

TREATMENT OF MTBE IN WASTEWATER BY AIR STRIPPING AND
CARBON ADSORPTION.

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ABSTRACT

A study was conducted on the efficiency of the combined system for removal of the Methyl-tert-butyl ether (MTBE) from wastewater by simultaneous use of air stripping and carbon adsorption. MTBE which is widely used in industrial may cause environmental concern due to its presence in waste water. Two main processes involve in this research. These processes are air stripping and carbon adsorption. Compressed air is used in air stripping process and the Granular Activated Carbon is for adsorption where adsorption of MTBE occurs on the GAC. This research is about to use combine system and remove pollutant from the wastewater, where combination of air stripping and activated carbon adsorption in remove MTBE from wastewater was analyzed. The experimental rig experiments conducted at different flow rates 4 and 6 (L/min). It conducted at different open valve time that is 30s, 40s, 50s, 60s, 120s, 180s and 240s. The highest removal for flow rate 4 is 85% at cycle time 240s and for flow rate 6 is 90% for cycle time 240s. The removal of the surfactant MTBE from water by simultaneous use of air stripping and powdered granular carbon, GAC adsorption shows better performance than other system. From this research It can be concluded that, the overall project achieve the objectives by completion. The combine system effectively removes MTBE from waste water. Hope the environmental problem also will be reduced by treat the waste water contain MTBE before it is release to natural water sources.

ABSTRAK

Sebuah penelitian dilakukan untuk mengkaji kecekapan sistem gabungan untuk merawat eter Methyl-tert-butyl (MTBE) dari air buangan industri dengan menggunakan serentak *air stripping* dan *carbon adsorption*. MTBE yang banyak digunakan dalam industri boleh menyebabkan masalah persekitaran kerana kehadirannya di dalam air buangan. Di dalam kajian ini, dua proses utama yang terlibat, iaitu *air stripping* dan *carbon adsorption*. Udara yang dikompresi digunakan dalam proses *air stripping* dan butiran *Activated Carbon* adalah untuk *adsorption* di mana jerapan MTBE terjadi pada GAC itu. Penyelidikan ini adalah tentang menggunakan menggabungkan dua sistem untuk menghilangkan bahan pencemar dari air buangan, di mana kombinasi *air stripping* dan *carbon adsorption* dalam menghilangkan MTBE dari air buangan dianalisis. Percubaan *experimental rig* dilakukan di peringkat aliran udara yang berbeza; 4 dan 6 (L / minit). Ini dilakukan pada waktu injap terbuka yang berbeza yang 30s, 40s, 50s, 60s, 120s, 180s dan 240s. Kecekapan tertinggi bagi aliran udara 4 adalah 85% pada 240s masa kitaran dan untuk aliran udara 6 adalah 90% pada 240s masa kitaran. Perawatan MTBE dari air dengan menggunakan *air stripping* dan *carbon adsorption* menunjukkan prestasi lebih baik daripada sistem ini secara bersendirian. Dari penelitian ini dapat disimpulkan bahawa, keseluruhan projek mencapai tujuannya. Penggabungan dua sistem ini berkesan menghilangkan MTBE dari air buangan. Hendaknya masalah persekitaran juga akan dikurangkan dengan memproses air buangan yang mengandungi MTBE sebelum didedahkan kepada sumber air semulajadi.

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CHAPTER 1

INTRODUCTION

1.0 Background of study

Water pollution is a major problem in the global context. It has been suggested that it is the leading worldwide cause of deaths and diseases. The effect of water pollution are varied which is to humans, animals, plants and ecosystem. They include poisonous of drinking water, poisonous of food animals, unbalanced river and lake ecosystem that can no longer support full biological diversity, deforestation from acid rain and many other effects. So it's not a weird when wastewater discharged from diverse industries plays an important role in environmental pollution; wastewater recycling is now an emerging global issue, and contributes critically to the sustainability of environment. Based on research by Japanese Consulting Institute (JCI) on water pollution in Malaysia, rivers in Malaysia generally appear to have high organic pollution loads and high SS concentrations. Low rainfall, which resulted in reduced

flow rates in the rivers, was cited as one of the reasons for the increased pollution. In addition, the agriculture-based industries (natural rubber and palm oil production, for instance), manufacturing industry, and livestock industry was identified as the sources of pollution that contributing to BOD loading in water in Malaysia. Figure below shows the water quality in Malaysia:

