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Research on Pressure Swing Adsorption of Resin for Treating Gas Containing Toluene

Ruixia Wei and Shuguo Zhao
Hebei Polytechnic University, Tangshan, Hebei
China

1. Introduction

1.1 Introduction of volatile organic compounds

Volatile organic compounds (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.

Volatile organic compounds or VOCs are organic chemical compounds whose composition makes it possible for them to evaporate under normal indoor atmospheric conditions of temperature and pressure. This is the general definition of VOCs that is used in the scientific literature, and is consistent with the definition used for indoor air quality.

Since the volatility of a compound is generally higher the lower its boiling point temperature, the volatility of organic compounds are sometimes defined and classified by their boiling points. For example, the European Union uses the boiling point, rather than its volatility in its definition of VOCs.

A VOC is any organic compound having an initial boiling point less than or equal to 250° C measured at a standard atmospheric pressure of 101.3 kPa. VOCs are sometimes categorized by the ease they will be emitted. For example, the World Health Organization (WHO) categorizes indoor organic pollutants as very volatile, volatile, and semi-volatile. The higher the volatility (lower the boiling point), the more likely the compound will be emitted from a product or surface into the air. Very volatile organic compounds (VVOCs) are so volatile that they are difficult to measure and are found almost entirely as gases in the air rather than in materials or on surfaces. The least volatile compounds (SVOCs) found in air constitute a far smaller fraction of the total present indoors while the majority will be in solids or liquids that contain them or on surfaces including dust, furnishings, and building materials.

Many VOCs are dangerous to human health or cause harm to the environment. VOCs are numerous, varied, and ubiquitous. They include both man-made and naturally occurring chemical compounds. Anthropogenic VOCs are regulated by law, especially indoors, where concentrations are the highest. VOCs are typically not acutely toxic, but instead have compounding long-term health effects. Because the concentrations are usually low and the symptoms slow to develop. The main hazard is as the following aspects:

1. The ability of organic chemicals to cause health effects varies greatly from those that are highly toxic, to those with no known health effect. As with other pollutants, the extent and nature of the health effect will depend on many factors including level of exposure

and length of time exposed. Eye and respiratory tract irritation, headaches, dizziness, visual disorders, and memory impairment are among the immediate symptoms that some people have experienced soon after exposure to some organics. At present, not much is known about what health effects occur from the levels of organics usually found in homes. Many organic compounds are known to cause cancer in animals; some are suspected of causing, or are known to cause, cancer in humans. Eye, nose, and throat irritation; headaches, loss of coordination, nausea; damage to liver, kidney, and central nervous system. Some organics can cause cancer in animals; some are suspected or known to cause cancer in humans. Key signs or symptoms associated with exposure to VOCs include conjunctival irritation, nose and throat discomfort, headache, allergic skin reaction, dyspnea, declines in serum cholinesterase levels, nausea, emesis, epistaxis, fatigue, dizziness.

- 2. The reaction of photochemical smog in the sunlight will occur among nitrogen oxides, hydrocarbons and photochemical oxidants of the atmosphere. The main component of photochemical smog is ozone, peroxy acetyl nitrate (PAN), aldehydes and ketones and so on. They stimulate people's eyes and respiratory system, endangering people's health and even harm plant growth.
- 3. Halogenated hydrocarbons VOCs may destroy the ozone layer and change the Earth's heat balance. According to the Indian National Academy of Sciences report, the emissions of chlorofluorocarbons into the atmosphere have increased the atmospheric methane and chloride absorption of infrared radiation and heat hinder the discharge of the Earth which will make the Earth's temperature, climate change.

VOCs	environmental acceptable concentration (mg/m ³)	health hazards
Toluene	100	Headache, dizziness, nausea, pulmonary emphysema
Benzene	5	Cancer, leukemia, respiratory paralysis
Xylene	100	Anemia, leukemia, red blood cells reduced, skin and mucous
Methanol	200	membrane irritation Neurological disorders, vomiting, insomnia, headaches,
Acetone	750	Cramps
Ethyl acetate	150	Irritate the eye, skin, numbness, headache, cough, nausea
Carbontetrachloride	5	Eye irritation, paralysis Abdominal pain, nausea, vomiting, cancer
Acetaldehyde	10	Mucosal erosion, blurred vision, pulmonary edema
Ether	400	Paralysis, nervous system damage, liver and kidney damage
Acetonitrile	40	Headache, dizziness, breathing difficulties, damage the central nervous
Acrylonitrile	20	Nausea, vomiting, difficulty breathing

Table 1. Common VOCs environmental acceptable concentration and human health hazards

As the VOCs harmful environmental effects, many countries have developed a corresponding law to limit emissions of VOCs. "Clean Air Act 1990" of the United States

requires 90% reduction in emissions of the 189 kinds of toxic chemicals which of about 70% belongs to VOCs. In 1996 Japan adopted legislative restrictions of 53 kinds of VOCs emissions and limited 149 kinds of VOCs emissions in 2002. China also enacted in 1997 and implemented the "Integrated emission standard of air pollutants" which limits 33 pollutant emission limits, including benzene, toluene, xylene and other volatile organic compounds. The VOCs harmful environmental effects and human health can not avoid in terms of current technology, so there is an urgent need for effective technology to control VOCs.

1.2 Vocs treatment technology

VOCs treatment technology is divided into two categories: Destruction processes and Recuperation processes. VOC controls include all technologies which either collect the VOCs for recovery and reuse, or destroy the VOCs. If the VOCs have recovery value, which typically implies single-VOC exhaust streams, and if the cost of recovery is less than the cost of purchasing new VOC, which typically implies relatively concentrated exhaust streams, then recovery makes sense. Carbon adsorption, scrubbing, and condensation are typical recovery techniques. Note that the installation and operation of a recovery technology may more than pay for itself if the recovery value of the VOC is high enough. If the VOC stream has no recovery value, if, for example, it is a mixture, or if there are disposal concerns, such as for toxic compounds, then destruction probably makes the most sense. Thermal and catalytic oxidation and biofiltration would be useful in this case.

