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Phytoremediation on Air Pollution

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1. Introduction

Air pollution has been becoming a necessary evil with rapid industrialization and urbanization around the world, after it results in kinds of human health problems, such as ophthalmic, respiratory and cardiovascular diseases (Brunekreef & Holgate, 2002; Giles et al., 2011; Gudmundsson, 2011; Jamrozik & Musk, 2011; Miller et al., 2007; Nandasena, 2010). The direst threat posted by air pollution may be its hard controlling caused by its strong flowability. Either could it be spread from one source location to a larger region, even the whole planet, and the sweeping radiation pollution in air originated from Fukushima in Japan is unfortunately in this case, or conversely diluted with changes of climatic conditions (Sample, 2007).

Among all types of treatments of contaminants, including microbial bioremediation, phytoremediation stands out for its benefits yielded from self-maintaining, soil stabilization and other advantages to meet greater public approval (Doty et al., 2007). And different phytoremediation process is responsible for specific pollutant. Air pollutants can be divided into anthropogenic and natural pollutants according to their sources, or primary and secondary pollutants, which stem from reactions of primary pollutants, when taking production process into account (UNEP, 2004). However, physical, chemical and biologic pollutants belong to three general categories as usually discussed in air pollution treatment, and particulate matters, organic and inorganic chemicals, and microorganism were referred to the above categories respectively. This chapter will start from conception of phytoremediation, current state of phytoremediation of air pollutants, such as particulate matters, inorganic and organic pollutants, and a case study from recent authors' research on phytoremediation of benzene and toluene of indoor air will be finally presented.

2. Phytoremediation

Phytoremediation is a way to mitigate environment pollutions, such as in air, water and soil pollution in virtue of plants, more often than not, combined with their associated microorganisms. This concept has been widely applied to treat pollutants in soil and water (Cunningham & Ow, 1996; Schröder et al, 2002).

2.1 Principles of phytoremediation

Briefly, for phytoremediation, roles from roots to shoots are played in phytostabilization, rhizodegradation, phytoextraction, phytodegradation, phytovolatilization and phytofiltration

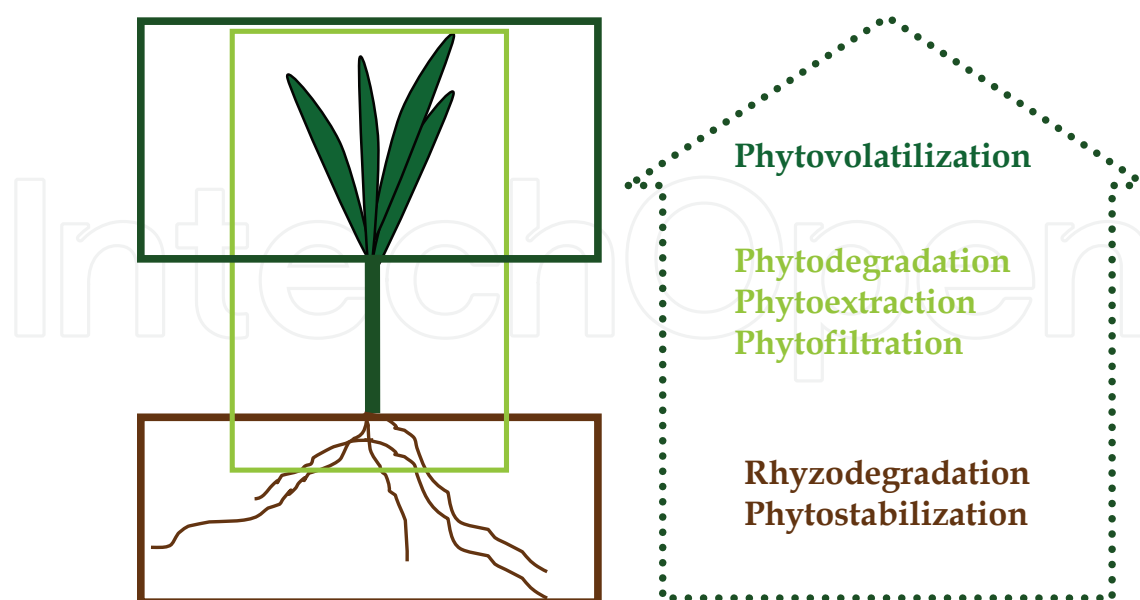


Fig. 1. Different parts of the plants are responsible for different processes of phytoremediation.

