Vol. 8, No. 2, 2023

DYNAMICS OF CARBON DIOXIDE ADSORPTION BY CARBON NANOTUBES

Vira Sabadash[1], Jaroslaw Gumnitsky[1], Oleksiy Lopushansky[1], Oksana Matsuska[2], Anna Nowik-Zając[3]

[1]Lviv Polytechnic National University,
12, S. Bandery Str., Lviv, 79013,Ukraine
1Department of Ecology, S. Gzhytskyi National University of Veterinary Medicine and Biotechnologies,
50, Pekarska Str,. Lviv, 79010, Ukraine,
[3]Academy of Jan Dlugosz in Czestochów,
4/8, J. Washington Str., 42200, Częstochowa
virasabadash@gmail.com

https://doi.org/10.23939/ep2023.02.101

Received: 01.05.2023

© Sabadash V., Gumnitsky J., Lopushansky O., Matsuska O., Nowik-Zając A., 2023

Abstract. This article is devoted to the study of the carbon dioxide adsorption process. The relevance of using carbon nanotubes for adsorbing carbon dioxide from industrial emissions is that carbon nanotubes have a high surface area and can effectively interact with carbon dioxide molecules. In addition, they have high mechanical strength and chemical resistance, which makes them attractive for industrial use. Carbon nanotubes have the potential to reduce carbon dioxide emissions and reduce the negative impact on the environment. Using carbon nanotubes in the industry can help reduce greenhouse gas emissions and the environmental impact of burning fossil fuels. Purpose. The work aimed to study the prospects of using carbon nanomaterials to purify industrial emissions from carbon dioxide in a fluidized state. The scientific novelty of the topic "Dynamics of carbon dioxide adsorption by carbon nanotubes" is the study of the influence of temperature and gas velocity on the initial curves of CO_2 adsorption dynamics in the fluidized state.

Keywords: adsorption, greenhouse gases, adsorbent, carbon nanotubes.

1. Introduction

Carbon nanotubes are one of the most promising materials for storing and transporting carbon dioxide. Carbon nanotubes as sorbents are relevant due to their high surface area and unique properties. The study of the dynamics of adsorption by carbon nanotubes makes it possible to understand the mechanism of the process and to find optimal conditions for the effective purification of carbon dioxide. This is due to their high surface area and possible interaction with gas molecules due to adsorption properties. Adsorption is the process of retention of gas molecules on the surface of a solid body (Hyvlud et al., 2019).

Carbon nanotubes can adsorb carbon dioxide by increasing the number of active sites on their surface. At the same time, the concentration of gas molecules on the surface nanotubes increases the volume of adsorbed gas (Cinke et al., 2003).

One of the ways of increasing the active surface of carbon nanotubes is the creation of defects on their surface. Defects were formed due to changes in the structure of nanotubes, which leads to the appearance of new surface sites. These defects can be created by heat treatment, irradiation, or chemical exfoliation.

Another way to increase the surface area of carbon nanotubes is to add functional groups to their surface. This can be done using chemical methods, for example, the treatment of nanotubes with acids or a reaction with functional molecules.

Carbon dioxide adsorption by carbon nanotubes can be used to store carbon dioxide produced by work industrial enterprises (Peng et al., 2021).

A review of literature sources on the adsorption of carbon dioxide by carbon nanotubes shows that this

For citation: Sabadash, V., Gumnitsky, J., Lopushansky, O., Matsuska, O., Nowik-Zając, A. (2023). Dynamics of carbon dioxide adsorption by carbon nanotubes. *Journal Environmental Problems*, *8*(2), 101–107. DOI: https://doi.org/10.23939/ep2023.02.101

issue is the subject of many studies in the scientific community.

In the article "Carbon dioxide removal through physical adsorption using carbonaceous and non-carbonaceous adsorbents: a review ", the authors are considered the main aspects adsorption of carbon dioxide gas on carbon nanotubes. They are investigating influence parameters such as temperature, pressure, size and shape of nanotubes on adsorption. The article also considers using carbon nanotubes to store carbon dioxide.

