Biofiltration of volatile compound mixtures from pulp and paper industries

Doctoral thesis

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Biofiltración de mezclas de compuestos volátiles de industrias de pasta y papel

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corroboran

Que el trabajo titulado **Biofiltration of volatile compound mixtures from pulp and paper industries,** ha sido realizado por la Licenciada en Química **Mirian Estefanía López Gómez** en el Departamento de Química Física e Enxeñaría Química I y que, como directores del mismo, **autorizan** su presentación para optar al grado de **Doctora**.

Y para que así conste, expiden y firman la presente en A Coruña, a de de 2015.

Christian Kennes María del Carmen Veiga Barbazán

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ABSTRACT

A two-stage bioreactor, comprising a biotrickling filter (BTF) as the first-stage and a biofilter (BF) as the second-stage, operated under steady-and transient-state conditions, was tested to remove gas-phase hydrogen sulphide, methanol and α-pinene. Hydrogen sulphide and methanol were removed in the first-stage, while α-pinene, was removed predominantly in the second-stage. The bioreactors were tested with two types of shock loads, long-term (66h) low to medium concentration loads, and short-term (12h) low to high concentration loads. Their performances were modelled using artifitial neural network (ANN), in order to predict the removal efficiencies (REs). It was observed that, a multi-layer perceptron with the topology 3-4-2 was able to predict RE of methanol H_2S in the BTF, while a topology of 3-3-1 was able to approximate RE of α-pinene in the BF. The same gaseous mixture was later examined in a biotrickling filter (BTF), inoculated with a highly adapted microbial consortium. The presence of methanol showed an antagonistic removal pattern for α-pinene, but the opposite did not occur. α-Pinene, removals were affected by itself. H_2S did not show any declining effect on the other compounds. This BTF was also modeled using ANNs and subjected to different types of short-term shock-loads. It was observed that, short-term shock-loads of individual pollutants (methanol or hydrogen sulfide) did not significantly affect their own removal, but the removal of α-pinene was affected by 50%.

RESUMEN

Un biorreactor en dos etapas, consistente en un biofiltro percolador (BTF) como primera etapa y un biofiltro (BF) como segunda etapa, se operó bajo estados estacionario y transitorio, para purificar una mezcla gaseosa compuesta por sulfuro de hidrógeno, metanol y α-pineno. El sulfuro de hidrógeno y el metanol se eliminaron en la primera etapa, mientras que el α-pineno se eliminó fundamentalmente en la segunda etapa. Los biorreactores fueron sometidos a dos tipos de sobrecargas: a largo plazo (66h) con cargas bajas-medias y de corto plazo (12 horas) con altas cargas. Utilizando redes de neuronas artificiales (ANNs), se realizó un modelado para predecir las respectivas eficiencias de eliminación (EEs). Se observó que un perceptrón multicapa con topología 3-4-2 fue capaz de predecir la eliminación del H_2S y del metanol en el BTF, mientras que una topología de 3-3-1 fue capaz de aproximar la eliminación del α-pineno en el BF. La misma mezcla gaseosa fue posteriormente examinada en un BTF inoculado con un consorcio microbiano altamente adaptado. Se observó que la presencia del metanol afectó negativamente a la eliminación del α-pineno, sin embargo lo opuesto no sucedió. La eliminación del α-pineno se vió afectada por su propia presencia. El H_2S no mostró ningún efecto sobre la eliminación de los otros compuestos. Este BTF también fue modelado usando ANNs y fue también sometido a diferentes tipos de sobrecargas a corto plazo, de cada contaminante por separado. Para el metanol y el sulfuro de hidrógeno, se observó que estas sobrecargas no afectaron significativamente a su propia eliminación, pero la eliminación del α-pineno se vio afectada en un 50%.

RESUMO

Un biorreator en dúas etapas consistente nun biofiltro percolador (BTF) como primeira etapa e nun biofiltro (BF) como segunda etapa, foi operado baixo estados estacionario e transitorio, para a purificación dunha mestura gasosa formada por sulfuro de hidróxeno, metanol e α-pineno. O sulfuro de hidróxeno e o metanol foron eliminados na primeira etapa, mentres co α-pineno foi principalmente eliminado na segunda etapa. Os biorreactores foron sometidos a dous tipos de sobrecargas: a longo prazo (66h) con cargas medias-baixas, e de curta duración (12 horas) a cargas elevadas. Utilizando redes de neuronas artificiais (ANNs), realizouse unha modelaxe para prever as correspondentes eficiencias de eliminación (EEs). Observouse que un perceptrón multicapa con topología 3-4-2 foi capaz de prever a eliminación do H_2S e do metanol no BTF, mentres que unha topoloxía 3-3-1 foi quen de aproximarse á eliminación do α-pineno no BF. A mesma mestura gasosa foi examinada posteriormente nun BTF inoculado cun consorcio microbiano altamente adaptado. A presenza do metanol afectou negativamente a eliminación do α-pineno, con todo, o contrario non aconteceu. A eliminación de α-pineno, foi afectada pola súa propia presenza. O H_2S non mostrou ningún efecto sobre a eliminación dos outros compostos. Este BTF tamén foi modelado utilizando ANNs e tamén foi suxeito a varios tipos de sobrecargas a curto prazo, de cada contaminante por separado. Para o metanol e o sulfuro de hidrógeno observouse que estas sobrecargas non afectaron significativamente as súas eliminacións, pero a eliminación do α-pineno foi afectada nun 50%.

