

Nanoporous Materials for Environmental Applications

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NANOTECHNOLOGY is a scientific field that concerns the exploitation of minutely sized synthetic materials, which can be applied in various processes and benefit humans. In scientific terms, 'nano' is a prefix in the SI system of units and corresponds to 10^{-9} meter. Nanoporous materials are highly useful materials in various industrial processes due to their unique physical and chemical characteristics. The word 'porous' derives from the Greek word 'πορος' (poros) meaning 'passage' [1].

A nanoporous material consists of either an organic and/or inorganic framework, which maintains a porous structure with a typically large surface area in excess of $400\text{m}^2/\text{g}$. Based on the definition by the International Union of Pure Applied Chemistry (IUPAC), porous materials may be classified according to their pore diameters, namely, micropores ($<2\text{nm}$), mesopores (between 2nm and

50nm) and macropores ($>50\text{nm}$).

Nanoporous materials are highly versatile and can be used in various industrial applications ranging from catalytic reactions, adsorption and environmental processes due to the presence of voids of controllable dimension at the atomic, molecular and nanometer scales [2]. As such, they are of interest to both chemical and environmental engineers, and with rising environmental concerns worldwide, the use of nanoporous materials in the removal of polluting species from different media as well as the recovery of useful ones has become more significant. This paper provides a general overview of the various types of nanoporous materials and their respective applications.

TYPES OF NANOPOROUS MATERIAL

The synthesis, development and application of nanoporous materials

are exclusively focused on the micro- and mesoscales, since the adsorptive ability contributed by macropores is negligible. Microporous materials are generally used for gaseous applications while mesoporous materials are usually used in aqueous-based media, since gaseous molecules (CO_2 , methane and hydrogen) are smaller in size compared to aqueous-based species (heavy metals and organics).

Zeolites, which represent the largest group of microporous materials, are crystalline inorganic polymers based on a three-dimensional tetrahedral arrangement of SiO_4 and AlO_4 (aluminosilicate) connected through their oxygen atoms [2]. Some of the best known mineral zeolites are clinoptilolite, chabazite, phillipsite, mordenite and analcite. Synthetic microporous zeolites, which usually have pore diameters in the range of 0.3nm to 1.8nm , are of great importance industrially as they are powerful acid-base catalysts and are one of the most used nanoporous materials in the world today [3].

Activated carbon (AC) is also a very established nanoporous material, which is basically an amorphous organic material with an extensive network of micro- and mesopores. The conventional precursor of AC is coal, although biomass sources such as wood and agricultural wastes are being increasingly used as substitutes. AC is typically produced via a two-step process, namely, charring to produce black carbon and subsequent physical (thermal) and/or chemical activation to produce pores. A typical porous texture of a biomass-based AC is shown in Figure 1.

In addition to zeolites and AC, there are plenty of novel synthetic

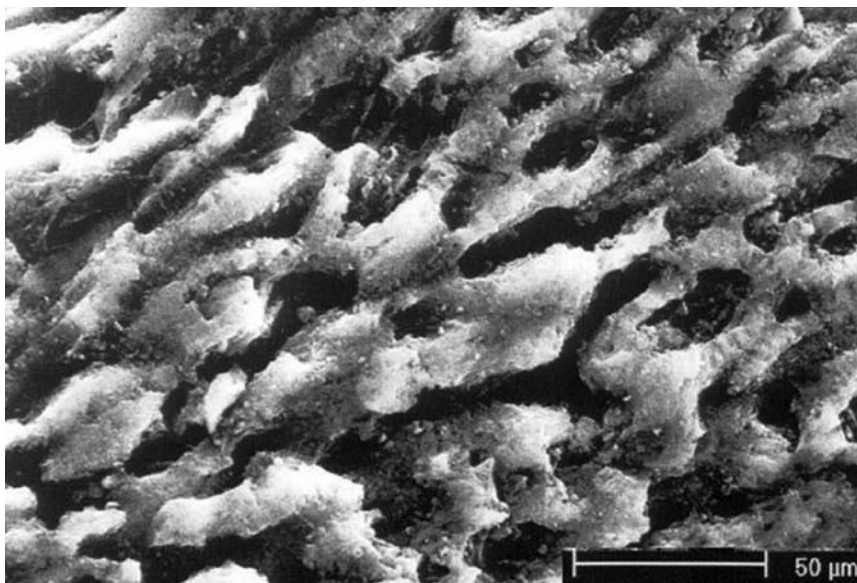


Figure 1: Pilot structural tests on (a) 8.6m Dura® X650 prestressed beam and (b) 8.7m Dura® T875 bridge girder in the 5000kN stiff frame of heavy structural laboratory of DTSB