And the second considered different methods of creating carbon nanotubes and their use as materials for storing carbon dioxide. They describe the main methods of synthesis of nanotubes and their chemical modification, which increases their efficiency in carbon dioxide gas adsorption (Abd et al., 2020).

In the article "Chemically modified carbonaceous adsorbents for enhanced CO_2 capture: A review", the authors investigate the possibilities of modifying carbon nanotubes to increase their efficiency in carbon dioxide adsorption. They considered different methods of functionalization nanotubes and described the effectiveness of using functionalized carbon nanotubes in the resp storage of carbon dioxide gas (Cinke et al., 2003).

So, a review of literary sources shows a high interest in the problem of carbon dioxide adsorption.

A review of the literature shows that many types of sorbents can be used for carbon dioxide adsorption. Some of them were discussed below.

Activated carbon. Activated carbon is one of the most widely used sorbents for carbon dioxide adsorption. Its high surface area and porosity ensure effective gas adsorption.

Silica gel. Silica gel is a chemically resistant material with a high surface area. He can be used as a sorbent for carbon dioxide adsorption in different conditions (Park et al., 2020).

Zeolites. Zeolites are microporous materials with a complex structure that provides high surface area and porosity. They can be used to adsorb carbon dioxide and other gases.

Metal-organic frameworks. Metal-organic frameworks (MORs) consist of metal ions and organic ligands. They have a big superficial area and porosity, which allows them effectively adsorb carbon dioxide [7]. (Wijaya, Lee, 2020). I am a technologist producing materials with a metal-organic framework (MOK) that can be used to produce sorbents for the adsorption of carbon dioxide. It was found that this sorbent has high efficiency and can be used to reduce emissions of greenhouse gases in industry.

Carbon nanomaterials. Carbon nanomaterials, such as carbon nanotubes and graphene, have high surface area and porosity, which allows them to efficiently adsorb carbon dioxide.

Polymer sorbents. Polymeric sorbents can be made from different polymers and matrices and can be designed for different types of adsorption, including carbon dioxide. For example, polymer sorbents based on polyacrylonitrile and its derivatives can be effective for carbon dioxide adsorption (Arista, 2023).

Modified sorbents. Modified sorbents can be made of different materials, such as activated carbon, silica gel, or zeolites, and modified to improve their carbon dioxide adsorption efficiency. For example, modified silica gels can contain amino derivatives that provide interaction with carbon dioxide.

Hybrid sorbents. Hybrid sorbents can be made of different materials, such as polymers and mineral sorbents, and can be effective for carbon dioxide adsorption. For example, hybrid sorbents based on polymer and zeolite can have increased efficiency adsorption of carbon dioxide gas (Li et al., 2023).

In summary, many sorbents can be used to adsorb carbon dioxide. Each of these types has its advantages and limitations, so the choice of the optimal sorbent depends on specific situations and conditions of use. The last five years were rich in research in the field of the adsorption of carbon dioxide and the development of effective sorbents. Some of the most significant research during this period:

Group researchers developed a new sorbent based on mixing green tea and the mineral montmorillonite. It was found that this sorbent has increased the efficiency adsorption of carbon dioxide and can be used to reduce emissions of greenhouse gases in industry (Wang et al., 2021).

Group researchers from the University of Pennsylvania in the USA developed a new methodology for evaluating the sorbents' efficiency for carbon dioxide adsorption. This method allows us to evaluate not only sorbent efficiency but also the release of carbon dioxide with its regeneration (Gautam, Mondal, 2023).

It is also known about the use of sorbents based on graphene and ions calcium _ It was found that this sorbent has increased efficiency adsorption of carbon dioxide and can be used to reduce emissions of greenhouse gases in the industry (Wang et al., 2023).

It is known that the development of a sorbent based on palm oil and activated coal was found to have increased efficient carbon dioxide gas adsorption (Hayawin et al., 2023).

Mesoporous materials silicon also can be used as sorbents for carbon dioxide adsorption. It was found that this sorbent has high efficiency and high technical and economic indicators that make it an inexpensive alternative to synthetic ones zeolites (Yuan et al., 2023).