(Morikawa & Erkin, 2003) (see Fig. 1.). It is the process for phytostabilization that contaminants were sequestered, but not degraded, in the root zones. The narrow region of 1-3 mm from root surface is rhizosphere, where there are much more profuse microorganisms than in bulk soil. Root secretions and rhizospheric microorganisms are joint-agents to degrade the pollutants in soil in the process of rhizodegradation. Phytoextraction is with regard to extracting pollutants from soil and translocating them from the roots to shoots by plants. Phytodegradation is to transform and/or degrade pollutants, which enter the plants from soil, water or air. Phytovolatilization means the pollutants are volatile out of the stoma of the plants and degraded by hydroxyl radicals, otherwise they will become air pollutants. It is phytofiltration that particulate matters in air are reduced through the surface of plants (Singh & Tripathi, 2007).

2.2 Characteristics of phytoremediation

2.2.1 Main advantages

Phytoremediation is proved to be helpful to reduce pollutants in soil, water and air; it is energy-economizing and cost-effective compared with those physical or chemical methods since it is solar-energy driven cleanup technology; it is a preference for people as its aesthetic value and less environment disruption, which letting nature take its course.

2.2.2 Primary disadvantages

Plants are also living things, and there exists tolerance limits for the toxicity of pollutants; it is a kind of “leave it to chance” thing since it is too natural to disrupt the environment: optimum concentrations of pollutants for remediation varying with species of plants, intermediates possibly leading to second pollutants, time-consuming when considering growth period of plants.

2.3 Examples of phytoremediation of air pollutants

2.3.1 Particulate matters

Vegetation has been used to shield dust in many countries, and the process is called phytofiltration. A 8-m wide green belt may reduce 2 to 3 times of dust fall (Novoderzhikina et al., 1966 as cited in Singh & Tripathi, 2007). For phytofiltration, morphological characteristics, such as orientation of leaf on the main axis, size and shape, surface nature, the presence or absence of trichomes and wax deposition, are factors to trap or capture dust from ambient air.

2.3.2 Inorganic pollutants

NO_x

NO_x are air pollutants, and they are one of precursors of photochemical reaction. They can reach plant system through wet/dry deposition to foliar or roots. Plant species, plant age, NO_x concentration and other environmental conditions are factors which influence the leaf penetration of NO_x. After NO₂ enter into the plant, most of them are metabolized to organic compounds, e.g. amino acid, through nitrate assimilation pathway. The enzymes in plants, such as nitrate reductase, nitrite reductase or glutamine synthetase may play an important role in this process. Genetic engineering could turn plants into magic sink for NO_x by making the enzymes overexpressed.

SO₂

Nearly 70% SO₂ in the atmosphere originates from fossil fuel combustion. SO₂ enters into plants mainly through stoma, and can be utilized in a reductive sulfur cycle in plants. They are changed into SO₄²⁻ or SO₃²⁻ in cell walls. Adenyl-5-phosphosulphate, carrier protein, carrier protein with bound sulphite and carrier protein with bound sulphide are the intermediates in the reduction pathway. The final products are cysteine or other organic compounds.