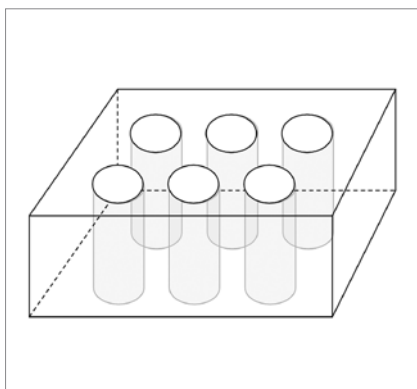


Figure 2: Hexagonal MCM-41

nanoporous materials that, in the future, may be used prominently alongside the aforementioned adsorbents. One such novel synthetic nanoporous material is the Mobil Crystalline Material number 41 (MCM-41), first reported in 1992. This is basically an inorganic, hexagonal mesoporous material initially synthesised to be applied as a catalyst support (Figure 2). The synthesis of mesoporous silicas MCM-41 and MCM-48 in 1992 used a supramolecular surfactant system as a template and provoked a boom in the development of synthetic nanoporous materials [2].

Porous coordination polymers built from metal ions connected by organic linkers referred to as metal-organic frameworks (MOFs), and molecular frameworks consisting of light elements (carbon, boron, hydrogen and oxygen) referred to as covalent organic frameworks (COFs), are more recent additions to the ranks of ordered porous materials [4]. MOFs are highly diversified materials composed of metal atoms (ions) linked together by multifunctional organic ligands.

The high diversity is a consequence of the linkage between inorganic and organic chemistry where the whole substitution chemistry of organic synthesis can be coupled with inorganic elemental and cluster chemistry [5]. These relatively novel nanoporous materials, though not readily available in the commercial market as yet, may have huge market potential due to their proven high surface area and pore volume in addition to their highly ordered and robust porous frameworks.

WATER AND WASTEWATER TREATMENT

Malaysia relies considerably on strong industrialisation initiatives to boost its global economy competitiveness. Concurrently, remarkable economic growth, which is spurred by robust manufacturing industries, has also generated a significant quantity of hazardous waste. Organic and inorganic contaminant-laden industrial wastewaters are examples of such wastes, which are potentially highly damaging to public health. Nanoporous materials, particularly zeolites and AC, have been extensively used as adsorbents to remove contaminants from wastewater due to their unique structural, surface physico-chemical and ion-exchange properties.

Zeolites are predominantly used in a wide spectrum of water and wastewater treatment processes in which the presence of heavy metal and ionic contaminants is inherent, although in some cases, organic contaminants can be removed as well. Most technologies using zeolites for water treatment are based on the unique cation-exchange behaviour of zeolites, which removes dissolved cations from water through the cation exchange at zeolites exchange sites and through chemisorption, *i.e.* the formation of stable inner-sphere or outer-sphere complexes, where functional groups on the zeolite framework (mainly OH-) form strong chemical bonds with metal ions [2].

In the majority of zeolites, the ion-exchange mechanisms usually dominate over chemisorption. Due to this ion exchange ability, zeolites are widely used to 'soften' hard water, *i.e.* water that contains significant amounts of bivalent cations such as Ca^{2+} and Mg^{2+} . This is particularly useful when treating highly mineralised groundwater in order to prevent the 'scaling' or build-up of mineral deposits in pipes and household appliances.

On the other hand, AC is an effective adsorbent for the removal of a wide variety of organic pollutants dissolved in aqueous media. As a porous carrier material, it is able to distribute chemicals on its large hydrophobic

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internal surface, thus promoting their reactivity [6]. Since AC is essentially derived from carbon, it is highly suited to adsorb organic contaminants from water streams such as phenol and other benzene derivatives.

In Malaysia, AC has been proven to be a popular and effective adsorbent to remove organics from industrial wastewater streams (polishing) before the final discharge into drainage systems. In many cases, AC can be tailored to enhance its effectiveness to remove certain pollutants [6]. For example, acidic treatment of AC using either sulfuric or nitric acid can enhance its effectiveness in the removal of metal contaminants, whereas basic treatment using gaseous ammonia will improve its adsorption capacity for organic contaminants.

In addition to zeolites and AC, recent studies have developed several novel alternatives for wastewater treatment. One promising alternative is the cross-linked sol-gel monoliths, which are mechanically strong and can absorb metal ions at a rate of the order of milligrams per hour, which is about eight times higher than that of conventional microporous gels [7]. In this case, the sol-gel method is a chemical process used to fabricate nanoporous materials, starting from colloidal particles, to produce gels composed of integrated pore networks.

