°C. As a result, they analysed that it had not much effect at a low temperature [11].Another study presented the NO_2 adsorption and reduction on pitch-based activated carbon fibres. The experiment parameters were determined as 250-1000 ppm concentrations; $O_2$was 0-10% and temperature was between 30 °C and 70°C. Pitch-based activated carbon fibres led to soar up of NO quickly; however, the adsorption of NO_2 remained the same up to the breakthrough time at 30 °C temperature. Meanwhile, it was also experienced a decrease in the adsorption and breakthrough time of NO_2 at 70 °C temperature [12].Nowicki et al. (2013) investigated the activated carbon character and adsorption properties. NO_2 gases were determined as adsorptive. Activated carbon surface area range was between 5 to 2,076 m2/g and pore volume is between 0.03 and 1.25 cm3/g. The outcomes of their studies have also pointed out that a proper selection of pyrolysis and activation process in the wastes of coffee sector pave the way for high amount of NO_2 production indicating 44.5 mg NO_2 in dry states and 84.1mg NO_2 in wet states [13].Lee et al. (2003), studied on impregnated activated carbon with KOH (KOH-AC) and examined the ratio of adsorption of NO_X and SO_2. The result indicated that the adsorption capacity of NO_X gas was much more than the capacity of SO_2 gas [14]. Long et al. (2008) made a study of the ammonia adsorption on activated carbon. In here, it was concentrated on two parameters: these are to bring out the effects of temperature and concentration over the adsorption of ammonia. The experimental results depicted that the adsorption rate of ammonia over activated carbon was tended to rise with the increasing concentration in these studies.

The adsorption rate is also tended to rise with the increasing temperature. Long et al. (2008) analysed the change over the carbon surface with dimethylamine on

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the adsorption of NO_X [15]. The wood-based activated carbon was tried with dimethylamine aqueous solution. In order to get it together with the nitrogen groups, it is modified in this way. This modification was considered as NO_2 adsorbents. In this context, breakthrough time and concentration was observed. While examining the nitrogen adsorption, it was also made element and temperature test together with potentiometric titration and the modifications were handled after exposing to NO_2. As a result, it was seen that the adsorption rate of NO_2 increased; on the other hand, NO release decreased [16]. Toops et al. (2006) analysed the adsorption of NO_X over $Pt/K/Al_2O_3$ with different period of times and temperatures. While the adsorption of NO_X is 6.4 $\mu mol/m^2$ at 150 °C, the adsorption is observed as 1.8 $\mu mol/m^2$ at 400 °C in their study [17]. Zhu et al. (2000) investigated the adsorption behaviour of NO on activated carbon at low temperatures (between 30°C and 250 °C), and NO showed a decrease with the increasing temperature in these temperature ranges. Here, the activated carbon was treated with NH_3 [18]. Hofmann and Pietrzak (2011) used waste tires as adsorbents in their experiments and put them through a chemical process between 550 °C and 800 °C. Besides, it was also researched the pyrolysis based on the performances of waste tiresas adsorbents through the effects of modification such as chemical and physical activation in addition to the room temperatures and dry states. As a consequence, it was understood that the surface of the adsorbent has the indicative feature in the adsorption capacity and also it affected the NO_2 adsorption [19]. Zhang et al. (2008) studied the reduction of NO gas on activated carbons having porous structures and they realized it under 100 °C. In this sense, it can be described that there is not any NO reduction without any existence of oxygen [20]. Kazmierczak-Razna et al. (2016), in their study, tested the pyrolysis analysis, the surface structure and adsorption characteristics on activated carbon. The outcomes also justified that the appropriate pyrolysis and activation process enables the adsorbents' production within this scope [21]. Sager et al. (2016) presented that NO_2 gas reduction with the help of activated carbon can be advanced via metal oxide nanoparticles infiltration into sorbents at ambient temperatures. The adsorption of $NO_2$was reduced in a catalytic way to physiological neutral substances through metal oxides after adsorbed by activated carbon. The amount of reduction was quite slow at usual ambient temperatures [22].

