Adsorption of Nitrogen Dioxide (NO₂) for Different Gas Concentrations, Temperatures and Relative Humidities by using Activated Carbon Filter: An Experimental Study

Adnan Görgülü¹, Yıldız Koç², Hüseyin Yağlı², Ali Koç²∗

¹Siemens AG, Duisburg, Germany
²İskenderun Technical University, Hatay, Turkey
∗Corresponding author: Ali Koç, İskenderun Technical University, Faculty of Engineering and Natural Sciences, Department of Mechanical Engineering, 31200 İskenderun, Hatay, Turkey. Tel: +90 326 613 5600-2416
E-mail addresses: adnan.goerguehue@siemens.com, yildiz.koc@iste.edu.tr, huseyin.yagli@iste.edu.tr, ali.koc@iste.edu.tr

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 NO₂ 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 NO₂ evaluated from experiments have been used in the present study. Results show that the humidity has not a remarkable effect on the adsorption of NO₂; however, increasing relative humidity causes to a decrease in the capacity of the activated carbon for NO₂ adsorption. Additionally, NO₂ adsorption is exothermic, therefore it increases the air temperature.

Keywords— adsorption of NO₂, filtration, activated carbon, air pollution, NO₂.

I. INTRODUCTION

Our environment is polluted by many different noxious gases owing to the production of -among others-the corrosive exhaust gases NOₓ, NO+NO₂. 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 (NO₂). Besides, N₂ 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 NO₂ 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 NOₓ it is. In catalytically non-affected combustion processes, NO develops as a main product with a percentage of between 90-95% of NOₓ [1].

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

| Sources of NOₓ         | Proportion |
|------------------------|------------|
| Road transport         | 42%        |
| Energy production and distribution | 20%        |
| Energy use in industry  | 13%        |
| Commercial institutional and households | 14%        |
| Non-Road Transport     | 7%         |
NO\textsubscript{2} amount around the world poses a great danger to human health and environment. According to a study about NO\textsubscript{2} and other waste gases’ effect on human health by Chaloulakou et al. (2008), it is ascertained that the regions where the NO\textsubscript{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\textsubscript{2} has a triggering effect on cancer [4]. Moreover, Murphy et al. (1964) have seen that NO\textsubscript{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\textsubscript{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\textsubscript{2}. For this reason, minimising the emission of NO\textsubscript{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\textsubscript{2} is impossible to eliminate.

The reduction of NO\textsubscript{2} gas in the available systems is provided with adsorbed filtration systems. The adsorption term denotes to the cleaning of air from NO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} includes the reduction of NO\textsubscript{2} to NO actuated via the carbon surface oxidation [8]. Dantaset al. (2009) presented the adsorption behaviours of Carbon dioxide (CO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} adsorption and reduction on pitch-based activated carbon fibres. The experiment parameters were determined as 250-1000 ppm concentrations; O\textsubscript{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\textsubscript{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\textsubscript{2} at 70 °C temperature [12]. Nowicki et al. (2013) investigated the activated carbon character and adsorption properties. NO\textsubscript{2} gases were determined as adsorptive. Activated carbon surface area range was between 5 to 2,076 m\textsuperscript{2}/g and pore volume is between 0.03 and 1.25 cm\textsuperscript{3}/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\textsubscript{2} production indicating 44.5 mg NO\textsubscript{2} in dry states and 84.1mg NO\textsubscript{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\textsubscript{2} and SO\textsubscript{2}. The result indicated that the adsorption capacity of NO\textsubscript{2} gas was much more than the capacity of SO\textsubscript{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
the adsorption of NOx [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 NO2 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 NO2. As a result, it was seen that the adsorption rate of NO2 increased; on the other hand, NO release decreased [16]. Toops et al. (2006) analysed the adsorption of NOx over Pt/K/Al2O3 with different period of times and temperatures. While the adsorption of NOx is 6.4 μmol/m2 at 150 °C, the adsorption is observed as 1.8 μmol/m2 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 NH3 [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 tires 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 NO2 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 NO2 gas reduction with the help of activated carbon can be advanced via metal oxide nanoparticles infiltration into sorbents at ambient temperatures. The adsorption of NO2 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 NOx adsorption have been made; however, they are generally studying the NOx adsorption for limited parameters. In this study, adsorption capacity of NO2 by activated carbon is determined. During the experiment, the NO2 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 NO2, air temperature and relative humidity. NO2 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, NO2 is always found in a fluid phase at room temperature. In order to achieve its gas phase, NO2 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
The adsorption behaviour of the Nitrogen Dioxide (NO\textsubscript{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\textsubscript{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\textsubscript{2} gas concentration, F=50% air relative humidity](image)

The figure above shows the breakthrough curves for 18 °C, 23°C and 33°C at a 30 ppm NO\textsubscript{2} gas 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\textsubscript{2} gas concentration, F=50% air relative humidity](image)
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 noticeable change in the increase or decrease of temperature can not be seen at 20 ppm like in the 30 ppm.

As above it is shown in Figure 4, it is examined adsorption behaviour of NO2 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, 5 ppm, 10 ppm, 20 ppm, 30 ppm. The experiment time is 300 minutes. While it reaches 37% saturation point in 1 ppm of NO2 at the end of the 300 minutes, it reaches 84% saturation point in 20 ppm of NO2. And, it reaches 92% saturation point in 30 ppm of NO2 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.

As in the shown Figure 5, it is examined the adsorption behaviour of NO2 gas at constant concentrations and constant temperature, but at different relative humidity. And, in this way, we can see the effect of different relative humidity 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 successess 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.
quicker than before. This diagram also shows that if we have higher concentration range, then it is faster than lower concentration at the NO₂ adsorption at same temperature and relative humidity and concentration range between 5 ppm and 30 ppm.