1.2.1 Destruction processes

1.2.1.1 Thermal oxidation processes

Thermal oxidation is the process of oxidizing combustible materials by raising the temperature of the material above its auto-ignition point in the presence of oxygen, and maintaining it at high temperature for sufficient time to complete combustion to carbon dioxide and water. Time, temperature, turbulence (for mixing), and the availability of oxygen all affect the rate and efficiency of the combustion process. These factors provide the basic design parameters for VOC oxidation systems.

There are three basic types of thermal oxidation systems: direct flame, recuperative, and regenerative.

Direct flame systems or flares rely on contact of the waste stream with a flame to achieve oxidation of the VOCs. These systems are the simplest thermal oxidizers and the least expensive to install, but require the greatest amount of auxiliary fuel to maintain the oxidation temperature, thus entailing the highest operating cost. Flares are useful for destruction of intermittent streams.

Recuperative thermal oxidation systems use a tube or plate heat exchanger to preheat the effluent stream prior to oxidation in the combustion chamber. Thermal recovery efficiencies typically are limited to 40-70% to prevent auto-ignition in the heat exchange package, which could damage the package. Supplemental fuel therefore is usually required to maintain a high enough temperature for the desired destruction efficiency. Recuperative systems are more expensive to install than flares, but have lower operating costs.

Regenerative thermal oxidation systems typically incorporate multiple ceramic heat exchanger beds to produce heat recovery efficiencies as high as 95%. An incoming gas stream passes through a hot bed of ceramic or other material, which simultaneously cools

the bed and heats the stream to temperatures above the auto-ignition points of its organic constituents. Oxidation thus begins in the bed, and is completed in a central combustion chamber, after which the clean gas stream is cooled by passage through another ceramic heat exchanger. Periodically the flow through the beds is reversed, while continuous flow through the unit is maintained. Regenerative thermal oxidation systems are the most expensive thermal oxidizers to build, but the added capital expense is offset by savings in auxiliary fuel.

ESOCOV is a regenerative thermal oxidation process on ceramic beds. The process is especially well adapted to a mixture of gases with concentrations between 1 and 10 g/Nm³ and flows from 1.000 to 100.000 Nm³/h. The gas passes over a ceramic bed in which air is progressively heated and the VOC's are destroyed by oxidation above 800 C. The direction of the airflow is changed on a regularly basis in order to charge and discharge the calories in the bed(s). The thermal efficiency amounts to 90 - 98 %. In this way the regenerating systems are autothermal, so, without additional energy for concentrations higher than 1,5 g/Nm³. Addition of a catalyst to have the oxidation at a lower temperature (between 200 and 400 C).

1.2.1.2 Catalytic oxidation

Catalytic oxidation converts volatile organic compounds (VOC) into carbon dioxide and water, as do other oxidation processes, with no byproducts requiring disposal. Catalytic oxidation is well suited to applications with VOC concentrations ranging up to 25% of the lower explosion limit. With proper selection of catalyst, operating conditions, and equipment design, catalytic oxidation can attain VOC conversions of up to 99%. Advantages of this technology are low fuel usage, particularly with the proper choice of heat exchanger, little nitrogen oxide formation, given low operating temperatures, and little formation of partial oxidation products, such as carbon monoxide and aldehydes. Disadvantages include susceptibility to catalyst poisons, and the sensitivity of the catalysts to high temperatures.

Catalysts for VOC oxidation typically are either precious metals supported on ceramic or metal monoliths (honeycombs) or on ceramic pellets, or base metals supported on ceramic pellets. Catalyst life exceeds five years with the proper choice of catalyst, and may be extended with catalyst washing and regeneration techniques. Recent generations of catalysts have much longer lives and greater poison resistance than their forebears, and have greater capabilities, including the destruction of chlorinated organics.

As with any process, proper equipment design is essential to performance and operating cost. Typical catalytic oxidizer components include the catalyst housing, blower, burner, heat exchanger, controls, and stack. Small units are often skid-mounted and delivered to the site ready for installation.

As vent streams are often below the temperature at which catalytic oxidation is effective, most oxidizers use burners to preheat these streams to reaction temperatures, often from 400-800 °F. Heat is recovered using either recuperative or regenerative heat exchangers. As the latter can provide 95% heat recovery, streams with low VOC levels can be processed with minimal fuel usage.

1.2.1.3 Biological treatment processes

Biological method is essentially the use of microbial life activities to the emissions of VOCs into simple inorganic (such as CO₂ and H₂O) and microbial composition of the material itself. Common processes are biological filtration, biological washing. The biggest difference of biological filtration from biological wastewater treatment process is: in the

exhaust gas through the organic material must first transfer to the liquid (or solid surface of the film) in the mass transfer process, and then in the liquid (or solid surface of the biological layer) adsorption by microbial degradation. Biological method is particularly suitable for processing gas is greater than 17000m³ / h, the gas concentration is less than 1000ppm.

Biological method has many advantages compared to other technologies, it's simple, low operation cost, low investment relative to other methods, wide range of applications, while not easy to produce secondary pollution. Especially for low concentrations of VOCs (for example, when only a few ppm) the results of treatment is good. However, biological method is related to gas and liquid (or solid) mass transfer and chemical and biological degradation processes. The influencing factors are many and complex. Now, biodegradable technology is not enough in-depth theoretical study, so the biological treatment of VOCs present the design and operation is still basically remain in the level of experience. At the same time it also requires a larger footprint, which is limiting the biological treatment of extensive use of VOCs.