As it was shown in the research above, several experiments and examinations of NO_X adsorption have been made; however, they are generally studying the NO_X adsorption for limited parameters. In this study, adsorption capacity of NO_2 by activated carbon is determined. During the experiment, the NO_2 concentration is varied from 5ppm to 50ppm while temperature and relative humidity are varied from 10°C to 20°C and from 30% to 70%, respectively.

II. TESTING SYSTEM

In this experimental setup, different parameters and materials are used. The aim of the study is to observe the adsorption behaviour of activated carbon while changing the concentration of NO_2, air temperature and relative humidity. NO_2 gas supplied to the experimental setup as toxics gas. DIN 71460 standard, which describes the cabin air filtration standard, is used in this experiment. Schematic view of the experimental setup is given in Figure 1.Normally, NO_2 is always found in a fluid phase at room temperature. In order to achieve its gas phase, NO_2 was heated prior to dosage in filters. We used 0.79 µg activated carbon, which complies with the average amount of filtered carbon as equivalent. An activated carbon layer was built into the trial lane. Together with filtered air, the dosage introduced from outside the trial lane. The measurements were conducted via using measurement device type AC 31M.

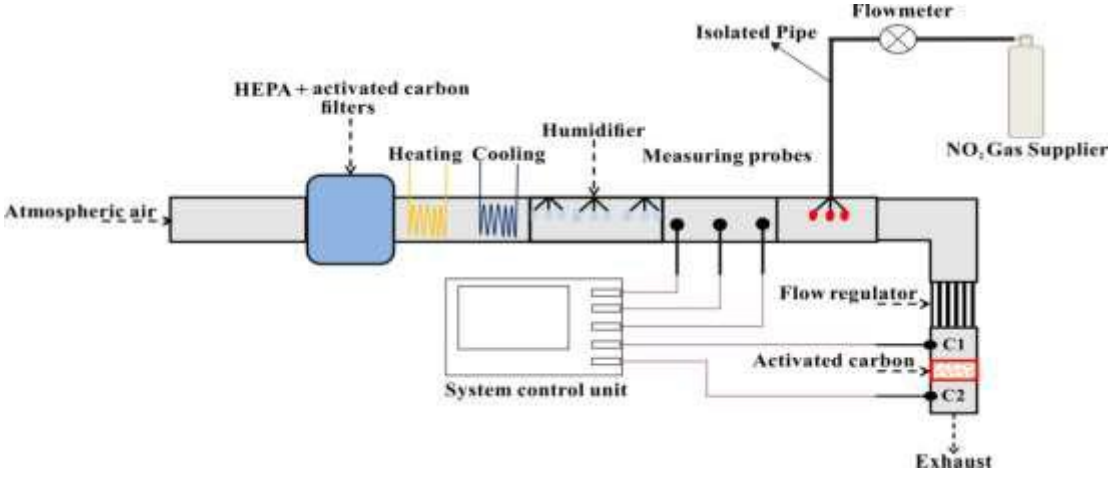

Fig.1: Schematic view of the experimental setup

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The adsorption behaviour of the Nitrogen Dioxide (NO_2) on activated carbon is examined at different concentrations and relative humidity as a result of the research. Initially, the experimental parameters, that can be seen in the experimental setup in Figure 1, was set and then the instruments are calibrated and requested amount of NO_2 gas concentration is injected into the system after reaching the requested ratios of temperature and relative humidity. After filling of activated carbon, the adsorption test starts with transmitting of gas concentration in the experiment on the activated carbon. The gas inlet is called as raw gas while the gas outlet is called as clean gas. The point where the gas inlet and outlet become equal is called as breakthrough point, that is the adsorption is not going ahead and activated carbon reaches at saturation point.

III. RESULTS AND DISCUSSION

The results of the experiments are investigated in detail and given in figures. The results of the experiments are investigated in detail and given in figures. The x-axis of the diagram shows the time duration of an experiment in minutes, the y-axis of the diagram shows the change in the raw gas and clean gas concentration range.

