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EFFICIENCY OF ALUMINIUM-BASED NANOADSORBENTS FOR CARBON MONOXIDE ADSORPTION: MINI-REVIEW

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Background: Today, scientists are exploring the best technology to improve air quality for human health, which is especially important in conditions of actively developing technogenic activity and following emergencies. Planning and development of towns and regions should include adequate gas cleaning to minimize the amount of CO in the atmosphere, as this gas is responsible for the ozone layer's depletion and other atmospheric negative impacts. **Objectives:** The current study aims to explore some of the features and the characteristics of such nanoadsorbents for the CO adsorption from atmospheric air, with an emphasis on their potential prospects. **Methods:** A review of studies based on publications in peer-reviewed scientific journals was conducted. Mostly the most recent publications and the most cited ones were taken into account. **Results:** It has been established that among several phases (δ-, η-, θ-, and γ-) of alumina, γ-alumina that is recognized as transition alumina is the suitable choice for capturing CO gas because it has a large surface area, an excellent catalytic activity, pore-volume. The roll-coating method leads composite films to have special properties, such as a high mechanical property and surface area, simplicity to produce, and needless to pre-treated before use. It was found that the maximum adsorption efficiency for different alumina-doped adsorbents is about 94 – 98%. **Conclusion:** The roller coating method for the production of composite films has proven to be a simple, cheap and reliable method for producing an effective nanoadsorbent. Alumina-doped adsorbents deserve serious attention for further development, since they are quite capable of competing in efficiency, ease of manufacture and cost with commercial adsorbents available on the market.

Keywords: CO adsorption; atmosphere; aluminium-based materials; nanoadsorbents; composite films.

INTRODUCTION

Carbon monoxide (CO), which is an odourless, colourless, and flavourless gas, is responsible for global warming (Cleland, 2013). CO gas can be released by natural ways like bushfires, volcanoes (Wang et al., 2023) and also by human activities, that includes fossil fuel use, activities of industrial enterprises, vehicle exhaust and even cigarette smoke (Yeom et al., 2018; Chen et al., 2018). The release of CO possesses severe impacts on the environment, namely ozone depletion, climate change, global warming, and acid rain (Bobbitt et al., 2017). Besides, it also causes dizziness, asthma, and death arise from CO emission in the atmosphere with high concentrations (Mozaffari et al., 2020).

Consequently, the evolution of effective techniques to adsorb CO toxic gas has attracted significant interest. Investigations have been conducted on CO removal by metal-organic frameworks (Yeom et al., 2018; Glover et al., 2011), mesoporous silica (Hanif et al., 2015), and mesoporous alumina (Yeom et al., 2018) because of their particular properties, namely large surface area, porous form, pore size distribution, and wall thickness (Yeom et al., 2018; Hung & Bai, 2008). Furthermore, their uniform porosity, wide joint pores, and the large volume of the pore are noticeable to capture molecules of gas selectively (Yeom et al., 2018; Yin et al., 2007). Considering some scientific publications like (Thote et al., 2012; Walcarius & Mercier, 2010), mesoporous alumina has been recently the centre of attention among metal-organic frameworks as well as mesoporous silica due to its effectiveness in gas removal. Notwithstanding its prominent properties, the progress of adsorption technology for CO capture is of great interest and more systematic study and optimization is required (please add reference, you can keep Mozaffari et al 2020, Yuliusman et al 2020).

Metal-organic frameworks are also well-known in the gas adsorption process. Munusamy et al. (2012) reported the capability of MIL-101(Cr) to capture CO gas. MIL-101(Cr) is the metal organic framework with a large surface area, large pore volume, and harmonic pore size, which can capture a wide range of toxic gases, namely carbon monoxide, carbon dioxide, methane, and so on (Munusamy et al., 2012; Chowdhury et al., 2009). Given the adsorption capacity of CO gas obtained by Munusamy et al. (2012), adsorption capacity had a decreasing trend with increasing temperature, in which the adsorption capacity at 288 k, 303 k, and 313 k was 1.13, 1.00, and 0.89 mmol g^{-1}, respectively.