1.2.2 Recuperation processes

(1) Cryogenic Condensation processes

Low temperature or cryogenic condensation is a process that can be used as an effective means for VOC emissions control. Cryogenic condensation technology is based on lowering the vapor pressure of a component by reducing the temperature of the process stream thus increasing the recovery of the components in the liquid phase.

Since nitrogen gas is widely used in the chemical process industry, is inert and is typically transported and stored in it's liquid state at low temperature and high pressure, it is a convenient media to use. The low temperature capability of liquid nitrogen allows for the design of highly efficient condensation systems. At temperatures below -120°F, the vapor pressure of most organic compounds is depressed sufficiently to condense 95 to 99+% of the compounds from a typical emissions stream. In addition, the vented nitrogen can be recycled for reuse within the plant.

Cryogenic condensation is well suited for VOC emission control because of its ability to respond instantly to changes in VOC flow rate and solvent loading. It can recover virtually any VOC species even under varying conditions. Cryogenic condensation can deal with all organics (even in the presence of water) and can function when the concentration and composition are changing over time. This flexibility makes it particularly suitable for VOC control in multi-product, multi-purpose plants where batch or continuous processes are employed.

(2) membrane

Volatile organic compounds (VOCs) are involved in atmospheric pollution and green house effect. Some of these compounds might be recovered, instead of being released to the atmosphere, by several methods such as condensation, absorption, adsorption, etc. Among these processes, vapor permeation has several advantages since it requires compact equipment, it is non destructive and it is not energy-intensive. Over the past ten years, vapor permeation has been proven to be a feasible alternative to conventional processes in the recovery of several halogenated VOCs and monomers. In recent years, this process has found other applications such as in the recovery of hydrocarbon VOCs from the petroleum industry facilities; these applications are still under development.

Within the membranes used for the recovery of volatile organic compounds, composite membranes offer several advantages over other kinds. They are composed of a selective, defect-free layer that performs the vapor separation while another porous layer gives mechanical strength. Poly dimethyl siloxane (PDMS) is one of the most used polymers as selective permeation layer. It can be easily fabricated and thus is readily available for its use on large scales. The use of dimensionless solubility parameters showed that PDMS has good selectivities towards a wide variety of VOCs (e.g., hydrocarbons).

The recovery of toluene, propylene and 1,3-butadiene, which are compounds of particular concern in the petroleum industry, is focused on in this study. Since several petroleum activities such as oil storage or distribution, emit pollutants at low flow rates and variable concentrations, vapor permeation appears to provide a flexible recovery solution.

(3) absorption processes : ESOLAV

ESOLAV is a range of absorption processes or washers which transfers the VOC's into a liquid phase in order to be solubilized, oxidized or separated. It is especially well suited for VOC's soluble in the washing solution with weak and low concentrations ($< 1 \text{ g/Nm}^3$) and for gasflows between 500 and 50.000 m^3/h .

(4) adsorption with regeneration processes : ESOSORB

ESOSORB is a solvent adsorption process on beds of activated carbon with recuperation by desorption through steam. The process is very well adapted to gases containing 1 or 2 solvents in a concentration lower than 30 g/Nm^3 and gas flows between 200 and 200.000 Nm^3/h . These units are built out of several adsorbent beds containing activated carbon. The air to be treated is guided over the activated carbon where the VOC's are adsorbed until the activated carbon is saturated. If one of the adsorbing beds is saturated, a regeneration process is set in motion. After passage of the steam for the desorption a fan dries and cools the activated carbon beds, which makes them ready for a new adsorption cycle.

Adsorption on activated carbon is useful for recovery of VOCs with intermediate molecular weights (typically about 45-130): smaller compounds do not adsorb well, and larger compounds cannot be removed during regeneration, which typically is by steam stripping. Adsorption is most effective at lower temperatures, so that cooling of hot exhaust gas streams may be necessary. Further, dehumidification of very humid streams may be necessary for the carbon to have the greatest capacity. While carbon is the dominant adsorbent used, alumina, zeolites, and polymers have been used in some processes. Carbon can also be used to remove compounds in a once-through process with off-site regeneration.

1.3 Adsorption with regeneration processes and its principles

1.3.1 Adsorption

Adsorption refers to the binding of a dissolved solute onto the surface of a solid adsorbing material. It is a surface phenomenon and should not be confused with absorption, which is a term with a much broader meaning and generally deals with penetration of species into material. Adsorption can be used to separate a solute from a mixture of solutes, or a solute from a solvent. This is achieved by contacting the solution with the adsorbing material which is also called the adsorbent. The solute/s, which adsorb on the adsorbent, is/are referred to as adsorbate/s. The release of adsorbed material from an adsorbent is called desorption which is the reverse of adsorption.

Adsorption is a selective process and this selectivity is due to differences in the following: Molecular weight or size; Solute shape; Polarity; Electrostatic charge.

The physical binding of an adsorbate onto an adsorbent takes place due to non-covalent interactions such as: van der Waals forces; Electrostatic interactions; Hydrophobic interactions; Hydrogen bonding.

This type of adsorption takes place at ordinary temperature and is called physical adsorption or simply adsorption. Certain types of adsorption take place at much elevated temperatures when activation energy is available to break chemical bonds and facilitate chemical changes. Such processes are referred to as chemical adsorption or chemisorption.

The adsorbent material can be natural or synthetic. These generally have amorphous or microcrystalline structure and thus have very high specific surface area (surface area per unit amount of adsorbent). Commonly used adsorbents include clays like kaolin and bentonite, activated carbon, silica gel, activated alumina, zeolite (molecular sieves), etc.