Figure 6: The comparison of the breakthrough curves for a varying air relative humidity from 30% to 50% at NO₂ gas concentrations of 1 ppm and air temperatures of 23°C

IV. CONCLUSION

In this study, NO₂ 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 CO₂, SO₂ etc. Simultaneously, it was demonstrated how a change in temperature had little influence on NO₂ adsorption. After all, the NO₂ adsorption rate increased together with increased concentrations; however, it was analysed that adsorption rate decreased at lower concentrations together with increased relative humidity.

ACKNOWLEDGMENT

The authors are thankful to the Prof. Dr.-Ing Klaus Gerhard Schmidt, Dr.-Ing Uta Sager and Prof Dr.Habil - Ing Frank Schmidt due to their kind helps for experiments in the Institute of Process Engineering of the University of Duisburg-Essen.

REFERENCES

[1] European Environment Agency, Publications on Air Quality. (Accessed 19.11.2018). Source: https://www.eea.europa.eu/publications/#c7=en&c11=5&c14=&c12=&b_start=0.

[2] European Environment Agency, Nitrogen Oxides (NOx) Emissions Report. (Accessed in 18.11.2018). Source: http://www.eea.europa.eu/data-and-maps/indicators/eea-32-nitrogen-oxides-nox-emissions-1/assessment.2010-08-19.0140149032-1.

[3] Chaloulakou, A., Mavroidis, I., & Gavril, I. (2008). Compliance with the annual NO2 air quality standard in Athens. Required NOx levels and expected health implications. Atmospheric Environment, 42(3), 454-465.

[4] Al-Ahmadi, K., & Al-Zahrani, A. (2013). Spatial autocorrelation of cancer incidence in Saudi Arabia. International journal of environmental research and public health, 10(12), 7207-7228.

[5] Murphy, S. D., Ulrich, C. E., Frankowitz, S. H., & Xintaras, C. (1964). Altered function in animals inhaling low concentrations of ozone and nitrogen dioxide. American Industrial Hygiene Association Journal, 25(3), 246-253.

[6] Börger, G. G. (1989). Adsorption aus der Gasphase. Ingenieurwissenschaftliche Grundlagen und Technische Verfahren. Von W. Kast. VCH Verlagsgesellschaft, Weinheim 1988. XV, 279 S., geb. DM 220.00.–ISBN 3-527-26719-0. Angewandte Chemie, 101(5), 650-651.
[7] Mahzoul, H., Brilhac, J. F., & Gilot, P. (1999). Experimental and mechanistic study of NOx adsorption over NOx trap catalysts. *Applied Catalysis B: Environmental*, 20(1), 47-55.

[8] Zhang, W. J., Bagreev, A., & Rasouli, F. (2008). Reaction of NO2 with activated carbon at ambient temperature. *Industrial & Engineering Chemistry Research*, 47(13), 4358-4362.

[9] Dantas, T. L., Amorim, S. M., Luna, F. M. T., Silva Jr, I. J., de Azevedo, D. C., Rodrigues, A. E., & Moreira, R. F. (2009). Adsorption of carbon dioxide onto activated carbon and nitrogen-enriched activated carbon: surface changes, equilibrium, and modeling of fixed-bed adsorption. *Separation Science and Technology*, 45(1), 73-84.

[10] Bazan, A., Nowicki, P., & Pietrzak, R. (2016). Removal of NO2 by carbonaceous adsorbents obtained from residue after supercritical extraction of marigold. *Adsorption*, 22(4-6), 465-471.

[11] Gao, X., Liu, S., Zhang, Y., Luo, Z., Ni, M., & Cen, K. (2011). Adsorption and reduction of NO2 over activated carbon at low temperature. *Fuel processing technology*, 92(1), 139-146.

[12] Shirahama, N., Moon, S. H., Choi, K. H., Enjoji, T., Kawano, S., Korai, Y., ... & Mochida, I. (2002). Mechanistic study on adsorption and reduction of NO2 over activated carbon fibers. *Carbon*, 40(14), 2605-2611.

[13] Nowicki, P., Skubiszewska, P., & Pietrzak, R. (2013). NO2 removal on adsorbents prepared from coffee industry waste materials. *Adsorption*, 19(2-4), 521-528.

[14] Lee, Y. W., Kim, H. J., Park, J. W., Choi, B. U., Choi, D. K., & Park, J. W. (2003). Adsorption and reaction behavior for the simultaneous adsorption of NO–NO2 and SO2 on activated carbon impregnated with KOH. *Carbon*, 41(10), 1881-1888.

[15] Long, X. L., Cheng, H., Xin, Z. L., Xiao, W. D., Li, W., & Yuan, W. K. (2008). Adsorption of ammonia on activated carbon from aqueous solutions. *Environmental Progress*, 27(2), 225-233.

[16] Delianni, E., & Bandosz, T. J. (2010). Effect of carbon surface modification with dimethylamine on reactive adsorption of NO x. *Langmuir*, 27(5), 1837-1843.

[17] Toops, T. J., Smith, D. B., & Partridge, W. P. (2006). NOx adsorption on Pt/K/AI2O3. *Catalysis today*, 114(1), 112-124.

[18] Zhu, Z., Liu, Z., Liu, S., & Niu, H. (2006). Adsorption and reduction of NO over activated coke at low temperature. *Fuel*, 79(6), 651-658.

[19] Hofman, M., & Pietrzak, R. (2011). Adsorbents obtained from waste tires for NO2 removal under dry conditions at room temperature. *Chemical engineering journal*, 170(1), 202-208.