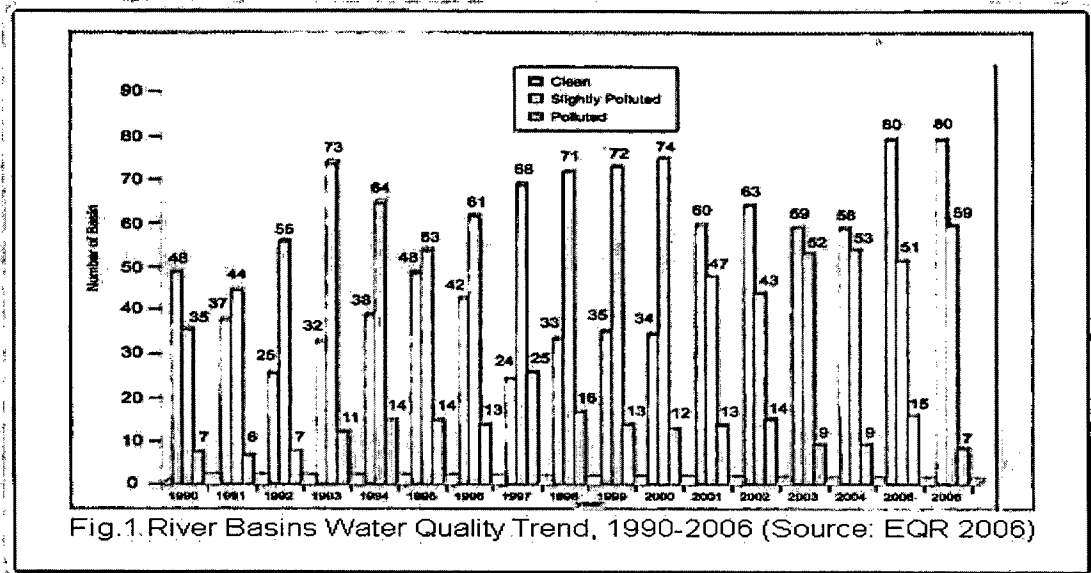


Figure 1: River Basins Water Quality Trend, 1990-2006

Most wastewater contains heavy metals and organic compounds, which are not only harmful to human health but also dangerous to nature life. One of them is Methyl-Tert-Butyl-Ether (MTBE). Technology for treating industrial wastewater can be divided into three categories: chemical methods, physical methods and biological methods. Chemical methods are include chemical precipitation, chemical oxidation or reduction, formation of an insoluble gas followed by stripping, and other chemical reaction that involve exchanging or sharing electrons between atoms. Physical treatment methods include sedimentation, floatation, filtering, stripping, ion exchange, adsorption, and other process that accomplish removal of dissolved and undissolved substance without necessarily changing their chemical structure. Meanwhile biological treatment methods are those that involve living organism using organic or in some instances, inorganic, substances for food, completely changing their chemical and physical characteristics.

In this experiment, I have focus on physical treatment method: air stripping and powdered activated carbon (PAC) adsorption. Air stripping was shown to have the lower unit treatment costs for higher flow rates, although relatively tall towers were required for greater treatment requirements. PAC was examined using rapid small-scale column tests (RSSCT). PAC was effective at most conditions, although it was also the most costly alternative for most waters.

1.1 Problem Statement

The practice of adding methyl tert-butyl ether, MTBE, to gasoline started in the late 1970s and increased dramatically in the 1990s in an effort to increase combustion efficiency and reduce air pollution. With advantage, much industry has opened to produce MTBE to fulfill the demand. Wastewaters from this industry that contain MTBE have to be treated before it being release to river.

The common method, air stripping, has a low cost operational, but efficiency of this method is lower than any other method. While, carbon adsorption is most effective method at most condition, but to operate this method, it consumes a lot of operational cost. This study is purpose to maximize the advantage and minimize the disadvantage at each method by combining this two methods.

1.2 Objectives

The major objectives in this study are:

- To renew previous methods to get optimum advantage in treating the MTBE by combining air stripping and carbon adsorption.
- To reduce the operational cost and to increase efficiency method of treating the MTBE.