Researchers (Quan et al., 2023) developed a new sorbent based on a mix of graphene and biomass. It was found that this sorbent has increased the efficiency adsorption of carbon dioxide and can be used to reduce emissions of greenhouse gases in industry.

Of them, this research is an essential contribution to the industry adsorption of carbon dioxide and the development of effective sorbents. Thanks to as a result of this research managed to develop new technologies and materials that can be used to reduce greenhouse gas emissions in industry and other spheres of activity. It is expected that even more sophisticated and progressive research will be conducted.

2. Experimental part

Methodology research of the process of carbon dioxide adsorption. Selection of the sorbent. At the beginning of the study, the sorbent was selected, considering its properties and efficiency of carbon dioxide adsorption.

Sample preparation: The sorbent samples should be prepared and cleaned before starting the study.

Determination of the temperature range: determination of the temperature range was carried out for the carbon dioxide adsorption study, which depends on temperature and pressure.

Determination of concentration. We determined the initial concentration of carbon dioxide and other parameters such as humidity and sample size. We carried out a determination of the sorption capacity of the studied adsorbent.

Analysis of results was carried out by data processing and analysis of results, including the determination of adsorption kinetics, isotherms and other parameters.

The volumetric method of studying carbon dioxide adsorption is one of the most common and accurate methods of measuring the volumetric adsorption of gas on the surface of solid materials. Below is the method of carrying out the study of the adsorption of carbon dioxide by the volumetric method (Gautam, Mondal, 2023).

Equipment:

chamber for adsorption;

vacuum pump ;

manometers for measuring gas pressure;

gas pressure regulator;

manometer for measuring gas pressure in the tank;

a computer with software for processing the results.

Characteristics of the sorbent.

Table 1

Technical characteristics of the sorbent Multi-Walled Carbon Nanotubes (long) Powder 5-15 nm MWCNTs

Name product	**Multi-walled carbon nanotubes (long)**
External appearance	Black powder
Outer diameter (nm)	5...15 nm
Length, µm	10-30 microns
Purity, %	>95 %
SSA	>200 m2/h
EC = Electrical conductivity (s/cm)	>100
Density is specific	0.27 g/cm3
Density	~2.1 g/cm3

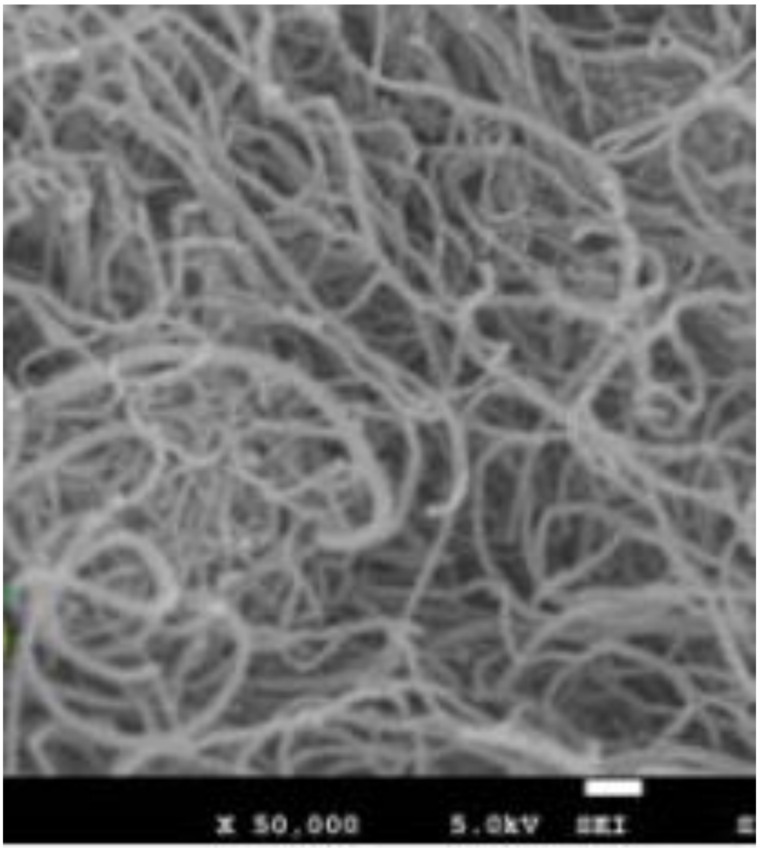

Fig. 1. Photomicrograph of the sorbent 1x50

Research procedure:

All instruments must be checked for proper operation and calibrated before beginning the study.