2.3.3 Organic pollutants

Formaldehyde

Formaldehyde, a ubiquitous air pollutant, is so harmful that it is classified as a mutagen and carcinogen. In the 1980's, an NASA's research in the USA revealed that low level of formaldehyde in air could be removed by plant leaves alone, while higher concentrations of the toxic chemical can be filtered by activated carbon firstly and the plant roots and associated microorganisms degrade and assimilate remained chemicals (Wolverton, 1988). In cell-culture experiments (Giese, 1994), when the concentration of formaldehyde is low enough (8.5 mg · m⁻³), spider plants (*Chlorophytum comosum* L.) shoot can metabolize it to organic acids, amino acids, free sugars, lipids and cell-wall components. In soybean (*Glycine max* L.) cell cultures, serine and phosphatidylcholine are the major metabolic products for formaldehyde. NAS⁺-dependent formaldehyde dehydrogenase and glutathione-dependent formaldehyde dehydrogenases have been isolated from cell-suspension cultures of some plants. It appears that formaldehyde can be oxidized and then degraded in C1 metabolism in phytodegradation.

Benzene and toluene

As members of VOCs (Volatile Organic Compounds, VOCs), benzene is genotoxicity and carcinogenicity while toluene is a neurotoxic chemical (Pariselli et al., 2009). Benzene and toluene have been reported to be removed from air and be assimilated by plants (Porter, 1994; Ugrekhelidze, 1997). Porter (1994) suggested at the lower toluene exposure, a fairly

modest amount light change was credited with significant increase or decrease of removal rate and the plant, the only photoresponsive organisms in the system, may be responsible for the phenomenon. Furthermore, hydroxylation is considered to be the first step of the aromatic ring cleavage of benzene and toluene in higher plants (Ugrekheldidze, 1997). Besides, a substantial role of microorganisms in the growth medium in removing benzene and toluene was also reported by previous researches (Orwell et al., 2004; Orwell et al., 2006; Wood et al., 2002; Wood et al., 2006).

Two compartments Model

Foliage-air exchange is believed to be the primary route of plant uptake particularly for semi-volatile and volatile organics. Two-compartment model has been used to explain atmosphere-foliage bioaccumulation phenomenon, namely a relatively fast initial uptake followed by a period of slower uptake (Keymeulen, 1995; Mackay et al., 2006). In the model, the leaf was divided into two compartments according to its structure. The first compartment can be referred to the non-living plant cuticle, where physico-chemical sorption of airborne lipophilic compounds can occur. The second compartment is within the leaf interior, where further sorption and metabolism of organic compounds may exist.

3. Removal of benzene and toluene from indoor air by ornamental houseplants—a case study (Yang, 2010)

3.1 Indoor air pollution

Indoor air pollution in urban environments has become a significant health concern, as city dwellers often spend over 90% of their time indoors (USEPA, 1987; Abbritti & Muzi, 1995; American Lung Assoc., 2001). “Sick building syndrome” (SBS) or “building-related illness” is partly attributed to the indoor chemicals, particularly in air-conditioned buildings (Burge et al., 1987; Mendell and Smith, 1990; Carpenter, 1998; Brasche et al., 1999; Carrer et al., 1999; Jones, 1999; Sundell, 2004). As indoor pollutants, volatile organic compounds (VOCs) with 300 species having been detected, should not be negligible (Orwell et al., 2004), after the cocktail of VOCs might lead to additive effects on human health (Wolkoff, 1995; Weschler and Shields, 1997; Pariselli *et al.*, 2009). Thus, removing these chemical mixtures from indoor air merits serious consideration. Many experimental studies have investigated the effects of plants on VOCs (Cape, 2003). This part presents a study on applicability of phytoremediation of benzene and toluene from indoor air.

3.2 Experiments design

Indoor ornamental plants were purchased from flower markets for experiments. Plants were well watered and allowed to drain for 24 hours before fumigation.

A series of experiments were designed as follows (see Fig. 2.):

1. Plants-Screening experiments

This experiment aimed to acquire plants which are capable of effective-removing binary mixture of benzene ($0.26 \text{ mg} \cdot \text{m}^{-3}$) and toluene ($0.3 \text{ mg} \cdot \text{m}^{-3}$). For this purpose, initial screening experiment and replication experiment for validation were carried out in sequence. Allowing for vast amounts of species of plants, only one individual for every species of plants was fumigated in the initial screening experiment. After some ineligible ones could inevitably have slipped into candidates in the initial screening experiment, further three replicates for those species which showed relative high removal rates were