Some of the advantages of adsorption over competing separation technologies are: High selectivity (e.g. affinity adsorption); Ability to handle very dilute solute concentrations. Major disadvantages are: It is a surface phenomenon, therefore the interior of the adsorbent material is not involved; Batch or semi-batch operations generally have to be used; In certain cases adsorbents have to be regenerated;

In certain cases adsorption results in loss of product quality (e.g. with certain bioproducts)

Some of the common applications of adsorption are: Gas separation using molecular sieves by pressure swing adsorption; Removal of toxic gases from air (e.g. gas masks); Fractionation of industrial chemicals using gas or liquid chromatography; Removal of trace amounts of CS₂ and H₂S; Removal of phenolic and other toxic chemical from waste water; Removal of chlorinated hydrocarbons from waste gas streams; De-hydration or de-humidification of gases; Water purification by deionization and ion-exchange; Fractionation and recovery of protein bio-products; Affinity separations of bio-products.

1.3.2 PSA

Pressure swing adsorption (PSA) is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It operates at near-ambient temperatures and so differs from cryogenic distillation techniques of gas separation. Special adsorptive materials (e.g., zeolites) are used as a molecular sieve, preferentially adsorbing the target gas species at high pressure. The process then swings to low pressure to desorb the adsorbent material.

Pressure swing adsorption principle can be illustrated in Figure 1. The gas component in a defined adsorption on the adsorbent is a function of temperature and pressure, usually available as shown below those adsorption isotherms. The figure shows the A, B two gases at the same temperature in a certain adsorbent adsorption isotherms on. Obviously, the same pressure A is more easily adsorbed than B. If A and B mixture through the adsorption column filled with the adsorbent, under relatively high pressure PH adsorption, at relatively low pressure PL desorption. The partial pressure of component A easily adsorbed are respectively PAH, and PAL, and the partial pressure of component B hard adsorbed are respectively PBH and PBL. The figure shows that under the relatively high-pressure component A is preferentially adsorbed, while the component B-rich gas stream in the outflow set. It is due to the equilibrium adsorption amount of q_{AH} of component A is much higher than the equilibrium adsorption amount of q_{BH} of component B. To make the adsorbent regeneration, the bed pressure is reduced to PL, the equilibrium adsorption

capacity of the component A and B are respectively q_{AL} and q_{BL} . In the process which a new equilibrium is reached, the amount of desorption are $q_{AH}-q_{AL}$ and $q_{BH}-q_{BL}$. This change in bed pressure periodically, the A, B mixture can be separated.

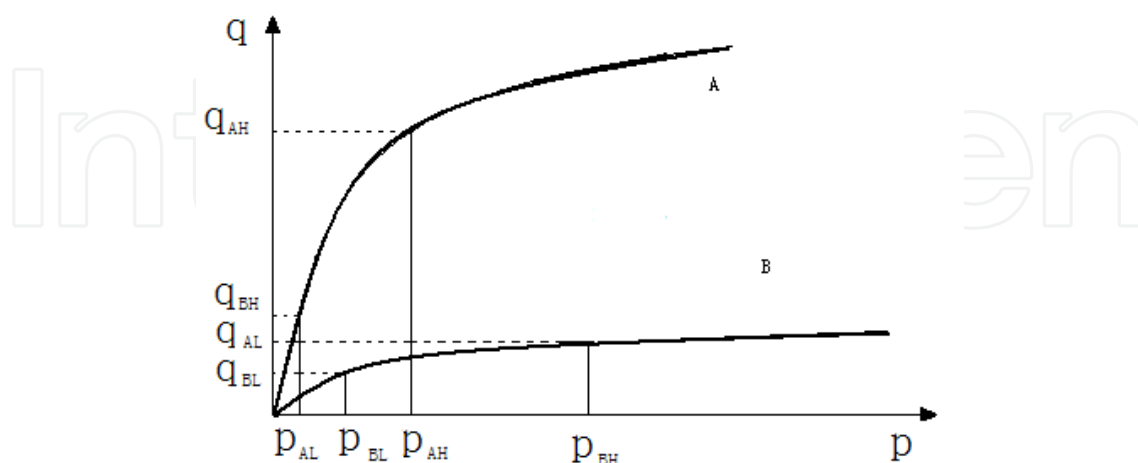


Fig. 1. The basic principle of pressure swing adsorption

Pressure swing adsorption processes rely on the fact that under pressure, gases tend to be attracted to solid surfaces, or "adsorbed". The higher the pressure, the more gas is adsorbed; when the pressure is reduced, the gas is released, or desorbed. PSA processes can be used to separate gases in a mixture because different gases tend to be attracted to different solid surfaces more or less strongly. If a gas mixture such as air, for example, is passed under pressure through a vessel containing an adsorbent bed that attracts nitrogen more strongly than it does oxygen, part or all of the nitrogen will stay in the bed, and the gas coming out of the vessel will be enriched in oxygen. When the bed reaches the end of its capacity to adsorb nitrogen, it can be regenerated by reducing the pressure, thereby releasing the adsorbed nitrogen. It is then ready for another cycle of producing oxygen enriched air. This is exactly the process used in portable oxygen concentrators used by emphysema patients and others who require oxygen enriched air to breathe.

Using two adsorbent vessels allows near-continuous production of the target gas. It also permits so-called pressure equalisation, where the gas leaving the vessel being depressured is used to partially pressurise the second vessel. This results in significant energy savings, and is common industrial practice.

Aside from their ability to discriminate between different gases, adsorbents for PSA systems are usually very porous materials chosen because of their large surface areas. Typical adsorbents are activated carbon, silica gel, alumina and zeolite. Though the gas adsorbed on these surfaces may consist of a layer only one or at most a few molecules thick, surface areas of several hundred square meters per gram enable the adsorption of a significant portion of the adsorbent's weight in gas. In addition to their selectivity for different gases, zeolites and some types of activated carbon called carbon molecular sieves may utilize their molecular sieve characteristics to exclude some gas molecules from their structure based on the size of the molecules, thereby restricting the ability of the larger molecules to be adsorbed.