A portion of the sorbent was weighed and placed in the adsorption chamber.

The sample size must be sufficient to obtain accurate results and ensure adequate contact between the sample surface and the gas.

A vacuum pump was started to create a discharge in the chamber.

The supply of carbon dioxide to the tank was started, and the gas pressure regulator was adjusted to the required level.

The chamber was filled with gas at a certain temperature and pressure. In the experimental conditions, at the beginning and end of the study, the pressure and temperature in the chamber and in the tank were recorded after reaching equilibrium.

By reducing the gas pressure in the tank, the gas volume in the chamber was fixed for each pressure value. The processing of the obtained adsorption research data includes the construction of adsorption isotherms, which is the dependence of the amount of adsorbed gas on the pressure at a certain temperature. Isotherms allow us to determine the maximum amount of gas that a given porous substance can absorb at a given temperature and pressure, as well as adsorption characteristics such as equilibrium and detection constants and possible mechanisms of adsorption.

3. Results and Discussion

Experiments were held on experimental installation, the main device was a quartz tube with a lower perforated grid with a heating and thermostatic system. The system allows the creation of a fluidized bed of adsorbent. A gas mixture of the required concentration was supplied from air and CO_2 cylinders to the mixer. Volume flow rates of gases were set and recorded by rotameters, and the concentration of CO_2 in the initial mixture and at the exit from the apparatus using a measuring device Finor 710 of the Mahiak company, which is connected to a computer. The measurement system provided both numerical analysis results and their graphical interpretation in the form of an output curve. The device works in the CO_2 concentration range of 0–100 % and in the range of 0–20 %, with an accuracy of +/- 1 %. The parameter for evaluating the adsorption activity of zeolite was the value a, which represents the mass of adsorbed CO_2 per

100 g of zeolite. The initial gas mixture corresponded to the composition of flue gases of power plants and contained 15 % vol. CO_2. A certain amount of zeolite was loaded into the adsorber. The system was brought to the specified temperature and hydrodynamic mode, after which the gas supply was turned on, and the time was fixed with a stopwatch. The duration of the experiment was chosen in such a way as to ensure complete saturation of this amount of adsorbent. Integration of the initial curve to the saturation state makes it possible to determine the static activity of the adsorbent for the given temperature conditions.

The experimental data are presented graphically in the form of the dependence of the adsorption activity of zeolite on the adsorption time *t* for three temperature values: 20, 50, and 100 ^{0}C. The choice of such high temperatures, which is not typical for adsorption, is explained by the fact that in energy, gases have significant temperatures, which would require significant costs for their cooling. At the same time, as mentioned above, it is necessary to absorb only a certain part of CO_2.

The back through curves of CO_2 adsorption dynamics in the fluidized state depending on the temperature (20 °C, 50 °C and 100 °C) can be presented in the form of graphs (Fig. 2).

The obtained dependences have the form of characteristic initial adsorption curves. An increase in temperature leads to a decrease in adsorption capacity.

It can be seen from the graphs that as the temperature increases, there is a decrease in the adsorption capacity of coal materials to CO_2. At the same time, the higher the temperature, the faster desorption occurs. It can also be seen that at low temperatures (20 °C), the adsorption capacity of coal materials for CO_2 is higher compared to high temperatures (50 °C and 100 °C). From the presented dependence (Fig. 2), it follows that the saturation time of the adsorbent during the process in the fluidized state is within 40–60 seconds, which is essential when calculating the adsorber, where this time will be taken as the time the adsorbent grains stay in the apparatus.