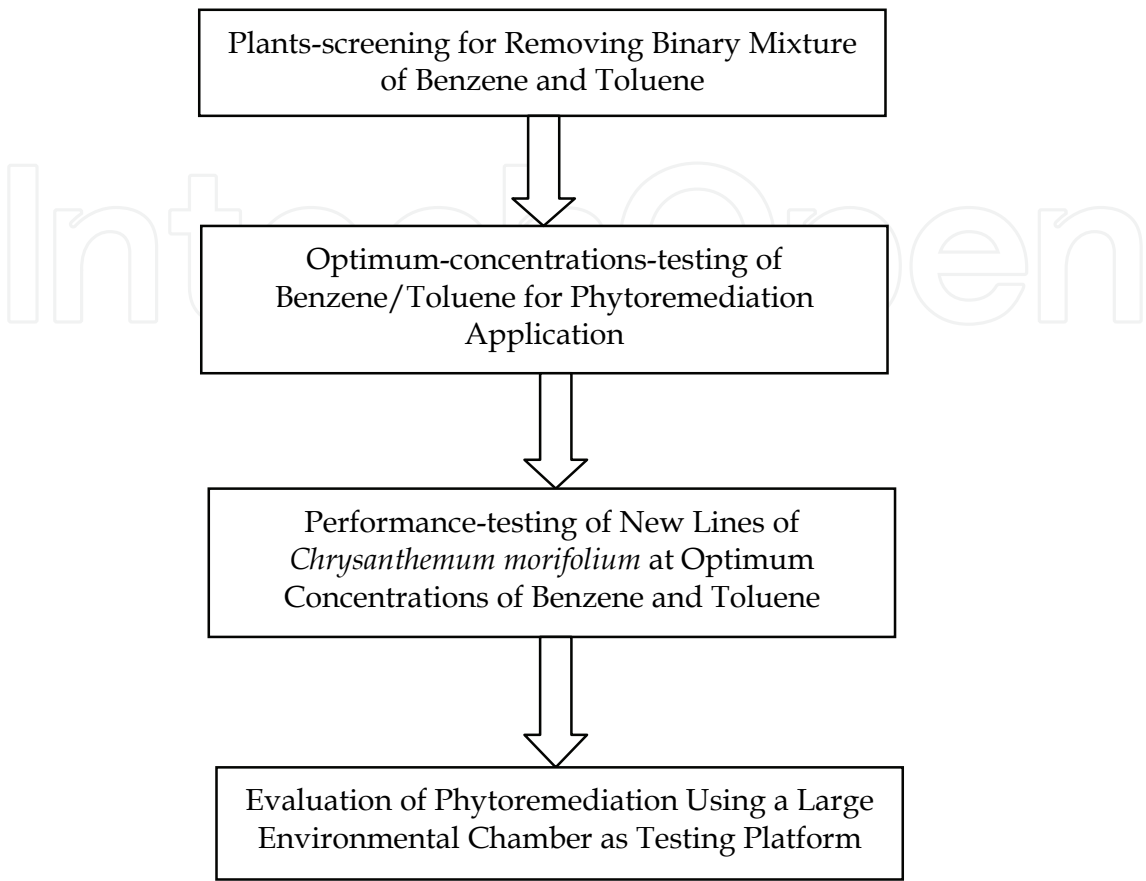


Fig. 2. Processes of the case study on Removal of Benzene and Toluene from Indoor Air by Ornamental Houseplants

established in replication experiment to confirm the removal effects and to quantitatively estimate the rate and efficiency of phytoremediation.

2. Fumigating-experiments at gradient concentrations

The gradient concentrations (Table 1.) were set up to investigate optimum concentrations of benzene and toluene for phytoremediation application. The plants were chosen from those plants with relatively high removal efficiency from plants-screening experiment.

3. Evaluating-experiments for new lines of *Chrysanthemum morifolium*

It is one object in the experiments to evaluate removal performance of new lines of *Chrysanthemum morifolium* at the optimum concentrations of benzene and toluene acquired in the experiments mentioned above. *Chrysanthemum morifolium*, a Chinese traditional flower, has been so popular they are available everywhere in the country. The phytoremediation on indoor air pollution is believed to be easy to be promoted, if *Chrysanthemum morifolium* demonstrates ideal removal effects.