The release of 260,000 barrels of crude oil into the Gulf of Alaska by the Exxon Valdez prompted scientists to extensively study and invent novel materials capable of absorbing oil spills. Some of the nanoporous materials, which can be used to clean up oil spills, are silica aerogels and zeolites [8]. These materials are attractive for oil spill cleanups because of the possibility of the collection and complete removal of the oil from the oil spill site. Aerogels are nanoporous materials made using the sol-gel process followed by drying under supercritical conditions, which yield special properties including large surface areas ($>1000\text{m}^2/\text{g}$), high porosity, low density and low thermal conductivity [8].

CAPTURE OF GASES

Since the turn of the new millennium, the human populace has been very concerned with the effect of global warming deemed to be caused mainly by anthropogenic activities. The foremost concern has always been the rising concentration of CO_2 as well as other polluting species such as NO_x and SO_x gases that contribute to acid rain. As such, scientists and engineers have been developing new technologies to efficiently capture these gases before they can escape into the atmosphere. Usage of nanoporous materials to capture these gases is very common in Malaysian industries and this is reflected in the popular use of AC in the industrial scrubber systems for the removal of polluting gases such as flue gas.

The main mechanism in the nanoporous material capture of gases is physisorption – the adherence to pore surfaces via weak intermolecular forces, which is normally aided by appropriately sized micropores ($<2\text{nm}$) which can trap the gas molecules. Various studies have investigated physisorption mechanisms in nanoporous materials with respect to the removal of CO_2 from gas streams. These studies have focused mainly on the application of zeolites, since they are well characterised for this purpose and many framework topologies and compositions have been analysed from pure siliceous silicalite (MFI) to aluminosilicates containing different ion-exchange cations [4].

That said, it is the relatively novel MOFs that are making the greatest impact on CO_2 adsorption. Recent MOF research indicates a remarkable CO_2 adsorption capacity (e.g. MOF-177 exhibits a CO_2 capacity of $33.5\text{mmol}\cdot\text{g}^{-1}$) which exceeds the capacities of zeolites and activated carbons [9]. A separate development indicates that COF systems also have high CO_2 storage potential. Barbarao and Jiang [10] reported that COF-102 exhibited high capacity even at considerably low pressures.

In the context of the application of nanoporous materials for the capture of gases, it is very important

Table 1: Gas separation processes and their suitable adsorbent relevant to environmental applications (adapted from Keller [11]; Dabrowski [3])

Separation	Suitable adsorbent
CO ₂ /C ₂ H ₄ , natural gas, etc.	Zeolite
Sulfur compounds/natural gas, hydrogen, liquefied petroleum gas (LPG), etc.	Zeolite
Odors/air	Activated carbon
NO _x /N ₂	Zeolites, activated carbons
SO _x /vent streams	Zeolites, activated carbons
H ₂ O/olefin-containing cracked gas, natural gas, air, synthesis gas, etc.	Silica, alumina, zeolite
Hg/chlor-alkali cell gas effluent, other off gases	Zeolites, activated carbons

to consider gas separation processes. Gas separation is a very important process in many chemical industries and selective adsorption is one of the most common technologies used for this purpose. The key to selecting an appropriate nanoporous material for an environmental gas separation process is to ensure high selectivity of the adsorbent so that the intended gas removal (e.g. CO₂) from a gas stream (e.g. CO₂ and natural gas) via adsorption on the adsorbent is performed at a high rate or capacity without (relative) the absorbance of other species (e.g. natural gas) from the gas stream. Table 1 lists suitable adsorbents for various environmental gas separation processes.

CONCLUDING REMARKS

The synthesis and application of nanoporous materials is very exciting and is considered to be the fastest developing field in materials science. The multidisciplinary nature of research into these materials necessitates contributions from chemists, physicists and engineers in order to fully tap their potential for application in various industrial processes. In terms of environmental protection, the greatest challenges currently faced by the application of such materials are the transfer of laboratory studies to industrial application, as well as enabling cost-effective production of these materials.

The last factor is particularly crucial in developing countries, such as Malaysia, where the high cost of such materials often hinders their usage. AC and zeolites are undoubtedly still the preferred choices of nanoporous materials in terms of environmental protection in Malaysian industries. Nonetheless, it is hoped that in the near future, novel synthesised materials such as MCM-41, MOFs and COFs can be mass produced in a cost-effective manner so that their advantages, such as higher adsorptive capacities as well as lightweight properties, can be fully exploited in environmental applications. ■

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