Therefore, the backthrough curves of CO_2 adsorption dynamics in the pseudo-liquefied state depending on temperature indicate the dependence of the adsorption capacity of coal materials on temperature.

Fluidization speed on the adsorption capacity of natural zeolite showed that this value depends little on the gas speed. At the same time, there is a significant temperature dependence (see Table 2).

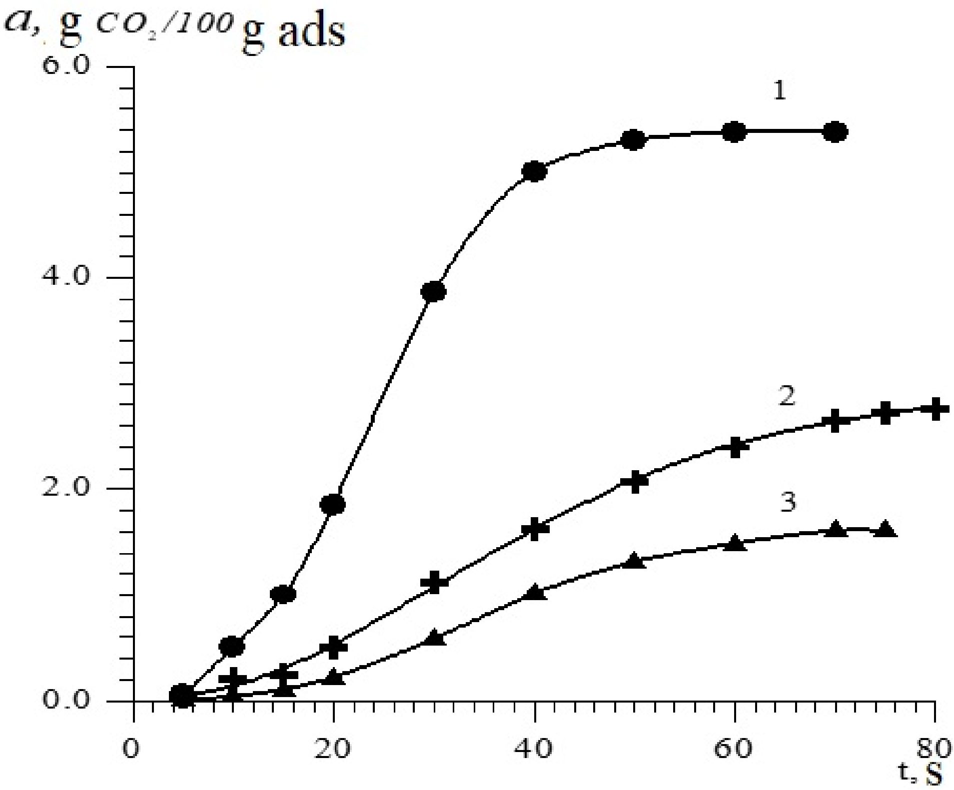

Fig. 2. Breakthrough curves of dynamics adsorption of CO_2 in pseudo liquefied in a state of dependence from temperature: 1 - 20°C; 2 – 50°C; 3– 100°C

Table 2

Adsorption activity of carbon nanotubes to CO_2

Speed of gas, m /s	Temperature, ^{0} C					
	20	50	70	100	120	150
0.064	5.38	2.76	1.81	1.6	1.31	1.19
0.08	5.18	2.15	1.68	1.59	1.4	1.12
0.16	5.37	2.06	1.68	1.49	1.68	1.12
Average value	5.31	2.31	1.72	1.56	1.46	1.14