The other object is to establish a large environmental chamber as a testing-platform to evaluate phytoremediation on indoor air pollution.

Gradient concentrations (mg · m ⁻³)	
Benzene	Toluene
0.26	0.31
0.64	0.76
1.3	1.5

Table 1. Gradient concentrations of benzene and toluene set up in the fumigating experiments

3.3 Fumigation system

A set of eight cylindrical, Plexiglas chambers (41 cm in diameter, 70 cm in height, ca. 0.09 m³ in volume) were lined with Teflon film to reduce possible absorption by Plexiglas material (see Fig. 3.). Stainless steel or Teflon Pipes were used to carry gasses in order to minimize the loss of benzene/toluene. Simultaneously, compressed purified air and standard mixture of benzene and toluene entered a cylindrical, stainless steel mixing chamber. The flow rate of air and benzene/toluene was regulated by Float Flow Meter and Mass Flow Meter respectively, which were calibrated by Bubble Flow Meter before use. Thus, air containing expected concentrations of benzene and toluene was continuously and evenly distributed to fumigation chambers through 8 Float Flow Meters. It took about 2 hours to achieve expected concentrations of benzene and toluene of outlet air based on the continuous measuring the benzene/toluene concentrations at the inlets and outlets of the eight empty chambers. Fig. 4. shows the fumigation system in the study.



Fig. 3. Photograph of a Plexiglas chamber housing one potted plant

Among the eight chambers, two chambers were designated randomly as controls, one holding only pots and soil similar to those used in the experimental chambers; another empty one used to monitor stability of gasses flow. And the other six chambers housed six different plant species per trial. After three hours (from 9 a.m. to 12 noon) and six hours