Activated carbon (AC) is another known material to capture CO gas because of its high adsorption capacity. Moreover, ACs are cost effective, flexible, and ease of use compared to other counterparts of CO gas adsorbents. Yuliusman et al. (2020) studied the ability of activated carbon with different lengths of the tube to capture CO gas, in which CO adsorption percentage with a tube length of 3 cm and 4 cm was 88.87% and 92.47%.

The well-known potential catalysts are noble metal-metal oxide or metal oxide-metal oxide for oxidation of carbon monoxide. However, they have had less attraction in gas adsorption in spite of their powerful performance because of their expensiveness and low accessibility in the market (Cai et al., 2021).

Considering the significant interest of scientists in the design and generation of effective aluminium-based nanoadsorbents, the purpose of this study is to explore some of the features and the characteristics of such nanoadsorbents for the CO adsorption from atmospheric air, with an emphasis on their potential prospects.

MATERIALS AND METHODS

A review of research resources and research techniques was conducted based on publications in peer-reviewed scientific journals. Since the current study is a mini-review, the most recent and most cited publications were predominantly taken into account.

During the review, it was observed that researchers were interested in developing a significant number of adsorbents to reduce the concentration of CO gas in the atmosphere. In many research studies, both experimental and theoretical aspects were considered to explore the adsorption capability of every adsorbent.

RESULTS AND DISCUSSIONS

Focus on the adsorbent composition

Liquid adsorbents for carbon monoxide have a smaller capacity, require special equipment for the absorption process and special methods for purifying the gas from absorbent vapours. Therefore, from a technological point of view, processes of absorption of carbon monoxide by solid substances are more practical. The most commonly used materials for such solids are those containing transition metal compounds (Lopez et al., 2021; Muñoz-Senmache et al., 2020). This allows carbon monoxide molecules to bind to the surface of the adsorbent.

The prospects of such adsorbents are limited due to low selectivity to carbon monoxide, which is accompanied by a significant decrease in their effectiveness in the presence of other compounds in the atmosphere, such as hydrogen sulphide, nitrogen oxides, and organic compounds. Due to contamination of adsorbents in this way, they are almost not regenerated. The use of transition metal compounds also increases the cost of gas purification and leads to the emergence of a large amount of waste with low concentrations of toxic elements, which are difficult to further dispose of.

Various researchers are discovering that increased CO adsorption efficiency can be achieved by using materials with a special zeolite structure. Although this raises problems with the location of active adsorption centres in the structure of zeolites. With an increase in the number of active compounds, the influence of the microporous structure on adsorption decreases, and with an increase in the amount of cellular structure, the overall adsorption activity of the material decreases. This problem can be partially solved by using various structural components as an additive to the adsorbent material (Thote et al., 2012; Lehman & Larsen, 2014).

The use of a mixture of zeolite and active carbon as the main component of the adsorbent demonstrates good performance (Bastos-Neto et al., 2011) due to the absence of alloying additives. Moreover, the high adsorption capacity is due to the fact that active carbon particles are both a carrier of the active substance and part of the structure of the adsorbent.

It was found that alumina-based materials can be considered advantageous adsorbents due to their uniform porous form, pore size, and interconnected channels inside their structure (Rengaraj et al., 2007). Among several phases (δ-, η-, θ-, and γ-) of alumina, γ-alumina that is recognized as transition alumina is the top choice for capturing CO gas because it has a large surface area, an excellent catalytic activity, pore-volume (Macêdo et al., 2007; Busca et al., 2014; Peng et al., 2018). Besides, alumina possesses high stability and durability which are its noticeable properties (Chen et al., 2011). The effect of type of electrolyte on the size and regularity of pores by anodization was also reported (Keshavarz et al., 2013). However, adding a small amount of a dopant enhances surface area as well as surface defect density (Zhou et al., 2018), which results in the improvement of the performance of adsorption (Chen et al., 2018).

