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A Review on Carbon Adsorbers and Activated Carbon-Based Composite Materials for the CO₂ Capturing

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ABSTRACT: Low to medium amounts of volatile organic chemicals can be removed from gas streams using a non-destructive control technique called adsorption. Adsorption is usually used when a high output concentration must be achieved and/or VOC recovery is desired. Metal oxides can enhance the CO₂ collection capacity of AC/metal composites by changing the surface area and pore structure of the carbon. Furthermore, AC may have more active sites for CO₂ collection thanks to the metal oxides' capacity to contribute electrons. The AC/zeolite composite also showed lower energy consumption than commercial AC during the ESA process. Details on carbon adsorbers and a few composite materials based on activated carbon that have good adsorption capability are included in this review work.

I. INTRODUCTION

A non-destructive control method called adsorption is used to eliminate volatile organic compounds (VOCs) from gas streams with low to medium concentrations. When a high output concentration needs to be reached and/or VOC recovery is sought, adsorption is typically utilized. Carbon adsorbers have many uses, ranging from reducing hydrogen sulfide and volatile organic compounds (VOCs) from municipal wastewater facilities to reducing VOC and HAP emissions from storage tanks and process vents in refineries, chemical manufacturers, and pulp and paper factories. Some smaller applications, such as portable soil remediation devices, have made use of carbon adsorber canisters. Adsorbers are employed as concentrators in certain industrial applications to reduce the expense of other air pollution treatments, such as condensers and thermal oxidizers. In order to reach VOC discharge restrictions, carbon adsorbers can also be employed as a last polishing step in combination with other less successful methods, such as condensation or biofiltration.

They are especially helpful in cases with moderate flow rates and relatively low VOC concentrations (less than 100 ppmv), which might be challenging or expensive to eliminate with other kinds of pollution controls. At input VOC concentrations of 500–2,000 ppm in air, carbon adsorbers can achieve high VOC removal efficiency of 95–99% when they are designed, run, and maintained appropriately. For diluted waste streams, removal efficiencies of over 98 percent can be attained.

The phenomenon known as adsorption occurs when gas molecules move across a bed of solid particles and are retained on the solid's surface by attraction forces that are less strong and specific than chemical bonds. When gas molecules actually create chemical bonds with the adsorbent surface groups, this process is referred to as chemisorption.

When a molecule from the gas stream sticks to the solid's surface, energy is released. Known as the "heat of adsorption," this energy usually matches or surpasses the heat of condensation. The concentration of the gas phase, molecular weight, diffusivity, polarity, and boiling temperature all tend to increase the solid's adsorbent capacity for the gas. By raising the temperature, lowering the pressure, or adding a more potent adsorbed substance to displace the volatile organic compounds, the majority of gases (also known as "adsorbates") can be eliminated (also known as "desorbed") from the adsorbent.

Carbon adsorbers typically have an equipment life of 15 to 25 years. However, because corrosion affects the adsorber components, systems that handle waste gases that contain corrosive elements, like hydrogen chloride or other acid gases, have shorter equipment life. For instance, the walls of the adsorber vessel, the carbon bed supports, and the outlet ducts may corrode if waste streams contain corrosive gases. When elements of the gas stream condense to generate corrosive liquids that accumulate on the bottom of the adsorber vessel, corrosion of the bottom of the vessel is typical. The carbon beds may eventually collapse due to corrosion of the carbon bed supports, which is also a possibility. Materials that are resistant to corrosion should be utilized to build carbon adsorbers, which are used to regulate gas streams that contain corrosive substances.

II. DIFFERENT TYPES OF ADSORBERS

Adsorption equipment comes in four varieties: fluid-bed adsorbers, moving bed adsorbers, disposable/rechargeable canisters, and fixed regenerable beds. Among these, canisters and fixed-bed systems were the first to be created and are still the most often used systems today.

1. Fixed-bed Units

Over a broad range of flow rates, from few hundred to several hundred thousand cubic feet per minute (cfm), fixed-bed units can be sized to regulate continuous streams that contain volatile organic compounds. For some dangerous chemicals, the VOC content of streams that can be handled by fixed-bed adsorbers can be as low as a few parts per billion by volume (ppbv), or it can reach up to 25% of the lower explosive limit (LEL) of the VOCs. In certain applications, the waste gas stream's VOC concentration might be higher than the LEL. The waste gas stream is diluted to keep the waste gas VOC concentration below 25% of LEL in order to lower the danger of ignite. The LEL for the majority of VOCs falls between 2,500 and 10,000 ppmv.

