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A review on common adsorbents for acid gases removal: Focus on biochar

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ABSTRACT

Biochar, a product of pyrolysis of biomass, represents an attractive alternative to non-renewable or unsustainably sourced biomass as an adsorbent material for treating gaseous effluents. Biomass from residues associated with agricultural and forestry operation, otherwise considered waste material or a storage issues, represents a potential sustainable source of adsorbent. There are several adsorbents for removal of contaminants from gases including carbon based, silica based, and metal oxide based adsorbents; however, availability of feedstock, low cost, and potential high adsorption capacity distinguish biochar from other adsorbents. This review includes common sorbents for removal of contaminants from gas, biochar production methods, and compares biochar with activated carbon as one of the most common commercial adsorbents. Adsorption isotherms, mechanisms, and process systems for removal of acid gases such as CO_2 and H_2S by biochars have been comprehensively reviewed. The application of molecular modeling to describe adsorption by activated carbons and possible extension to biochar were studied. There is still a lack of published information in the molecular modeling of biochars, and using these models to understand the complex adsorbent mechanisms on the very heterogeneous surfaces of biochar (relative to commercial adsorbent materials such as activated carbons). Therefore, further research needs to fill these gaps to identify all potentials of this promising adsorbent.

1. Introduction

Hydrogen sulfide (H_2S) and carbon dioxide (CO_2) are common contaminants in oil and gas production/processing, wastewater treatment plants, fossil fuel combustion, and landfill gases and can result in corrosion, problematic gaseous emissions, and represent a safety risk [1]. In addition to light hydrocarbons, natural gas can contain variable amounts of carbon dioxide, nitrogen, sulfur compounds, water, aromatics and small amounts of helium (less than 1 vol%) and mercury (generally 5–300 μgNm^{-3}) [2]. On offshore platforms, the treatment of any gas or liquid effluent is challenging due to space restrictions and/or manpower on the platform (this limits operator intensive processes). In platforms where the main product is oil, any produced gas is re-injected, used for utilities, and/or flared and must be treated to a level appropriate for these applications. These challenges are not restricted to the offshore, any remote location (e.g. landfills, small wastewater treatment plants etc.) require smaller scale and less operationally intensive alternatives to gas treatment, particularly if the gas is to be used as a fuel. There are a number of processes used to remove CO_2 and H_2S (acid gases) from natural gas, including absorption and adsorption. In absorption, the acid gases are removed using solvents such as monoethanolamine (MEA) and diethylamine (DEA). Although the selectivity of this form of separation is relatively high, it is costly due to high energy needs in solvent regeneration and space requirements [3]. An alternative approach to absorption is adsorption in which, the contaminants are removed from the gas mixture by porous solid adsorbents. The most common adsorbents used in natural or produced gas treatment to remove acid gases are carbon based, silica based, and metal organic frameworks (MOFs) [4–6] adsorbents. The porous solid adsorbents could have amorphous and/or crystalline structure at both the macro and nanoscale. The MOFs and silica are two common representative examples of ordered crystalline structure, while the structure of carbon based adsorbents such as biochar are amorphous but contain some local crystalline structures of aromatic compounds. As the feedstock and processing conditions determine the nature of the biochar, biochars will have different molecular architectures and variable topologies, making them difficult to characterize [5].

Biochar produced from thermochemical conversion of biomass has been used for a number of different applications including structural fill and soil stabilization for construction [4], soil /water decontamination [7] and as adsorbents in gas effluent treatment [8]. The application depends on the properties of the biochars which in turn depend on the

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feedstock type, pyrolysis temperature, and residence time [9]. Biochar can be generated through thermal treatment of lignocellulose biomass, such as coconut [10], almond [11], palm kernel [12], pistachio nut shell [13], and wood [14] as well as municipal and industrial waste and activated sludge [15,16]. Using biochar as an adsorbent in the gas treatment process could be a sustainable approach if the biomass source is a waste material.

In this article the application of biochar as an adsorbent for removal of contaminants from gaseous phase has been reviewed. This review includes a summary of the most common sorbents for removal of acid gases from natural or produced gas, processes used to produce biochar and the resulting properties, as well as research related to biochar adsorption isotherms and mechanisms. Research in process systems and molecular modeling of H_2S and CO_2 adsorption by biochar is also reviewed.

2. Common sorbents for removal of contaminants from gases

There are key criteria that a sorbent material must satisfy, for the sequestration of contaminants to be both economical and operational, including; high adsorption capacity to reduce both adsorbent quantity and equipment size, low friction rate and the ability to tolerate high temperatures, fast adsorption kinetics, stability in oxidizing/reducing environments such as acid gas, steam, and hydrocarbons, and regenerability [17]. Several types of sorbents have been developed over the last two decades which are capable of removing acid gases: (1) carbon based adsorbents (2) microporous and mesoporous silica and (3) metal organic frame works. These three groups are applicable for adsorption of many gaseous compounds, especially hydrogen sulfide and carbon dioxide.