Another potential adsorbent that attracted research interest is tin (IV) oxide due to its large bandgap, durability, high sensitivity, inexpensiveness, and high adsorption ability to capture CO gas (Kolmakov et al., 2003; Durrani, 2006; Chen et al., 2018). In addition, Canto et al. (2012) and Wiltner et al. (2008) have reported that transition-metal dopants, like nickel, increase the adsorption process of CO gas.

Zeolite is a crystalline aluminosilicate possessing uniform size, controllable pore size, large surface area, and large level of selectivity (Ackley et al., 2003; Wang et al., 2011; Bastos-Neto et al., 2011, Khalegh et al., 2020) which leads to being known as CO adsorbent.

The promise of adsorbents with this composition lies in their high adsorption capacity and the absence of alloying additives. However, at the same time, due to the significant difference in the physical and chemical properties of the components of such a composite material, this composite does not have very high mechanical properties.

The efficiency of adsorbents can be increased by using materials with a special zeolite structure. However, their progressive use is hampered by difficulties associated with the location of active adsorption sites in the structure of zeolites. With an increase in the amount of active compounds, the influence of the microporous structure on adsorption decreases, and with an increase in the amount of cellular structure, the overall adsorption activity of the material decreases.

The use of different structural components partially solves this problem by adding another structural component (Martens et al., 2014; Lehman & Larsen, 2014).

Therefore, Mozaffari et al. (2020) have suggested that alumina-doped with zeolite, or tin oxide, or nickel may enhance CO adsorption capacity. These problems can be overcome in order to create a progressive adsorbent by mixing zeolite and gamma aluminium oxide powders. A particularly positive effect can be achieved with a mass ratio of components of 0.7:1 to 1.4:1 for zeolite powder with a pore diameter of 15 – 25 nm (with particles of 60 – 100 nm) and gamma aluminium oxide powder with a pore diameter of 6 – 13 nm (with particles 15 – 45 nm) respectively.

These advantages can be justified as follows:

– uniform distribution of zeolite and aluminium oxide particles in the final material is achieved due to the use of particles of the same size;

– the highest specific adsorption capacity relative to carbon monoxide molecules is achieved due to the appropriate particle pore size;

– the simultaneous use of zeolite and aluminium oxide allows you to combine the high adsorption capacity of zeolite with selectivity towards carbon monoxide and the stability and mechanical properties of aluminium oxide;

– the environmental friendliness of the adsorbent increases and there are no alloying additives in the form of transition metal compounds, which makes such an adsorbent more environmentally friendly. Sixth, the use of these components makes the adsorbent more resistant to poisoning by other gases and easier to regenerate.

Experimental studies by Mozaffari et al. (2020) have shown that the adsorption capacity is determined by the ratio of the proposed components. More zeolite results in a larger total adsorption capacity, and more alumina results in stronger adsorption of carbon monoxide and therefore reduces the minimum equilibrium concentration of carbon monoxide in the gas.

When the zeolite: aluminium oxide ratio decreases to less than 0.7:1, the equilibrium degree of carbon monoxide in the mixture decreases to 1 mg/L, but at the same time the adsorption capacity

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is reduced by almost half. Conversely, when the zeolite: aluminium oxide ratio increases to more than 1.4:1, the adsorption capacity almost doubles, but at the same time the equilibrium degree of carbon monoxide in the mixture increases to 15 mg/L. Therefore, the optimal values of this parameter are (0.7 – 1.4):1.