1.3 Scopes of Study

In order to achieve the objectives, the following scopes have been identified:

- Synthetic wastewater
- Bench scale experiment
- Experimental rig

1.4 Rationale and Significance

There are some purposes why industrial wastewater entering collecting systems or wastewater treatment plants shall be subject to such pre-treatment. These because of in order to:

- Gain the highest efficiency of the process.
- Reduce the operational cost of treatment method.
- Protect the nearest population from pollution of MTBE.
- Ensure that discharges from the treatment plants do not adversely affect the environment, or prevent receiving water from complying with other Community Directives,

CHAPTER 2

LITERATURE REVIEW

In this chapter will discuss about what the wastewater and what is MTBE that contain in wastewater. For the next section, it will discuss more in detail on air stripping process description and carbon adsorption.

2.1 Wastewater

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. Wastewater can be divided in three categories:

1. Domestic (sewage) wastewater is the water that contains mainly human and animal wastes, household wastes, small amounts of groundwater infiltration and small amounts of industrial wastes.
2. Sanitary wastewater — consists of domestic wastes and significant amounts of industrial wastes. In many cases, the industrial wastes can be treated without special precautions. However, in some cases, the industrial wastes will require special precautions or a pretreatment program to ensure the wastes do not cause compliance problems for the wastewater treatment plant.
3. Industrial wastewater — consists of industrial wastes only. Often the industry will determine that it is safer and more economical to treat its waste independent of domestic waste.
4. Combined wastewater — consists of a combination of sanitary wastewater and storm water runoff. All the wastewater and storm water of the community is transported through one system to the treatment plant.
5. Storm water — contains a separate collection system (no sanitary waste) that carries storm water runoff including street debris, road salt, and grit.

2.2 Methyl-tert-butyl-ether (MTBE)

The oxygenate methyl tert-butyl ether (MTBE) is added to gasoline to increase the octane level and to reduce carbon monoxide and hydrocarbon emissions by vehicles. MTBE is the most commonly used fuel oxygenate.

In Europe, usage in gasoline has increased by 23% between the years 1995 and 1999. The annual demand for MTBE in Europe today is about 3 million tons (t), which is approximately equal to the production capacity (EFOA, 2004).

In Germany, MTBE is used mainly as an octane enhancer and therefore the concentrations in gasoline are nearly constant all year round in contrast to the United States, where MTBE is added either seasonally to control carbon monoxide (OXY areas) in winter time or year round to control troposphere ozone (RFG areas). The calculated usage of MTBE as a fuel additive in Germany in 2001 was 683,900 t (Sur et al., 2003). Typical concentrations are 0.43%, 3.0% and 10.2% (w/w) for regular, Euro super and super premium gasoline, respectively (Sur et al., 2003).

2.3 Risk of MTBE

The biotransformation of MTBE leads to the formation of tert-butanol (TBA) and formaldehyde which in turn are further metabolized. The toxicokinetic data do not indicate reasons for concern with regard to bioaccumulation of MTBE or its metabolites.

Transient central nervous system (CNS) depression and mortality occur at high-doses/concentrations only. Following acute exposures to MTBE skin and respiratory irritation are regarded as the primary concern. Labeling of MTBE as irritant (Xi) with the corresponding R-phrase 38 (irritating to skin) is proposed by the European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) Task Force.

MTBE causes loss of consciousness when inhaled at exposure concentration of 28800 mg/m³ and above. At lower exposures transient behavioral changes have been described in animal studies. The no observable adverse effect level (NOAEL) for these reversible functional CNS effects observed after 6 hours of exposure is 2880 mg/m³.

Principal effects identified for MTBE following repeat oral or inhalation exposure are local irritation at the site of entry, CNS effects (transient anesthesia), kidney effects (chronic nephropathy) and liver effects (hepatocellular hypertrophy). The NOAEL for sub-chronic oral exposure is 300 mg/kg. The NOAEL for chronic inhalation exposure is 400ppm or 1440 mg/m³. This corresponds to retain MTBE-doses in the body of 102 and 113 mg/kg/day for male and female F-344 rats, respectively, and 182 and 184 mg/kg/day for the male and female mouse, respectively.

Irritation observed after short-term exposure in humans as well as liver and kidney toxicity observed after long term exposure in experimental animals are considered to be the critical effects for the health risk characterization of MTBE. The basis for the risk characterization is a comparison of three different doses / concentrations for these effects with occupational and consumer exposure data.