One of the primary applications of PSA is in the removal of carbon dioxide (CO_2) as the final step in the large-scale commercial synthesis of hydrogen (H_2) for use in oil refineries

and in the production of ammonia (NH_3). Refineries often use PSA technology in the removal of hydrogen sulfide (H_2S) from hydrogen feed and recycle streams of hydrotreating and hydrocracking units. Another application of PSA is the separation of carbon dioxide from biogas to increase the methane (CH_4) content. Through PSA the biogas can be upgraded to a quality similar to natural gas. Nitrogen generator units employ the PSA technique to produce high purity nitrogen gas (99.5% or greater) from a supply of compressed air.

2. The part of experiment

2.1 Experimental materials and equipments

Granular activated carbon was from Takeda Pharmaceutical Chemistry Kabushiki Kaisha, Environmental Company). XAD-4, NDA-150 and ND-90 resin were made by Nan Da Ge De Environmental Protection Technology Co Ltd, and their characters were listed in Table 2. High performance liquid chromatography (Waters 600) was manufactured by USA Waters Company. Experimental device of pressure swing adsorption was made by Shanghai Tonguang Technology & Education Equipment Co Ltd..

2.2 Chemical properties of toluene

Toluene, formerly known as toluol, is a clear, water-insoluble liquid with the typical smell of paint thinners. It is a mono-substituted benzene derivative, i.e., one in which a single hydrogen atom from the benzene molecule has been replaced by a univalent group, in this case CH_3 . It is an aromatic hydrocarbon that is widely used as an industrial feedstock and as a solvent. Like other solvents, toluene is sometimes also used as an inhalant drug for its intoxicating properties; however, inhaling toluene has potential to cause severe neurological harm. Toluene is an important organic solvent, but is also capable of dissolving a number of notable inorganic chemicals such as sulfur.

Toluene reacts as a normal aromatic hydrocarbon towards electrophilic aromatic substitution. The methyl group makes it around 25 times more reactive than benzene in such reactions. It undergoes smooth sulfonation to give p-toluenesulfonic acid, and chlorination by Cl_2 in the presence of FeCl_3 to give ortho and para isomers of chlorotoluene. It undergoes nitration to give ortho and para nitrotoluene isomers, but if heated it can give dinitrotoluene and ultimately the explosive trinitrotoluene (TNT). With other reagents the methyl side chain in toluene may react, undergoing oxidation. Reaction with basify potassium permanganate and diluted acid (e.g., sulfuric acid) or potassium permanganate with concentrated sulfuric acid, leads to benzoic acid, whereas reaction with chromyl chloride leads to benzaldehyde (Étard reaction). Halogenation can be performed under free radical conditions. For example, N-bromosuccinimide (NBS) heated with toluene in the presence of AIBN leads to benzyl bromide. Toluene can also be treated with elemental bromine in the presence of UV light (direct sunlight) to yield benzyl bromide. Toluene may also be brominated by treating it with HBr and H_2O_2 in the presence of light.

Toluene is a common solvent, able to dissolve paints, paint thinners, silicone sealants, many chemical reactants, rubber, printing ink, adhesives (glues), lacquers, leather tanners, and disinfectants. It can also be used as a fullerene indicator, and is a raw material for toluene diisocyanate (used in the manufacture of polyurethane foam) and TNT. In addition, it is used as a solvent to create a solution of carbon nanotubes. It is also used as a cement for fine

polystyrene kits (by dissolving and then fusing surfaces) as it can be applied very precisely by brush and contains none of the bulk of an adhesive.

Industrial uses of toluene include dealkylation to benzene, and the disproportionation to a mixture of benzene and xylene in the BTX process. When oxidized it yields benzaldehyde and benzoic acid, two important intermediates in chemistry. It is also used as a carbon source for making Multi-Wall Carbon Nanotubes. Toluene can be used to break open red blood cells in order to extract hemoglobin in biochemistry experiments.

2.3 Experimental setup process

Air comes out of the air compressor filter which provides pressure for the experimental device, it filter out the oil, then into the organic gas generating device. The reaction had occurred after installation of benzene into the vapor mixing with air. Organic gases from the device comes into the adsorption column of the pipe with bypass for the determination of adsorption column inlet concentration. Adsorption column filled with resin and adsorption of gas access to outdoors by pipeline in the trachea on the road, passing through the bypass outlet to determine the concentration after adsorption. Experimental setup is as follows:

2.4 Experimental methods

1. The pretreatment of resin

The three kinds of resins were extracted by Soxhlet extractor with absolute alcohol to get rid of the porogen, catalyst, reaction solvent and other impurities. The process was stopped when the circumfluence liquid was colorless and transparent. Then the resins were washed with distilled water, filtered and dried in the ovens at 60°C after dried in the air. At last they were put into the dryer for a backup

2. Comparison of toluene adsorption between resin and activated carbon

XAD-4, NDA-150, ND-90 resin and activated carbon of same quality were taken as adsorbent, adsorbing 10 min at 0.1MPa pressure and room temperature, with flux of 3L/min, and selected the optimum adsorbing resin by comparing adsorbing effects of 3 types of resin and activated carbon.