Focus on adsorbent technology

The review shows that adsorption processes are most simple on solid materials. Granular materials or composite materials with an active layer applied to an inactive material are most often used as such materials. The future prospects for the use of granular sorbents are limited by their small specific surface area and high hydraulic resistance. Moreover, hydraulic resistance increases with increasing specific surface area. The problem of increasing hydraulic resistance can be solved by synthesizing composite film sorbents on some carrier. The transition metal thin films have a wide range of applications for various purposes (MacManus-Driscoll et al., 2020; Allag et al., 2024). The main advanced advantages of thin film technologies are the ease of preparation and the use of flexible substrates (Osuwa et al., 2009). The most promising adsorbents are composite materials, for which aluminosilicates, zeolites, aluminium oxide or mixtures thereof are used as carriers, and transition metal compounds are used as applied active substances (Hjiri et al., 2014; Poolakkandy & Menamparambath, 2020). But at the same time, problems arise with the adhesion of the active layer to the carrier, its strength, and differences in the physical properties of the carrier (MacManus-Driscoll et al., 2020), which can be accompanied by peeling and erosion in the flow of liquid and gas. By using chemical and electrochemical methods to form an active adsorption layer on stronger and more resilient materials, the likelihood of delamination and erosion can be significantly reduced. However, the problem of adhesion of the active layer to the carrier still remains.

Based on the analysis of published literature sources in this field of knowledge, alumina-doped zeolite, alumina doped-tin (IV) oxide, alumina doped-nickel, alumina doped-nickel-tin (IV) oxide composite films were prepared by the roll-coating method (Mozaffari et al., 2020, Mozaffari et al., 2021). The roll-coating method leads composite films to have special properties, such as a high mechanical property and surface area, simplicity to produce, and needless to pre-treated before use. Finally, four coated substrates were attached to fabricate a tunnel-like adsorbent, which was expected the molecules of CO are easily trapped, resulting in the enhancement of adsorption capacity as well as efficiency (Mozaffari et al., 2020, Mozaffari et al., 2021).

For the investigation of gas adsorption ability, designed and manufactured an experimental set-up, containing a two-way-valve container in which an adsorbent was placed. One valve is attached to a part installing a capsule of CO gas, which the right valve side is attached to a part installing a gas analyser. The use of this device for synthesizing a composite using the roller method made it possible to obtain a CO adsorbent with the following advantages:

– uniform physical properties;

– the use of a suspension of particles promotes uniform distribution of particles of the adsorbent layer of different compositions on the carrier;

– a large number of intermolecular bonds between particles, which provides a strong and uniform layer of active substances;

– as a result, the structure of the active layer has the highest density with open pores, optimal for the penetration of organic substances due to the gradual evaporation of the solvent, and as a consequence of an increase in the density of the layer; which is due to the capillary effect and the action of surface tension forces.

Discussion

Studies (Mozaffari et al., 2020, Mozaffari et al., 2021) found that for adsorbents doped with alumina, there is an increase in the contact surface area between adsorbent particles and CO molecules. This is clearly demonstrated by the concentration diagrams of adsorbed CO gas, which indicates an effective adsorption process and high adsorption capacity. For all adsorbents, there was a tendency for adsorption efficiency to increase from time to time until complete saturation. Adsorption stopped when all sites were filled with CO molecules. (Saber-Samandari et al., 2014) (Figure 1).