The mathematical description of this process bases on the system of differential equations of molecular diffusion inside the adsorbent grain written for spherical particles. The system involves the combination of mass flows in the volume of the pores of the adsorbent and on its surface, which makes it possible to introduce one effective diffusion coefficient. The system was supplemented with initial and boundary conditions. This system is given, for example, in (Peng et al., 2021). The system is supplemented with a material balance equation, which for the conditions of the process in a fluidized bed of the adsorbent when the apparatus acts as a reactor of ideal mixing in the solid phase and ideal displacement in the gas phase, has the form

$$V_c\left(c_{10}-c_1\right)=\frac{m}{\rho_{ad}}\varepsilon\,\overline{c}_2, \qquad (1)$$

where V_c - second gas consumption, m ^{3} /s; c_{10}, c_1 - initial and final CO_2 concentration; m - mass of adsorbent, kg; ρ_{ad} - density, kg /m ^{3}; - average concentration of CO_2 $\overline{c}_2$ by grain ; ε - porosity

The experimental data were compared with the theoretical solution, which for the average value, $\overline{c}_2$ has the form

$$\frac{\overline{c}_2}{\beta c_{10}}=\frac{1}{1+a}-\sum_{n=1}^{\infty}\frac{6e^{-\mu_n^2\tau}}{9a^2+\mu_n^2+9a} \qquad (2)$$

where β is the tangent of the angle of inclination of the isotherm; $a=\frac{m\varepsilon}{V\rho_{ad}}$ μ_n - the roots of the characteristic equation; $\tau=D_2 t/R^2$ - dimensionless time.

The use of a computer method of comparing experimental data with theoretical data according to equation (2) made it possible to establish that for zeolite particles with a diameter of 1 mm, the value of the effective coefficient of internal diffusion is 2.75*10 $^{-10}$ m^2 /s.

Carbon dioxide adsorption by carbon nanotubes is one of the potential methods of reducing greenhouse gas emissions in the industry. However, much work remains to develop efficient and sustainable carbon nanotube-based sorbents.

One of the areas of research is improving the properties of carbon nanotubes by changing their structure and chemical functionalization (Cinke et al., 2003; Peng et al., 2021). This mathod can help to increase their efficiency and resistance to high temperatures and other operating conditions.

Also, it is necessary to conduct more detailed studies on the mechanism of carbon dioxide adsorption by carbon nanotubes to understand the processes at the molecular level and ensure the efficient operation of sorbents. The volumetric research method is a powerful tool for studying the process of carbon dioxide adsorption and the characteristics of sorbents. It allows for obtaining accurate results and detailed data on the adsorption process, which allows for improving the quality and efficiency of the development of sorbents to reduce carbon dioxide emissions and combat climate change (Yuan et al., 2023).

Other issues that require attention include the recyclability and recycling of carbon nanotubes after their use. It is necessary to develop recovery and recycling methods that will be economically beneficial and environmentally safe (Wang et al., 2023).

Overall, research into using carbon nanotubes for adsorbing carbon dioxide from industrial emissions has great potential for reducing greenhouse gas emissions and the negative impact on the environment. However, for the effective use of this method, much work is still needed to improve the properties of carbon nanotubes.

4. Conclusions

Therefore, carbon nanotubes are potential materials for adsorbing carbon dioxide from industrial emissions. They have a high surface area and can be modified to improve their performance. Using different types of carbon nanotubes and sorbents can lead to improved adsorption properties and a decrease in carbon dioxide content in the atmosphere.

The research results showed that the adsorption efficiency depends on parameters such as the sorbent type, particle size, temperature and pressure. The manometric and volumetric methods of adsorption research allows for measuring the amount of carbon dioxide adsorbed on the surface of the sorbent.

Nanotubes and sorbents used for carbon dioxide adsorption were analyzed. We discovered that multi-layered carbon nanotubes coated with iron oxide are effective for removeing of carbon dioxide from the air, as they have a high surface area and adsorb gas molecules well.

The next steps in the research will include studying the effect of other factors, such as humidity, pH and other parameters, on adsorption efficiency. Also, the obtained results can be used to purify real industrial emissions from CO2 with the help of sorbents such as carbon nanotubes.