3. Experiment of the optimum adsorption flux

The resin and activated carbon were taken as adsorbent of toluene gas, under 0.1MPa pressure and room temperature, in-gas flux of 3, 4, 5, 6, 7L/min. After they adsorbed 10 min, removal rate of toluene in air were tested to confirm the optimum adsorbing flux of resin and activated carbon

4. Experiment on variance of desorption effect under different pressures

Desorbed resin and activated carbon after adsorption by the optimum adsorption flux and time under the pressure of -0.05Mpa, -0.04Mpa, -0.03Mpa, -0.02Mpa, -0.01Mpa, continued stable desorption for 12 min, tested desorption rate of toluene at 4, 6, 8, 9, 10, 11, 12 min, to confirm the optimum desorbing pressure and time

5. Experiment on stability

Under the optimum adsorption and desorption conditions of pressure swing confirmed by the above experiment, 100 batches of experiment on stability were conducted with resin and activated carbon as adsorbent, and removal rate of toluene each time and observed characters of resin and activated carbon were tested.

Gases treated in experiments of 1)-5) were all air containing toluene of 0.5178mg/L.

2.5 Analysis method

Toluene concentration was tested by Waters 600 High Performance Liquid Chromatograph (HPLC), and chromatographic column was C18 reversed phase column. Flowing phase was carbinol: water (80:20). Flow speed: 0.8ml/min, ultraviolet detector, 254nm in wavelength.

To investigate surface area and aperture distribution of resin and activated carbon, we adopted BET method, nitrogen gas as adsorbent, equipment type be Micromeritics ASAP2010 (USA). Infrared Spectroscopy was tested by Fourier transform infrared spectroscopy by using potassium bromide and pressed film method of resin powder. Element analysis was tested by Perkin-Elmer240c (USA) elemental analyzer.

resin	XAD-4	NDA-150	ND-90	granular activated carbon
structure	macroporous adsorption resin	hypercrosslinked	amino-modified hypercrosslinked	carbon build-up
geopolarity	non-polar	weak-polar	mid-polar	weak-polar
BET surface area (m ² /g)	850	906	819.1	880
average pore diameter (nm)	5.83	1.7	1.5	4.0
microporous surface area (m ² /g)	3.1	561.3	463.3	231.7
micropore volume (mL/g)	0.0051	0.2256	0.2186	0.1048
porosity (%)	40	53	52	42
granularity (mm)	0.4-0.6	0.4-0.6	0.4-0.6	0.4-0.5
oxygen content (%)	0	2.9	1.5	0.2
amino content (mmol/g)	0	0	1.51	0

Table 2. The nature of resin ND-900, NDA-101 and NDA-99

3. Results and discussion

3.1 The comparison of toluene adsorption of resin with activated carbon

Seen from Fig.2 evidently, the adsorption quantity of resin NDA-150 is the highest under the same condition, mainly relating to aperture, specific surface area and polarity of every adsorbent. Toluene is weak-polar molecule, so the adsorbability is minor on the non-polar resin XAD-4. In addition, from table1 we know that the aperture of resin XAD-4 is mainly big pore, but the other three kinds of sorbent have a certain amount of micropores.

Adsorbent with micropores adsorbs molecule not only depending on the high specific surface area, but also filling function of micro-aperture and capillarity, which both play significant role [8-10], so the adsorption quantity of resin XAD-4 for toluene is the lowest. Resin ND-90 is amino-modifying hyper-cross-linked resin, is mid-polar resin in spite of a lot of micropores, be adverse for the adsorption of toluene for higher polarity, so the adsorption quantity of toluene is less. The polarity of active carbon and NDA-150 matches with the polarity of toluene, the discrepancy of specific surface area between two adsorbents is not big, and the main distinguish is micropore volume. The micropore volume of NDA-150 is more than twice as activated carbon, so the adsorption quantity of resin NDA-150 for toluene is the highest. Therefore, resin NDA-150 and activated carbon were taken as adsorbent in the following experiment.

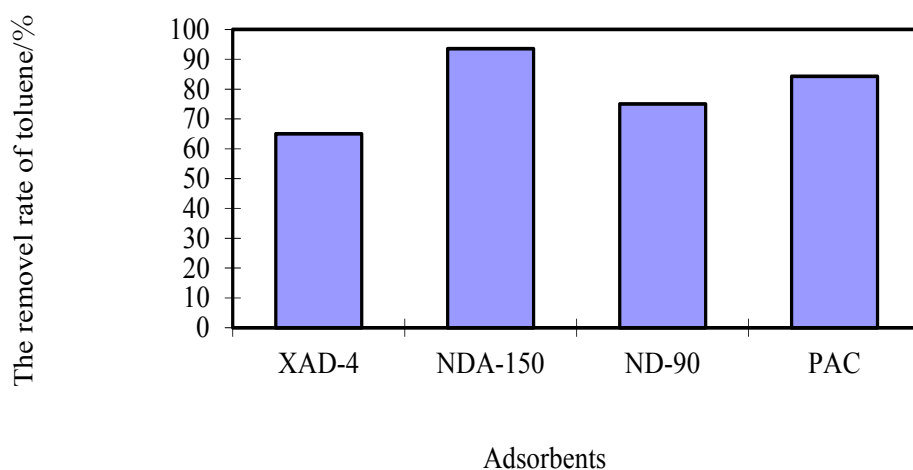


Fig. 2. The comparison of every adsorbent in toluene adsorption

3.2 The confirm of the best adsorption flow

According to the fig.3, we know that the removal of toluene reduced with the increase of intake flow. Adsorption process is very complicated, generally, can be divided into three phases: ①out-diffusion, gas molecules get on the surface of adsorbent form outside space; ②in-diffusion, gas molecules go deeply into adsorption surface along adsorbent channel; ③adsorption on the internal adsorption surface. Toluene molecules have no time to contact with adsorbent fully and be adsorbed when adsorption flux increased, and effuse from the adsorption column with airflow. Thereby, only by controlling the flow can toluene molecular absorbed by adsorbent. From fig.3, we learn that the resin NDA-150 has optimal adsorption effect when the adsorption flow is 3L/min, but the absorption effect at 5L/min has very small difference with that of 3L/min, however, adsorption efficiency reduced evidently when the gas flow increase from 5L/min to 6L/min. There are certain requests for adsorption volume in actual adsorption process, and the adsorption volume of exhaust gas was not great in the adsorption process when the adsorption efficiency is the highest, hence, confirmed the optimal adsorption flow was 5L/min considering the two factors, the absorption efficiency and the adsorption volume disposal gas. For activated carbon, adsorption efficiency declined evidently when the gas flow increased from 4L/min to 5L/min, so the optimal adsorption flow is 4L/min.