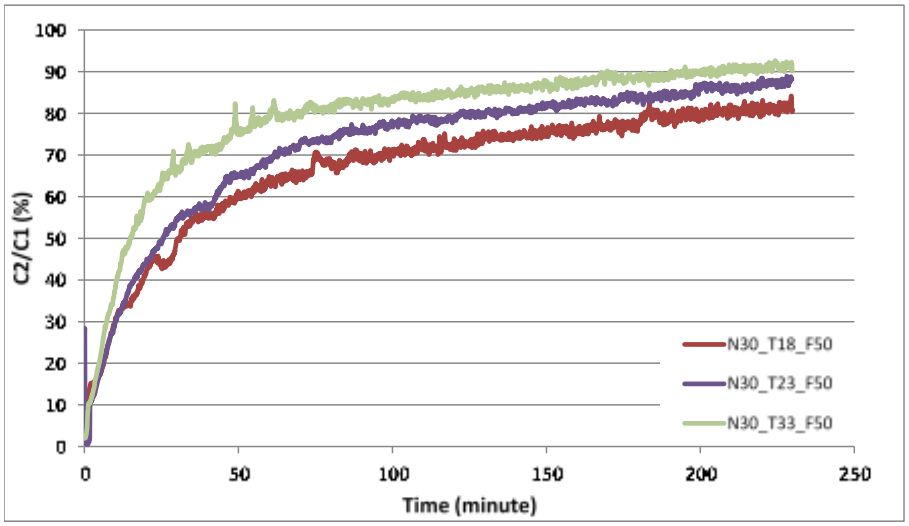

Fig.2: The comparison of the breakthrough curves for air temperatures of 18 °C, 23°C and 33°C at N=30ppm NO_2 gas concentration, F=50% air relative humidity

The figure above shows the breakthrough curves for 18 °C, 23°C and 33°C at a 30 ppm NO_2gas concentration and a constant relative humidity (50%). The experiment here has maintained until 230 minutes, and 18 °C curve has reached the saturation point at about 85 %. While the figure is reaching a 88% saturation point at 23 °C, it reaches 91% saturation point at 33 °C. A noticable change in the increase or decrease of temperature can not be seen at 30 ppm.

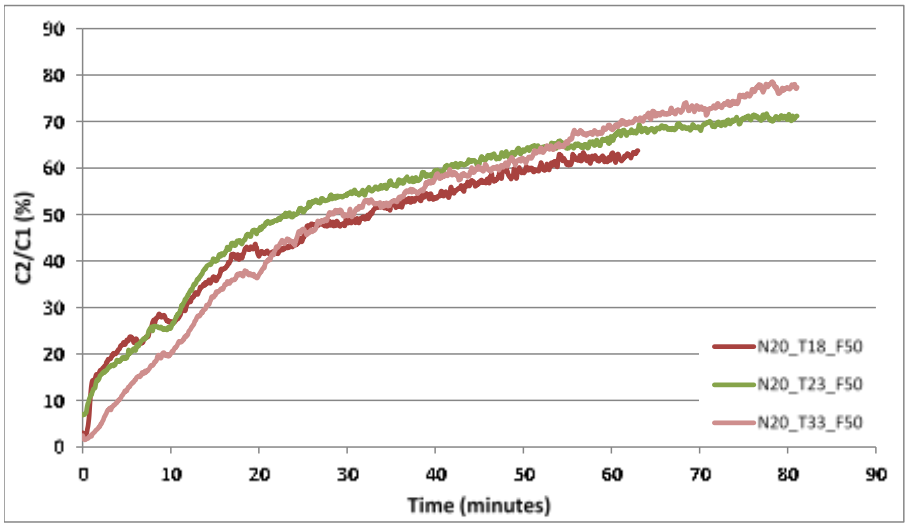

Fig.3: The comparison of the breakthrough curves for air temperatures of 18 °C, 23°C and 33°C at N=20ppm NO_2 gas concentration, F=50% air relative humidity

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Figure 3 shows the breakthrough curves for 18 °C, 23°C and 33°C NO2 gas concentration at a 20 ppm gas concentration and a constant 50% relative humidity. The experiment has maintained until 80 minutes and a noticable change in the increase or decrease of temperature can not be seen at 20 ppm like in the 30 ppm.