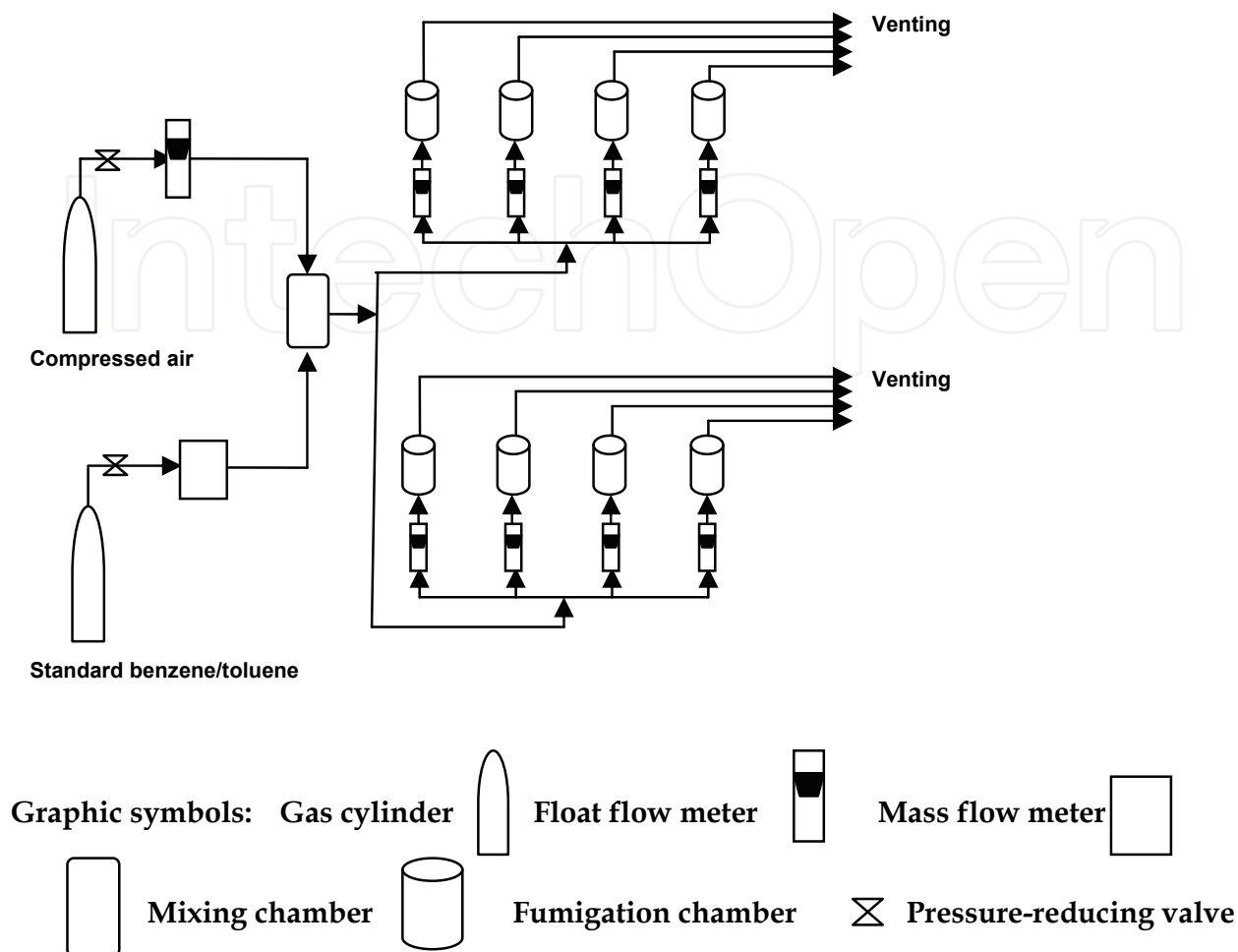


Fig. 4. Schematic diagram for fumigation system

(continue to extend from 12 noon to 3 p.m.) of exposure, gasses were sampled using a 100 mL gastight syringe for immediate analysis. The benzene/toluene removal rate was calculated as follows:

$$(C_{\text{control}} - C_{\text{sample}}) / C_{\text{control}} \times 100\% \quad (1)$$

Where C represents benzene or toluene concentration ($\text{mg} \cdot \text{mL}^{-1}$).

After sample collection, chambers were evacuated and prepared to test the next plants. The same sampling procedure with 8 empty chambers was inserted every 5 trials to test leak to guarantee uniform concentrations of benzene/toluene in all eight chambers.

14 m³ stainless steel of environmental chamber was made to meet ASTM 1333-96 (reapproved 2002) (see Fig. 5.). Parameters inside the chamber, such as temperature (25°C), relative humidity (45%) and air exchange rate (once every four hours), were maintained during the whole testing period. In the large chamber, concentrations in three steps, namely, background of empty chamber, only chemical evaporation and plants-fumigating were analyzed. 1 mL of benzene and toluene liquid were dropped in a 90 cm-high Petri dish to evaporate. The first sampling was taken after 10 minutes of evaporation, followed by next 8



Fig. 5. The photograph of inside of the environmental chamber

samplings every one hour. Gas samples were collected from 6 air sampling ports, each of them with 15 L of sample. When plants-fumigating, four replicates of the same species of *Chrysanthemum morifolium* were placed on the four corners of the chamber floor. Ventilation and scrubbing should be conducted between fumigation experiments.

3.4 Results and discussion

1. Plants-Screening experiments

In the initial screening experiment, 94 species and cultivars were tested, among which 15 species removed more than 30% of benzene or toluene at either 3-hour or 6-hour sampling. Eight species of plants, *Rhododendron hybrids*, *Hosta plantaginea*, *Ctenanthe oppenheimiana* cv. Tricolor, *Ficus elastica*, *Calathea rotundifolia* cv. Fasciata, *Codiaeum variegatum*, *Chrysanthemum morifolium*, *Hemerocallis fulva*, were chosen for the following replication experiment to confirm the removal effects, since they are more easily accessible. On the other hand, fixed time dependence on removal rates was not found for all species in this phase, just as Ugrekhelidze (1997) pointed out the ability of different plants to absorb and utilize exogenous hydrocarbons varied.