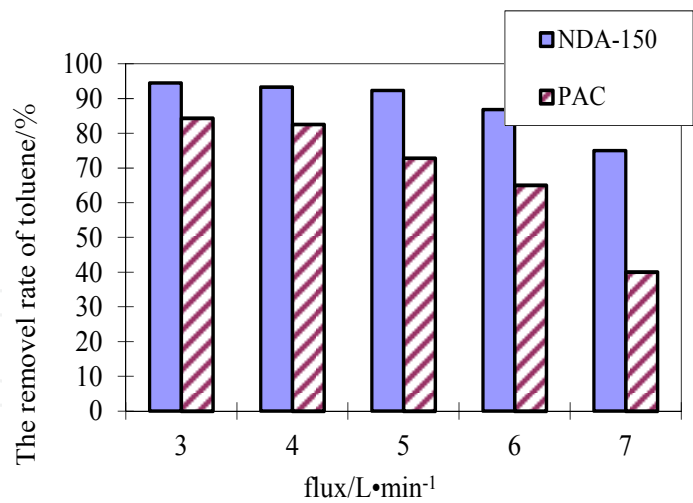


Fig. 3. The adsorption results of different adsorption flows

3.3 The confirm of the best adsorption time

As can be seen from the Fig4, the adsorption efficiency of adsorbent declined as time increased. It will take some contact time for toluene gas molecules entering into micropore of adsorbent; therefore, the longer the time, the much more amount of toluene entering micropore, tends to saturation in the end. Seen from Fig.4, the maximum absorption efficiency of NDA-150 resin and activated carbon are absorption for 5 minutes. There is slight difference of absorption effect between 10 min and 5 min for absorption time. At the same time, absorption efficiency descended significantly when the absorption time varying from 10 min to 12 min. Resin had the maximum adsorption efficiency when the absorption time was 5 min, but the volume of gas that resin dealt with was too small to satisfy the demand for the volume of gas that resin dealt with in actual process. Allowing for the two factors of absorption efficiency and absorption capacity, we determined the best adsorption time of NDA-150 resin and activated carbon were in 10 minutes.

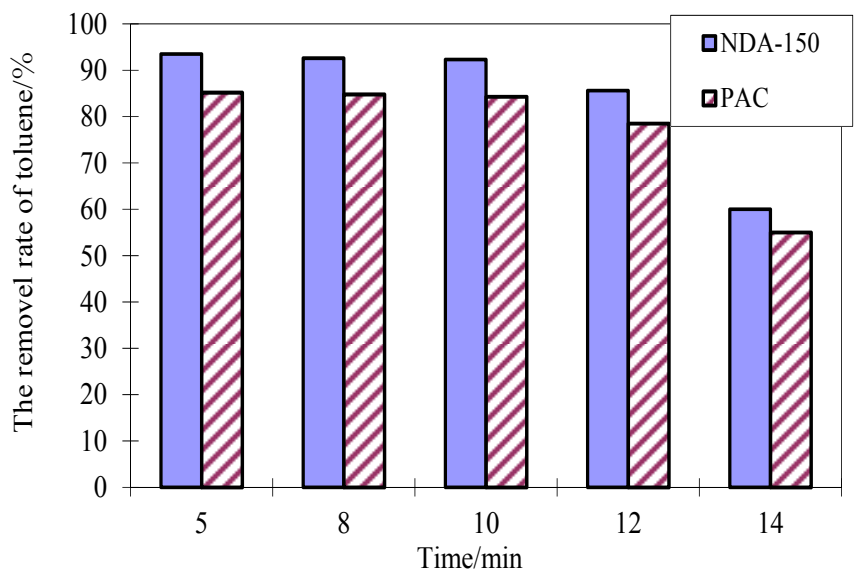


Fig. 4. Different absorption effects of different adsorption time

3.4 The confirm of desorption pressure and desorption time

From Fig. 5 and Fig. 6, we know that desorption efficiency of activated carbon increases with the time in the same condition of desorption negative pressure, and tends to balance gradually. With a certain desorption time, increasing desorption negative pressure makes desorption efficiency increased, and acquires the best desorption efficiency in -0.05MPa.

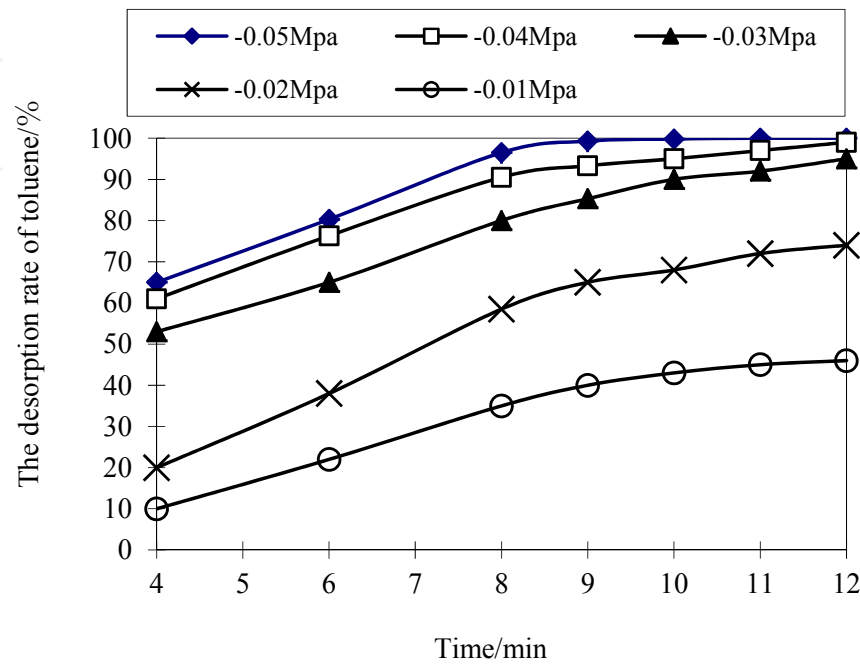


Fig. 5. The variation of desorption result of NDA-150 resin at under different desorption pressure with the time