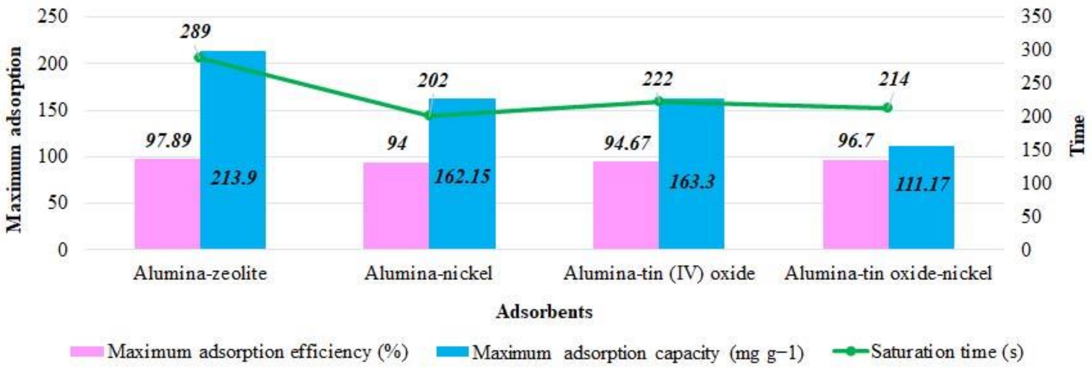

Figure 1. CO adsorption efficiency indicators for some alumina-doped adsorbents

Since the current mini-review revealed significant interest among researchers in the problem of synthesizing alumina-doped composite films for capturing CO gas, a comparative assessment of the adsorption capacity of such adsorbents was carried out. Yeom et al. (2018) found a significant decrease in the adsorption capacity of palladium-activated carbon (Pa-Ac), palladium-silicon (Pa-Si), Zeolite, Silicon, and Activated carbon from 77.60 to 25.20 mg/g in accordance with the specified order of materials.

This suggests that there is great promise for alumina doped adsorbents due to their higher adsorption capacity of adsorbents compared to more expensive commercial adsorbents. Figure 2 clearly demonstrates the advantages of alumina-doped composite films in terms of their adsorption capacity.

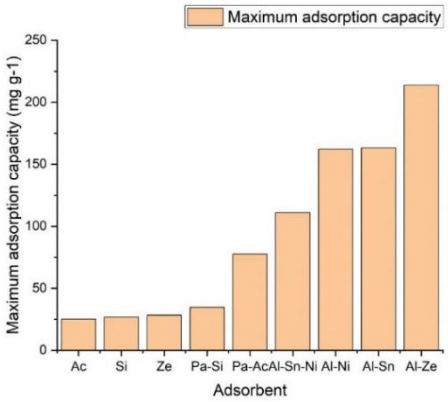

Figure 2. Maximum adsorption capacity limit of the studied adsorbents

CONCLUSION

The negative impact of CO on public health and components of the natural environment no longer requires proof. The natural protection of the atmosphere from the toxic effects of CO are green spaces, which are decreasing in quantity every year due to man-made activities. The current situation, as well as known trends and prospects in the field of atmospheric protection, motivate researchers to search for additional protection in the form of adsorbing filters. Current research identifies the use of γ-Al_2O_3 as a primary CO capture catalyst as promising. This is justified by the fact that γ-Al_2O_3 is a metastable alumina polymorph associated with unique characteristics related to the crystalline framework, surface chemistry and phase contribution. At the same time, modification of microstructures and surface frameworks can improve the performance of such nanoadsorbents even through additions in small quantities. Tin(IV) oxide (SnO_2) has emerged as the most suitable additive for nanoadsorbents designed to capture CO gas because it has excellent adsorption properties, including strong structure, potential sensitivity, and low cost.

The roller coating method for the production of composite films has proven to be a simple, cheap and reliable method for producing an effective nanoadsorbent. The results obtained through the testing mechanism showed that the nano-adsorbent produced by roll coating method has high adsorption efficiency and adsorption capacity due to obvious reasons such as the unique properties they have as well as their design since four nano-adsorbents are bonded together to form a hollow cubic shape. Besides, the concentration of adsorbed gas and also adsorption capacity were enhanced with passing time until it reached saturation level, confirming that all sites of adsorbents were filled by molecules of CO. The researchers found that the maximum adsorption efficiency of adsorbents doped with alumina was no less than 94%. Alumina-doped adsorbents deserve serious attention for further development, since they are quite capable of competing in efficiency, ease of manufacture and cost with commercial adsorbents available on the market.

Author's statements

Contributions

The authors declare that they made the following contributions to the current study, namely: Conceptualization, Formal Analysis, Investigation, Methodology, Validation, Writing – original draft: Ni.M. and Na.M.; Visualization, Writing – review & editing: A.V.

Declaration of conflicting interest

The authors declare no competing interests.

Financial interests

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No data were used for the current study.

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