There are two modes of operation for fixed-bed adsorbers: intermittent and continuous. When operating intermittently, the adsorber eliminates volatile organic compounds (VOCs) for a predetermined amount of time (referred to as the "adsorption time"), which is the same amount of time as the controlled source emits VOC. The unit starts the desorption cycle, which removes the collected VOC from the carbon, once the adsorber and the source are turned off (for example, overnight). Three steps make up this cycle in turn: (1) heating the bed to regenerate the carbon, usually by forcing steam through it in the opposite direction of the gas flow; (2) drying the bed with a fan or compressed air; and (3) using a fan to cool the bed to its working temperature. The majority of designs employ a single fan for both cooling and bed drying. The type of adsorbent, the regeneration technique, and the properties of the pollutants in the waste stream all affect how long the desorption cycle lasts. Until the emission source resumes operation (for systems with a single adsorber) or another adsorber is turned off-line for regeneration (for systems with two or more adsorbers), the unit remains inactive.

The emissions source can run constantly in fixed-bed adsorbers, which are made up of two or more carbon beds with at least one regenerated carbon bed always accessible for adsorption. Each carbon bed in a two-bed system needs to be big enough to accommodate the full gas flow during adsorption. Therefore, compared to an intermittent system managing the same flow, twice as much carbon must be supplied. It might be more cost-effective to have three, four, or even more carbon adsorption beds running simultaneously if the desorption cycle is much shorter than the adsorption cycle. This method lowers the amount of additional carbon capacity required and may offer some other advantages, such keeping the effluent's volatile organic compound (VOC) concentration low.

2. Canister Units

Unlike fixed-bed systems, canister-type adsorbers are often only used to regulate intermittent and lower-volume gas streams, as those released by storage tank vents, where off-site regeneration is appropriate due to process economics. Unlike the fixed-bed devices, the carbon canisters are not designed for in-situ desorption. Rather, they are regenerated at an on-site central desorption plant or sent back to the manufacturer. Canister adsorbers were originally used to describe relatively small returnable containers, including drums that held 55 gallons. However, since a substantial portion of the industry's growth is in larger vessels lacking regeneration capabilities, the word "canister" is starting to become rather misleading. One manufacturer, for instance, offers carbon capacities of 10,000 pounds and canister systems up to 18,000 cfm.

The machine is turned off and either the carbon or the canister is changed once the carbon reaches a specific VOC concentration. After that, either the whole canister or the used carbon is recycled at a reclamation facility or regenerated on-site at a central regeneration facility. A number of businesses offer canister carbon replacement services. These businesses examine the spent carbon that is sent back to them to see if any dangerous substances are present. According to 2018 rates, the average cost of testing spent carbon is between \$800 and \$1,000; however, the cost may increase based on the application for instance wood treating and DBCP or PCB treatment. A vessel, activated carbon, an intake connection to a distributor that leads to the carbon bed, and an outlet connection to link the unit to an exhaust stack make up each canister unit. In one arrangement (Calgon's Ventsorb®), 180 pounds of carbon are placed in a 55-gallon barrel with an internal collector on an 8-inch gravel substrate. The makeup of the VOC to be treated determines the kind of carbon that is utilized.

3. Moving-Bed Adsorbers

Moving-bed adsorbers, like fixed-bed adsorbers, are made up of a permanent adsorber vessel where the adsorbent is exposed to waste gases or vapors. Nevertheless, the spent adsorbent is continuously renewed in the moving-bed adsorber. The adsorbent is kept in two beds that are positioned on coaxial rotating cylinders in a standard moving bed adsorber. As the waste gas passes between the two spinning beds, VOC is adsorbed. The area of the adsorbent bed outside the waste gas stream is renewed as the cylinders spin, which raises the possibility that gas molecules may come into touch with the just regenerated adsorbent.