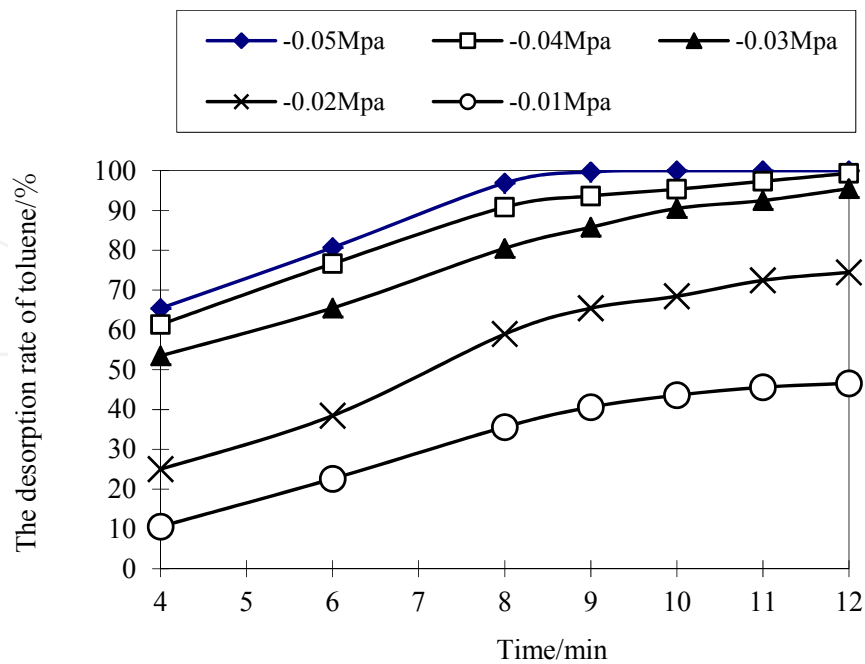


Fig. 6. The variation of desorption result of activated carbon at under different desorption pressure with the time

In theory, the greater desorption negative pressure, the higher desorption efficiency. However, in actual project, the greater negative pressure, the greater requirements of equipment and energy. As a result, we determined the best desorption negative pressure of resin and activated carbon is 0.05Mpa from this experiment. In the desorption pressure of -0.05Mpa, desorption rate could reach 99% after 9 minutes, while desorption efficiency didn't increase significantly when desorption time varied from 10 minutes to 12 minutes, closing to balance. Accordingly, chose the optimum desorption time for 10 minutes, and desorption efficiency were 99.8 percent at this point.

3.5 The stability test

It can be seen from the results of stability (listed in table 3): because of the weak mechanical strength of activated carbon, the more the number of repeated experiments, the greater impact under pressure, much seriously damaged, seriously affected its treatment. It is only by adding new activated carbon in time in order to guarantee treatment results. Conversely, the resin is synthetic organic polymer, has powerful mechanical strength. It didn't have damage within 100 batches of experiments and effect on the absorption efficiency of resin for toluene. Therefore, it is feasible to treat organic waste gas using resin as absorbent.

The number of experiments	Toluene removal (%)		Character	
	<i>activated carbon</i>	<i>NDA-150 resin</i>	<i>activated carbon</i>	<i>NDA-150 resin</i>
20	83.5	92.3	intact	intact
40	82	92.5	A portion of activated carbon had crack, and small particles of activated carbon emerged	intact
60	79.5	92	The amount of activated carbon that had cracking increased, walls of adsorption column are stuck by activated carbon powder.	intact
80	75	92	A small amount of active carbon powder appears at the bottom of adsorption column	intact
100	70	92.4	The quantity of activated carbon powder increased	intact

Table 3. The results of stability

4. Conclusions

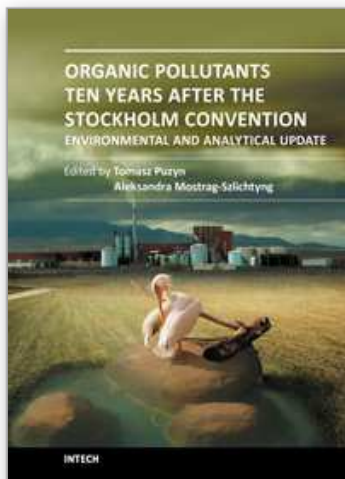
Having studied pressure swing adsorption for purifying toluene gas of low concentration by using activated carbon and resin as absorbent respectively, the experimental results indicate:
NDA-150 resin has the best adsorption effect on adsorption of air containing toluene. The optimum adsorption flow of resin and activated carbon is 5L/min and 4L/min respectively, the optimum adsorption time both are 10min, and the best adsorption efficiency respectively is 92.3% and 83.5%.
With desorption negative pressure be -0.05Mpa, the optimal desorption time of the resin and activated carbon both are 10min, and desorption rates can reach 99%.
It can be seen from the results of the stability test that resin as absorbent superior to activated carbon in treating air including toluene.

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Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update

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Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

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InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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