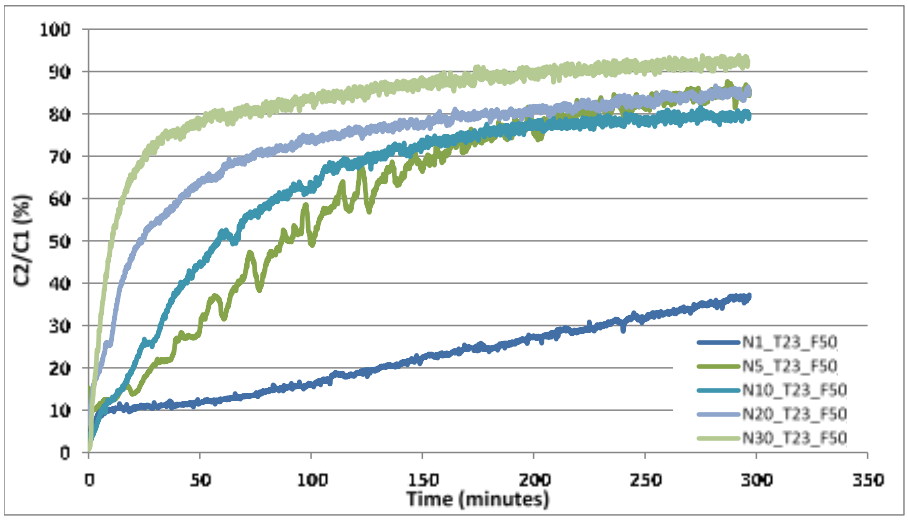

Fig.4: The comparison of the breakthrough curves for varying NO_2 gas concentrations of 1ppm, 5ppm, 10ppm, 20ppm, 30ppm at air temperatures of 23°C and air relative humidity of F=50%

As above it is shown in Figure 4, it is examined adsorption behaviour of NO_2 with changing concentrations and the same temperature and relative humidity. In here, while temperature is taken as 23 °C and relative humidity is 50%, the ratios of the concentration can be seen as 1 ppm, 5ppm, 10 ppm, 20 ppm, 30 ppm. The experiment time is 300 minutes. While it reaches 37% saturation point in 1 ppm of NO_2 at the end of the 300 minutes, it reaches 84% saturation point in 20 ppm of NO_2. And, it reaches 92% saturation point in 30 ppm of NO_2 at the end of 300 minutes. That is to say, it can be seen that the breakthrough point shortens when the gas concentrations are increased.

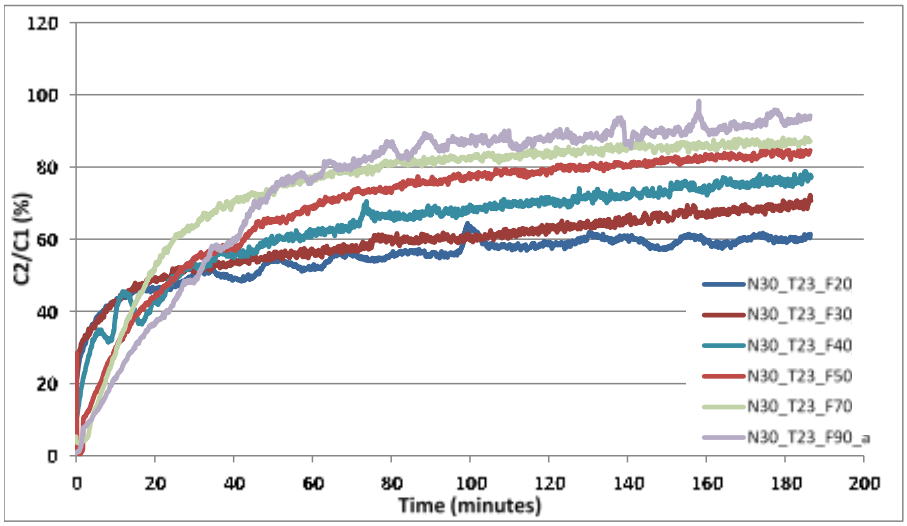

Fig.5: The comparison of the breakthrough curves for a varying air relative humidity from 20% to 90% at NO_2 gas concentrations of 30ppm and air temperatures of 23°C