4. Fluid-Bed Adsorbers

According to the counter-flow design of fluid-bed adsorbers, regenerated adsorbent enters the adsorber vessel from the top and gradually moves to the bottom, whereas waste gas normally enters the adsorber vessel from the bottom and flows up through the vessel. The adsorbent progressively becomes saturated as it passes through the vessel. At the bottom of the tank, the spent adsorbent is gathered and moved to a regeneration chamber. Fluid-bed adsorbers work more effectively and are less likely to encounter the breakthrough problems that come with fixed bed designs and canisters since spent adsorbent is continuously removed and replaced with fresh adsorbent.

III. DIFFERENT TYPES OF ADSORBENTS

In large-scale applications, three different kinds of adsorbents are used: polymers, synthetic zeolites, and activated carbon. Every kind of adsorbent has unique properties that make it useful in some situations but unworkable or unfeasible in others.

1. Activated Carbon:

The most widely utilized adsorbent nowadays is activated carbon, which was the first to be used. It is made from a range of resources, including wood, coal, and coconut husks, via high-temperature steam pyrolysis. Because of its high specific surface area for about 800–1,400 square meters per gram, and numerous tiny pores of different sizes which will be usually between 2 and 500 angstroms, the resultant carbon has exceptional adsorption properties. The type of material utilized determines the properties of the activated carbon that is created. Coconut-based activated carbon generally outperforms coal-based activated carbon at greater humidity levels. Additionally, activated carbon can be altered to enhance its ability to adsorb various contaminants, including ammonia, mercury, and hydrogen sulfide.

2. Zeolites:

Small, consistently sized pores and a high specific surface area characterize the homogeneous crystalline structure of zeolites. Because of their ability to trap molecules of particular sizes while permitting other molecules to flow past, zeolites are frequently referred to as "molecular sieves." The zeolite used for a particular application needs to be carefully chosen to fit the molecular diameter of the volatile organic compounds that need to be eliminated. Similar to activated carbon, zeolites have certain surface areas. Hydrophilic aluminosilicate minerals are examples of naturally occurring zeolites. On the other hand, synthesized zeolites with properties specific to a given application are also accessible. Certain synthetic zeolites, for instance, have a low affinity for water molecules and a high attraction for non-polar volatile organic compounds (VOCs) due to their hydrophobic nature. Zeolites work well to remove volatile organic compounds (VOCs) from waste streams with high relative humidity, in contrast to activated carbon. While activated carbon's adsorption capacity is greatly influenced at relative humidity levels below 50%, a hydrophobic zeolite's adsorption capacity is only affected at extremely high humidity levels.

3. Polymers:

Granules or beads composed of strongly crosslinked synthetic polymers that create a matrix of tiny pores and large surface areas are known as polymer adsorbents. Styrene, toluene, xylenes, aldehydes, ketones, alcohols, and chlorinated VOCs are just a few of the many volatile organic compounds (VOCs) that can be controlled with polymer adsorbents. However, strong oxidizing agents cannot be utilized with polymers. Polymers have a higher adsorption capacity than activated carbon, but a lower one than zeolites. They can achieve removal efficiency of over 95% and are less likely to catch fire than activated carbon adsorbents. To remove organic molecules selectively, polymers with a certain pore structure can be created.

The hydrophobic surface of polymeric adsorbents is one of its benefits. They can withstand a lot of water vapor because of this. VOC in waste streams with relative humidity more than 90% can be effectively treated with polymeric adsorbents. Therefore, in soil remediation operations and industrial wastewater facilities where the waste streams have high relative humidity, polymeric adsorbents have been employed to limit VOC emissions. VOCs and HAPs have been eliminated from soil vapor extraction (SVE) procedures using polymer adsorbents. Using a system with a flow rate of 271 ft³/min, relative humidity of 98%, and ambient temperature, the Dow Chemical Company demonstrated a 99% removal efficiency. Two beds held 191 pounds of Dowex OptiporeTM polymeric adsorbent, which was regenerated on-site by vacuuming with a low carrier gas flow and conductive heating to 250 degrees Fahrenheit. The system was expected to have yearly costs of \$2,732 and capital costs of less than \$160,000.