2.4 Air stripping

Air stripping is a full-scale technology in which volatile organics are partitioned from ground water by greatly increasing the surface area of the contaminated water exposed to air. Types of aeration methods include packed towers, diffused aeration, tray aeration, and spray aeration.

Air stripping involves the mass transfer of volatile contaminants from water to air. For ground water remediation, this process is typically conducted in a packed tower or an aeration tank. The typical packed tower air stripper includes a spray nozzle at the top of the tower to distribute contaminated water over the packing in the column, a fan to force air countercurrent to the water flow, and a sump at the bottom of the tower to collect decontaminated water. Auxiliary equipment that can be added to the basic air stripper includes an air heater to improve removal efficiencies; automated control systems with sump level switches and safety features, such as differential pressure monitors, high sump level switches, and explosion-proof components; and air emission control and treatment systems, such as activated carbon units, catalytic oxidizers, or thermal oxidizers. Packed tower air strippers are installed either as permanent installations on concrete pads or on a skid or a trailer.

Aeration tanks strip volatile compounds by bubbling air into a tank through which contaminated water flows. A forced air blower and a distribution manifold are designed to ensure air-water contact without the need for any packing materials. The baffles and multiple units ensure adequate residence time for stripping to occur. Aeration tanks are typically sold as continuously operated skid-mounted units. The advantages offered by aeration tanks are considerably lower profiles (less than 2 meters or 6 feet high) than packed towers (5 to 12 meters or 15 to 40 feet high) where height may be a problem, and the ability to modify performance or adapt to changing feed composition by adding or removing trays or chambers. The discharge air from aeration

tanks can be treated using the same technology as for packed tower air discharge treatment.

Modifying packing configurations greatly increase removal efficiency. A recent innovation is the so-called low-profile air stripper that is offered by several commercial vendors. This unit packs a number of trays in a very small chamber to maximize air-water contact while minimizing space. Because of the significant vertical and horizontal space savings, these units are increasingly being used for ground water treatment.

Air strippers can be operated continuously or in a batch mode where the air stripper is intermittently fed from a collection tank. The batch mode ensures consistent air stripper performance and greater energy efficiency than continuously operated units because mixing in the storage tanks eliminates any inconsistencies in feed water composition.

The eventual duration of cleanup using an air stripping system may be tens of years and depends on the capture of the entire plume from the ground water.

Limitations:

The following factors may limit the applicability and effectiveness of the process:

- The potential exists for inorganic (e.g., iron greater than 5 ppm, hardness greater than 800 ppm) or biological fouling of the equipment, requiring pretreatment or periodic column cleaning.
- Effective only for contaminated water with VOC or semi volatile concentrations with a dimensionless Henry's constant greater than 0.01.
- Consideration should be given to the type and amount of packing used in the tower
- Process energy costs are high
- Compounds with low volatility at ambient temperature may require preheating of the ground water.

Cost:

The key cost driver information and cost analysis was developed in 2006 using the Remedial Action Cost Engineering and Requirements (RACER) software.

➤ Low Profile Tray Stacks

The following table represents estimated costs (by common unit of measure) to apply ex situ air stripping using low profile tray stack technology at sites of varying size.

Table 1: Ex Situ Air Stripping--Low Profile Tray Stack

W TECHNOLOGY:	Ex Situ Air Stripping--Low Profile Tray Stack			
RACER PARAMETERS	Scenario A	Scenario B	Scenario C	Scenario D
	Small Site		Large Site	
	Easy	Difficult	Easy	Difficult
GALLONS TREATED	52,560,00	52,560,00	1,314,000,00	1,314,000,00
	0	0	0	0
COST PER GALLON	\$0.0020	\$0.0021	\$0.0004	\$0.0004
COST PER 10,000 GALLONS	\$20	\$21	\$4	\$4

➤ Packed Towers

The following table represents estimated costs (by common unit of measure) to apply ex situ air stripping using packed tower technology at sites of varying size and complexity.