In the initial screening experiment, *Crassula portulacea*, *Cymbidium Golden Elf*. and *Dieffenbachia amoena* cv. Tropic Snow did not display well as in previous experiment (Liu et al., 2007), less than 10% removal rate of benzene. Apart from toluene interference, fumigation fashion (kinetic/static and flow rate at inlet of each fumigation chamber), chamber size, concentration of benzene may all contribute to different removal effects

(Table 2.). In reference to studies on the effects of plants on VOCs, two main types of fumigation chambers were applied – static chambers and kinetic chambers. For a static chamber, more accessories have to be equipped with, such as thermostat and stirring devices needed to accelerate atmospheric equilibration, so that difference of concentrations at the same spot in the chamber at different time period can be evaluated effects of plants on VOCs, whereas effects of plants on VOCs can be determined by the difference of concentrations at inlet and outlet of a kinetic chamber with continuous gas-flow through (e.g. Liu et al., 2007).

For replication experiment, removal rates of 8 species of plants of benzene or toluene at either sampling (3-hour or 6-hour) were showed to be more than 30% in the replication experiment. Furthermore, for the convenience of comparison, the removal rates of benzene and toluene was normalized for leaf area (m^2). For most of 8 species of plants, the removal rates of benzene after 6-hour fumigation increased compared with those after 3-hour fumigation. The case of toluene reversed. A competitive reduction might exist when both benzene and toluene penetrating into leaves were under metabolic control, but combined removal remained essentially unchanged (Porter, 1994). This could be used to elaborate the reversal trend of removal rate with time showed by benzene and toluene.

Chrysanthemum morifolium displayed an excellent performance in removing both benzene and toluene at twice samplings in replication experiment. So it was chosen for further Evaluating-experiment.

2. Fumigating-experiments at gradient concentrations

From those 15 species which removed more than 30% of benzene or toluene at 3-hour or 6-hour sampling in the initial screening experiment, six species of plants such as *Rhododendron hybrids*, *Ficus elastica*, *Codiaeum variegatum*, *Hemerocallis fulva*, *Euphorbia pulcherrima* and *Cymbidium sinense* were chosen to test removal capacities at gradient concentrations of benzene and toluene (Yang et al., 2011) (see Table 1). The removal rates at different condition varied. At 0.64 mg m^{-3} of benzene and/or 0.76 mg m^{-3} of toluene, better removal effects were showed, and considering the household application, it is better to arrange some species of plants to achieve the best removal effects taking account of concentrations, fumigation time and pollutants.

3. Evaluating-experiment for new lines of *Chrysanthemum morifolium*

Not only did *Chrysanthemum morifolium* show an excellent performance in removing both benzene and toluene according to the results showed in plants-screening experiments, but also it is a kind of symbolic Chinese traditional flower. So it was chosen for evaluating-experiment. The new lines of *Chrysanthemum morifolium* were provided by Institute of Vegetable and Flower, the Chinese Academy of Agricultural Sciences. They are bred via anther culture and radiation mutation from breeding parents of *Chrysanthemum* with spray forms. It was the first performance-testing in China to remove gaseous benzene-toluene using new lines of *Chrysanthemum morifolium* (Yang et al., 2010).

While selective removal of benzene or toluene was not significantly showed in nine lines of *Chrysanthemum*, most of them removed more toluene than benzene. Removing rates varied significantly with lines. Samples from 6-hour of fumigation suggested that above 30% of removal rates of both benzene and toluene were reached by lines of the number 2, 4, 5, 9, in the meanwhile removal rate of toluene from line of the number 7 dropped to 0 from 13% at 3-hour of fumigation (Yang et al., 2010). From the results of removal amount, lines of the number 2, 4, 5, 8, 9 should be taken for application performance testing in real world considering better performance-testing results.