References

Abd, A. A., Naji, S. Z., Hashim, A. S., & Othman, M. R. (2020). Carbon dioxide removal through physical adsorption using carbonaceous and non-carbonaceous adsorbents: a review. *Journal of Environmental Chemical Engineering*, *8*(5), 104142. doi: https://doi.org/10.1016/j.jece .2020.104142

Arista, P. C. (2023). Peranan Microorganisms Pendegradasi Plastik: Tinjauan Biodegradation Plastik, Mekanismenya, serta Microorganisms yang Berperan. *Journal Pro-Life*, *10*(1), 743–755. doi: https://doi.org/10.33541/ jpvol6Iss2pp102

Cinke, M., Li, J., Bauschlicher Jr., CW, Ricca, A., & Meyyappan, M. (2003). CO_2 adsorption in single-walled carbon nanotubes. *Chemical physics letters*, *376*(5–6), 761–766. doi: https://doi.org/10.1016/S0009-2614(03)01124-2

Gautam, A., & Mondal, M. K. (2023). Review of recent trends and various techniques for CO_2 capture: Special emphasis he biphasic amine solvents. *Fuel*, *334*, 126616. doi: https://doi.org/10.1016/j.jclepro.2023.136568

Quan, C., Zhou, Y., Wang, J., Wu, C., & Gao, N. (2023). Biomass-based carbon materials for CO_2 capture: A review. *Journal of CO_2 Utilization*, *68*, 102373. doi: https://doi.org/10.1016/j.jcou.2022.102373

Hayawin, Z. N., Syirat, Z. B., Ibrahim, M. F., Faizah, J. N., Astimar, A. A., Noorshamsiana, A. W., & Abd-Aziz, S. (2023). Pollutants removal from palm oil mill effluent (POME) final discharge using oil palm kernel shell activated carbon in the up-flow continuous adsorption system. *International Journal of Environmental Science and Technology*, *20*(4), 4325–4338. doi: https://doi.org/ 10.1007/s13762-022-04268-8

Hyvlud, A., Sabadash, V., Gumnitsky, J., & Ripak, N. (2019). Statics and kinetics of albumin adsorption by natural zeolite. *Chemistry & Chemical Technology*, *1*(13), 95–100. doi: https://doi.org/10.23939/chcht13.01.095

Li, J. Y., Lin, Y. T., Wang, D. K., Tseng, H. H., & Wey, M. Y. (2023). The planetary cross-linked structure design of hybrid organosilica membrane by amine-driven polymerization for CO_2 separation. *Journal of Cleaner Production*, *398*, 136568. doi: https://doi.org/10.1016/j.jclepro.2023.136568

Park, D., Hong, S. H., Kim, K. M., & Lee, C. H. (2020). Adsorption equilibria and kinetics of silica gel for N_2O, O_2, N_2, and CO_2. *Separation and Purification Technology*, *251*, 117326. doi: https://doi.org/10.1016/j.seppur.2020.117326

Peng, X., Vicent-Luna, J.M., & Jin, Q. (2021). Water–gas shift reaction that capture carbon dioxide and separately hydrogen he single-walled carbon nanotubes. *ACS Applied Materials & Interfaces*, *13*(9), 11026–11038. doi: https://doi.org/10.1021/acsami.1c00145

Wang, L., Rinklebe, J., Tack, F. M., & Hou, D. (2021). A review of green remediation strategies for heavy metal contaminated soil. *Soil Use and Management*, *37*(4), 936–963. doi: https://doi.org/10.1111/sum.12717

Wang, F., Gu, Y., Zha, J., & Wei, S. (2023). Synthesis of Graphene Quantum Dots Enhanced Nano $Ca(OH)_2$ from Ammoniated $CaCl_2$. *Materials*, *16*(4), 1568. doi: https://doi.org/10.3390/ma16041568

Wijaya, D.T., & Lee, C.W. (2022). Metal-Organic framework catalysts: A versatile platform for bioinspired electrochemical conversion of carbon dioxide. *Chemical Engineering Journal*, *137311*. doi: https://doi.org/10.1016/ j.cej.2022.137311

Yuan, J., Liu, X., Wang, H., & Li, X. (2023). Evaluation and screening of porous materials containing fluorine for carbon dioxide capture and separation. *Computational Materials Science*, *216*, 111872. doi: https://doi.org/10.1016/ j.commatsci.2022.111872