2.1. Silica based adsorbents

Silica gels have been used commercially as an adsorbent since World War I. The surface areas range from 200 to 800 m^2/g [18]. Grafting amine functional groups to the pore walls of silica is a strategy for designing new adsorbents and catalysts for treatment of natural gas [19]. This sorbent is similar to aqueous alkaline amine based solvents where the amines covalently linked to the silica chemically bind to the target gaseous components. Amino-functionalized mesoporous silica provides large surface areas, pore volumes and well defined pore structures. Huang et al. [20] studied the feasibility of natural gas desulfurization by amine-grafted silica in 2003. Burwell and Leal [21] reported selective chemisorption of sulfur dioxide on amine modified silica gel, and Leal et al. [22] investigated carbon dioxide adsorption on amine-grafted silica gel. Table 1 illustrates some selected silica based adsorbents' function used in acid gas removal field.

The above experimental results indicate that the adsorption capacity of pure silica adsorbents is lower than amine functionalized silica. However, grafting amines to silica increases the cost and cannot increase the adsorption capacity notably compared with other adsorbents such as MOFs.

2.2. Carbon based adsorbents

One of the most important commercial adsorbents is activated carbon, typically derived from sources such as coals (e.g., bituminous coal, lignite), industrial by-products (e.g., scraps of polymeric materials, petroleum), and lignocellulose biomass (e.g., saw dust, coconut shells, olive stones) [27]. The first step in producing activated carbon (AC) is carbonization in order to produce char. All moisture and volatile compounds are removed thorough this process and physical or a chemical activation follows [67]. Activating agents such as CO_2, steam, and air, or a combination of these, at temperatures between 800 and 1250 K are used in physical activation, and alkaline metal and acids are used in chemical activation. Higher porosity increased surface area, and increased pore volume are the main advantages of the activation process [28]. Activated carbon is a widely used adsorbent in gas treatment, water purification, etc. The capacity of activated carbon decreases as the temperature increases; therefore, AC is suitable for low temperature application especially for CO_2 capture [29].

Table 1
Silica based sorbents for acid gas removal.

Silica based adsorbents	Adsorbed Gas	Uptake (mmol/g) Operating Conditions	Refs.
Silica Xerogel/ 3-aminopropyltriethoxy-silane	CO_2	1.12 25 °C, 1 bar	[23]
MCM–41 Silica/ Dimethyldecylamine	CO_2	2.5 25 °C, 1.4 bar	[24]
MCM–48 Silica/ Aminopropyl (3.42 wt%)	CO_2	0.8 25 °C, ~1 bar	[25]
Silica Xerogel	H_2S	0.01 30 °C, 1 bar	[26]
Silica Xerogel/ Diethylenetriamine (50 wt%)	H_2S	0.3 30 °C, 1 bar	[26]
MCM–41 Silica/ Dimethyldecylamine	H_2S	3.5 25 °C, 1.4 bar	[24]

The industrial application of commercial adsorbents such as zeolite and activated carbon as acid gas adsorbents is restricted because of low selectivity at high temperature, poor adsorption in presence of water vapour, and high cost of regeneration. The regeneration temperature of and AC zeolite is 400–500 °C and 200 °C, respectively [30,31].

Several research groups have investigated activated carbon for gaseous sulfur compounds removal. Table 2 highlights the impact activation conditions and source of activated carbon have on the sorption properties. For instance, despite the larger surface area in activated wood carbon under acidic conditions, the palm carbon activated under basic conditions with a lower surface areas showed a comparable (although lower) capacity for H_2S.

2.3. Metal oxide based adsorbents

Metal oxide based adsorbents can remove sulfur by forming insoluble metal sulfides. Pure metal oxides without a framework have

Table 2
Physical and chemical activation conditions and characteristics of activated carbon for removal of SO_2 and H_2S.

Raw material	Adsorbate	Activation Condition	S_{BET} [a] (m^2/g)	Sorption capacity (mg/g)	Refs.
Palm shell	SO_2	CO_2, 1100 °C	984	121.7	[32]
	H_2S	KOH, 30 wt%	1148	68	[33]
Coconut shell	SO_2	Steam, 800 °C Cu, 3 wt%	1054	24	[34]
	H_2S	Base impregnation	931	215.4	[35]
Wood	SO_2	H_3PO_4 activation	1708	120	[36]
	H_2S	H_3PO_4 activation	1470	30.9	[37]
Pistachio nut shell	SO_2	CO_2, NaOH activation	1064	89.6	[38]

[a] Surface area measurement method: Brunauer-Emmer-Teller (BET).