IV. DIFFERENT TYPES OF ACTIVATED CARBON-BASED COMPOSITES FOR CAPTURING THE CO₂

1. Activated Carbon/metal composites

CO₂ is an acidic gas, which shows strong affinity with a base. Therefore, the introduction of metal oxides to AC can effectively promote the preferential adsorption of acidic CO₂. The loading of metal oxides on the surface of AC is very effective for improving the surface properties and promoting the interaction of AC with CO₂. Therefore, AC/metal oxide composites are often synthesized to capture CO₂. Metal oxides most frequently loaded on the surface of AC for CO₂ adsorption mainly include CaO, MgO, CuO, NiO, and so on. To create composites for CO₂ collection, AC also supports metal hydroxide, metal carbonate, and metal oxides. The literature indicates that raising the adsorption pressure causes an increase in CO₂ absorption. This is because CO₂ molecules have a lower density when the adsorption pressure rises, which makes it easier for CO₂ to attach to the adsorption site.

Because of its high basicity, magnesium oxide (MgO) is frequently employed as a CO₂ adsorbent among metal oxides. Because of its low charge/radius ratio, MgO has a basic nature. Additionally, it was demonstrated that the basic O²⁻ of MgO in the corners and edges of the crystal surfaces was more basic than that in the planes. In order to collect the acidic CO₂, doping MgO on AC might improve the active sites and basicity. The use of MgO nanoparticles supported on AC for CO₂ adsorption was investigated by Wan et al. In comparison to fresh MgO, the AC/MgO composite demonstrated a significantly higher physical and chemical adsorption capacity (1.78 and 6.5 mmol g⁻¹). When compared to fresh AC, the physical adsorption increased by around 112%. It was discovered that the high dispersion of MgO nanoparticles on the surface of AC is connected to the composite's outstanding physical and chemical adsorption qualities. MgO nanoparticles increase the number of AC active sites. Furthermore, Li et al. created the AC/MgO composite for CO₂ adsorption by utilizing the synergistic effect of MgO self-dispersion and carbon produced from coconuts. At 100 and 150 degrees Celsius, the AC/MgO composite with 20% MgO demonstrated a high dynamic CO₂ capture capacity of 0.19 and 0.08 mmol g⁻¹, respectively, as a result of the hierarchical structure AC support's synergistic effect.

2. Activated Carbon/zeolite composite

A type of crystalline silica-aluminate, zeolite is made up of silicon-oxygen and silicon-aluminum tetrahedra. The zeolite exhibited numerous characteristics, including hydrophilicity, a large porous surface area, a high ion exchange capacity, molecular sieving, and a strong adsorption affinity, due to its crystallographical pentasil ring. Zeolites are therefore frequently employed in gas adsorption. Zeolites have been effectively employed in CO₂ adsorption and separation in flue gas in recent years. However, because some of the fine zeolite powders are easily suspended or aggregated, zeolites have limited practical applicability. However, zeolite's intrinsic drawbacks, like its slow rate of mineralization and ease of catalyst deactivation, result in considerable reaction uncertainty. Therefore, zeolite's structural characteristics must be enhanced in order to boost its adsorption performance. Zeolite support on the AC surface is a

viable choice. AC can significantly increase zeolite's mechanical characteristics, stability, and durability as well as its capacity for ion exchange and chemical migration. For this reason, AC/zeolite composites are typically created in order to collect CO₂.

Lee et al. investigated the CO₂ adsorption capacity of zeolite 13X and AC/zeolite X composite at various adsorption temperatures. The outcome verified that, within the experimental range, the AC/zeolite X composite's CO₂ uptake is less than that of zeolite 13X. In other words, the composite made of the two adsorbents does not absorb more CO₂ than the single adsorbent. The difference between the CO₂ uptake on zeolite 13X and the AC/zeolite X composite, however, diminishes as the pressure increases. At 100 kPa and 25°C, the absorption of the zeolite 13X and AC/zeoliteX combination was 3.5 mmolg⁻¹. Furthermore, at 100 kPa and 25°C, the AC/zeoliteX composite had a greater CO₂ adsorption capacity (3.5 mmolg⁻¹) than AC (2.2 mmolg⁻¹).

V. CONCLUSION

By altering the carbon's surface area and pore structure, metal oxides can improve the CO₂ collection capabilities of AC/metal composites. Additionally, the metal oxides' ability to donate electrons can give AC additional active sites for CO₂ capture. It was discovered, therefore, that not all ACs containing binary metal oxides showed a higher capacity for CO₂ adsorption than ACs containing single metal oxides. In the ESA process, the AC/zeolite composite also demonstrated reduced energy use than commercial AC.

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