Chrysanthemum morifolium and *Calathea rotundifolia* cv. Fasciata were chosen for performance evaluation in the large environmental chamber. After 10 minutes of evaporation, 10 mg m⁻³ of benzene and 8.5 mg m⁻³ of toluene were detected in the chamber. At first three hours, benzene and toluene were reduced significantly when fumigating *Chrysanthemum morifolium* compared with only chemical fumigation. It suggested that phytoremediation on indoor air pollution should be an effective way to remove organic pollutants. Besides, the environmental chamber is stable in performance, low in adsorption and background value of pollutants, convenient and safe in operation so that it could provide a testing platform for evaluating phytoremediation of gaseous pollutants.

Plant species	Fumigation fashion	Chamber size	VOCs member	Concentration level	Removal rate
<i>Crassula portulacea</i> <i>Cymbidium Golden Elf.</i> and <i>Dieffenbachia amoena</i> cv. Tropic Snow	Kinetic fumigation (0.5 L/min at inlet of each chamber)	Cylindrical; 40 cm in diameter, 60 cm in height,	Benzene	150 ppbv	More than 20% after 2-h fumigation
<i>Epipremnum aureum</i>	Static fumigation	Cubic; 60 × 60 × 60 cm	Benzene	25 ppmv	Less than 10% (Average removal rate in initial dose) after 3-h fumigation

Table 2. Fumigation methods and results in previous studies (Liu et al., 2007; Orwell et al., 2004)

4. Future perspective

As a technology, phytoremediation on air pollution is still in its infancy, and study on the applicability of phytoremediation is scarce. First, it is necessary that appropriate testing and evaluating platform should be established for different application. Static and kinetic fumigation fashion, fumigation box and large environmental chamber should be adopted according to goals of experiments. Second, pollutants-removing mechanism needs further studying from morphology to metabolism, from plant alone to associated microorganisms. Third, based on mechanism studies, prediction models can be established and accuracy be improved. In the meanwhile, the study of optimum concentrations of pollutants depending on species of plants should not be neglected for the technology promotion.

5. Conclusion

Phytoremediation is an eco-friendly, cost-effective way to remove pollutants from environment. Phytostabilization, rhizodegradation, phytoextraction, phytodegradation, phytovolatilization and phytofiltration are main principles of phytoremediation. As physical

and chemical air pollutants, phytoremediation of particulate matters, NO_x, SO₂, formaldehyde, benzene and toluene have been reported. Moreover, the authors studied applicability of phytoremediation from aspects of plants-screening, optimum concentrations and evaluation system. For all this, the study on the applicability of phytoremediation still needs work for future technology promotion.

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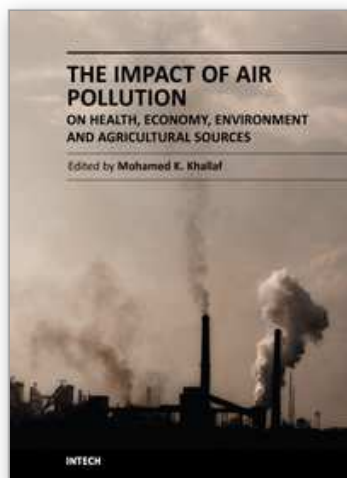
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The Impact of Air Pollution on Health, Economy, Environment and Agricultural Sources

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This book aims to strengthen the knowledge base dealing with Air Pollution. The book consists of 21 chapters dealing with Air Pollution and its effects in the fields of Health, Environment, Economy and Agricultural Sources. It is divided into four sections. The first one deals with effect of air pollution on health and human body organs. The second section includes the Impact of air pollution on plants and agricultural sources and methods of resistance. The third section includes environmental changes, geographic and climatic conditions due to air pollution. The fourth section includes case studies concerning of the impact of air pollution in the economy and development goals, such as, indoor air pollution in México, indoor air pollution and millennium development goals in Bangladesh, epidemiologic and economic impact of natural gas on indoor air pollution in Colombia and economic growth and air pollution in Iran during development programs. In this book the authors explain the definition of air pollution, the most important pollutants and their different sources and effects on humans and various fields of life. The authors offer different solutions to the problems resulting from air pollution.

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