As in the shown Figure 5, it is examined the adsorption behaviour of NO_2 gas at constant concentrations and constant temperature, but at different relative humidity. And, in this way, we can see the effect of different relative humditiy on adsorption. When it is observed at the end of the 185 minutes experiment, it reaches 60% saturation point at 20% relative humidity, constant temperature and concentration. While it is attained 70% saturation point at 30%, it successes 92% saturation point at 90% relative humidity. With the increasing relative humidity, the time to reach the saturation point shortens and the adsorption is realized

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quicker than before.This diagram also shows that if we have higher concentration range, then it is faster than lower concentration at the NO_2 adsorption at same temperature and relative humidity and concentration range between 5ppm and 30 ppm.

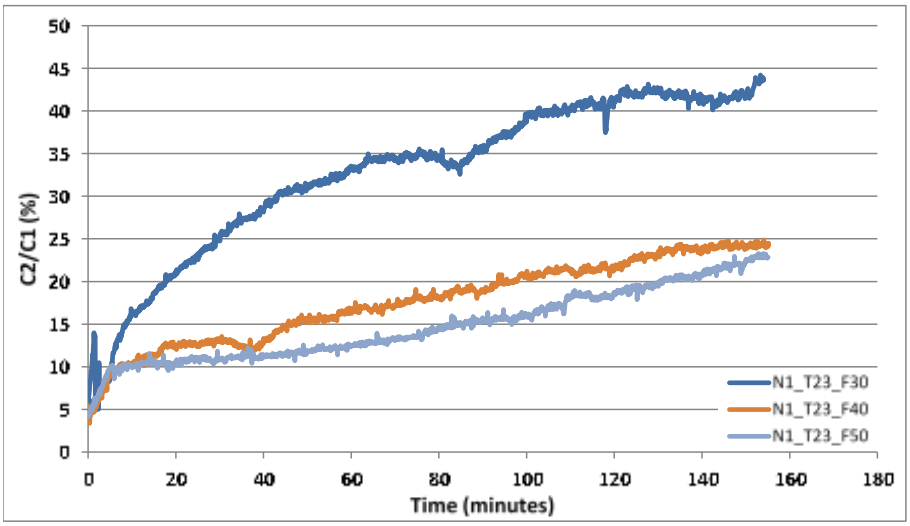

Fig.6: The comparison of the breakthrough curves for a varying air relative humidity from 30% to 50% at NO_2 gas concentrations of 1ppm and air temperatures of 23°C

Figure 6 indicates the adsorption behaviour of NO_2 gas at constant lower concentration, constant temperature and different relative humidity. Here it is taken as 1ppm of NO_2 gas concentration, the temperature as 23 °C and the relative humidity is taken as 30%, 40% and 50%. During 155 minutes experiment, while the time to reach the saturation point is 24% at 50% relative humidity, it is 45% at 30% relative humidity. Here we can see that the time to reach the saturation point increases together with the decreasing relative humidity. This is the direct opposite way of higher concentrations.

IV. CONCLUSION

In this study, NO_2 adsorption on active carbon was examined. We experienced that relative air humidity had not a remarkable influence on the adsorption in contrast to other gases like CO_2, SO_2 etc. Simultaneously, it was demonstrated how a change in temperature had little influence on NO_2 adsorption. After all, the NO_2 adsorption rate increased together with increased concentrations; however, it was analysed that adsorption rate decreased at lower concentrations together with increased relative humidity.

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