Table 2: Ex Situ Air Stripping--Packed Tower

W TECHNOLOGY:	Ex Situ Air Stripping--Packed Tower			
RACER PARAMETERS	Scenario	Scenario	Scenario C	Scenario D
	A	B		
	Small Site		Large Site	
	Easy	Difficult	Easy	Difficult
GALLONS TREATED	52,560,00	52,560,00	1,314,000,00	1,314,000,00
	0	0	0	0
COST PER GALLON	\$0.0023	\$0.0034	\$0.0004	\$0.0005
COST PER 10,000 GALLONS	\$23	\$34	\$4	\$5

2.5 Carbon adsorption

Vapor-phase carbon adsorption is a remediation technology in which pollutants are removed from air by physical adsorption onto activated carbon grains. Carbon is "activated" for this purpose by processing the carbon to create porous particles with a large internal surface area (300 to 2,500 square meters or 3,200 to 27,000 square feet per gram of carbon) that attracts and adsorbs organic molecules as well as certain metal and inorganic molecules.

Commercial grades of activated carbon are available for specific use in vapor-phase applications. The granular form of activated carbon is typically used in packed beds through which the contaminated air flows until the concentration of contaminants in the effluent from the carbon bed exceeds an acceptable level. Granular-activated carbon (GAC) systems typically consist of one or more vessels filled with carbon connected in series and/or parallel operating under atmospheric, negative, or positive pressure. The carbon can then be regenerated in place, regenerated at an off-site regeneration facility, or disposed of, depending upon economic considerations.

Carbon can be used in conjunction with steam reforming. Steam reforming is a technology designed to destroy halogenated solvents (such as carbon tetrachloride, CCl_4 , and chloroform, CHCl_3) adsorbed on activated carbon by reaction with superheated steam (steam reforming).

VOC Recovery and Recycle:

Another more recent technology related to vapor phase carbon adsorption is the Brayton-cycle heat pump (BCHP). This technology created by Idaho National Engineering Laboratory offers a method for VOC recovery and recycling. A Brayton-cycle heat pump can condense volatile organic compounds (VOCs) from an air stream, which offers the potential for both recovery and either on-site or off-site recycle of a

wide range of VOCs. The VOC-laden air stream can come from either vapor vacuum extraction of soil or air stripping of contaminated ground water.

The technology consists of activated carbon adsorbers located at each extraction well, plus a truck-mounted BHP to regenerate the adsorbers on a periodic basis. The VOC-laden air from the well is passed through the carbon bed, adsorbing the VOCs. When the bed becomes saturated, hot nitrogen from the regenerator is used to desorb the VOCs from the bed. The nitrogen passes through a chiller, is compressed, and is then cooled in a recuperator, where 50% to 80% of the organics are recovered. The partially depleted nitrogen stream is then expanded through a turbine, lowering the temperature to as low as -150oF and condensing the remaining organics. The now-clean nitrogen passes through the recuperator to cool the VOC-laden nitrogen before returning to the carbon bed. The only outputs will be the clean off-gas from the well and a small amount of recovered organics.

Applicability:

Vapor-phase carbon adsorption is not recommended to remove high contaminant concentrations from the effluent air streams. Economics favor pretreatment of the VOC stream, followed by the use of a vapor-phase GAC system as a polishing step.

Limitations:

Factors that may limit the effectiveness of this process include:

- Spent carbon transport may require hazardous waste handling.
- Spent carbon must be disposed of and the adsorbed. Contaminants must be destroyed, often by thermal treatment.
- Relative humidity greater than 50% can reduce carbon capacity.
- Elevated temperatures from SVE pumps (greater than 38° C or 100° F) inhibit adsorption capacity.
- Some compounds, such as ketones, may cause carbon bed fires because of their high heat release upon adsorption.

Data Needs:

Factors that affect adsorption are temperature, type and porosity of the carbon, the type and concentration of the contaminant, residence time in the bed; and in gas phase adsorption, temperature and humidity. At high temperatures, the volatility of compounds increases, thus reducing their affinity for carbon. Basic compounds are adsorbed better at high pH. Activated carbon is available from manufacturers in a variety of grades with different properties and affinities for adsorption of contaminants. Thus, it is often necessary to conduct adsorption tests with a particular contaminated stream on a variety of activated carbons from several manufacturers to identify a carbon that will be most effective for a particular application.

Cost:

Equipment costs range from less than \$1,000 for a 100-scfm unit to \$40,000 for a 7,000-scfm unit. Carbon cost is \$2 to \$3 per pound.

CHAPTER 3

METHODOLOGY

In this chapter, a detail experiment outline will be presented, which includes materials to be used, description of experimental rig and bench scale and also sequence of experimental procedures. The main purpose of this study is to investigate the efficiency to remove the Methyl tert-butyl ether (MTBE) by carbon adsorption and air stripping.