SUMARIO

La problemática de la contaminación atmosférica es un tema de primordial importancia y uno de los problemas ambientales más urgentes que todavía quedan por resolver en la mayor parte del mundo. Las estrategias y los reglamentos de control de la contaminación del medio ambiente se han centrado en los efectos agudos de los contaminantes del aire y del agua en la salud humana y el medio ambiente natural. En los últimos cincuenta años, sin embargo, los avances en las ciencias médicas y ambientales han dado lugar a una mejor comprensión de otros efectos nocivos de estos contaminantes. Contaminantes comúnmente presentes en actividades industriales, como el benceno, tolueno, xileno, estireno, sulfuro de hidrógeno (H_2S), amoniaco (NH_3), diclorometano (DCM), hexano y contaminantes del agua como fármacos, pesticidas, colorantes sintéticos, nitratos y fosfatos, con frecuencia pueden entrar en el medio ambiente natural a través de prácticas inadecuadas de manipulación y eliminación de residuos, tecnologías de tratamiento ineficaces, fugas durante el almacenamiento y el transporte y deshechos de derivados del petróleo. El efecto potencial para la salud causado por una fuga accidental depende del tiempo de exposición total de la especie en cuestión y la concentración del contaminante liberado.

La producción de papel es una industria en auge que cuenta en su haber con cerca de 5.000 plantas de pasta y papel a nivel mundial, las cuales producen cerca de 400 millones de toneladas de papel al año [1], [2], [3]. La industria de la pasta y el papel genera grandes cantidades de residuos, tanto en corrientes sólidas, así como en corrientes líquidas y gaseosas, a través de sus diferentes procesos. Las emisiones atmosféricas originadas en ciertos procesos de este tipo de industrias, especialmente en el proceso Kraft, incluyen tanto partículas como gases contaminantes. Las emisiones gaseosas suelen estar conformadas por mezclas de compuestos inorgánicos volátiles y orgánicos volátiles. Los compuestos orgánicos volátiles

(COV) más representativos de estas industrias incluyen alcoholes (principalmente metanol y algo de etanol), terpenos y cierta cantidad de acetona [3]. Por otra parte, los compuestos inorgánicos volátiles (CIV), integrados principalmente por compuestos de azufre tales como el sulfuro de hidrógeno (H_2S), el metil mercaptano, el sulfuro de dimetilo (DMS), el disulfuro de dimetilo (DMDS) y los óxidos de azufre, también se emiten a partir de la industria de la pasta y papel. Estos compuestos volátiles son extremadamente malolientes y su purificación es uno de los principales desafíos para este tipo de industria. Otros contaminantes peligrosos como las dioxinas y los furanos y otros compuestos clorados volátiles tales como el cloruro de metileno, el cloroformo, el clorometano, el diclorometano, etc., entre otros, también aparecen en las emisiones de la industria de pasta y papel [4], [5]. El metanol es un subproducto derivado del proceso Kraft de fabricación de pasta y, abarca alrededor de un 70% de la emisión total de sustancias químicas tóxicas. Aunque el metanol es muy hidrófilo, puede ser liberado a la atmósfera a partir de varias fuentes, como pueden ser los evaporadores, debido a la naturaleza estos procesos, a las temperaturas de operación relativamente altas y a la baja presión de vapor de metanol [6]. Los terpenos, que están presentes de forma natural en la madera, son el otro grupo de compuestos orgánicos volátiles emitidos por las industrias de pasta y papel. El α-pineno, un COV hidrófobo, es un mono-terpeno natural presente en los productos de madera. Su solubilidad en agua varía entre 2 y 22 mg L^{-1} a 25 ° C [7], y debido a su naturaleza volátil, está comúnmente presente en las emisiones de gases residuales procedentes de la industria de la pasta y el papel.

Otro problema ambiental importante que con frecuencia se asocia a las industrias de pulpa y papel es la generación de grandes cantidades de aguas residuales. Desde un punto de vista de valorización de residuos, una de las posibilidades para el tratamiento de aguas residuales sería el uso de un digestor anaerobio para la producción de biogás [3]. Sin embargo, hay que tener

en cuenta que este biogás también contendría una cantidad importante de contaminantes volátiles, como el sulfuro de hidrógeno. Por lo tanto, sería del todo necesario un proceso posterior de purificación, con el fin de mejorar la calidad del combustible. Las diferentes tecnologías de tratamiento de gases residuales descritos en esta tesis (biofiltros y biofiltros percoladores) también se pueden aplicar para la purificación de biogás, teniendo en cuenta ciertos ajustes necesarios.

El sulfuro de hidrógeno, el metanol y el α-pineno son contaminantes representativos de compuestos hidrófilos, hidrófobos e inorgánicos, respectivamente, generalmente presentes en las emisiones de las industrias de pasta y papel. De entre las distintas técnicas de tratamiento utilizadas para eliminar dichos compuestos de corrientes gaseosas contaminadas, los tratamientos biológicos son una de las opciones más versátiles y prometedoras, teniendo en cuenta el grado de depuración conseguido, así como a su bajo coste. La biodegradación explota las ventajas inherentes de los microorganismos mediante la transformación de contaminantes peligrosos en productos finales inocuos.

En el capítulo 1, se da una visión general de los problemas globales relativos a las emisiones atmosféricas. Así mismo, se presentan las diferentes tecnologías que se pueden utilizar para paliarlas. Por otra parte, se introducen los procesos industriales de pasta y papel y se analizan los distintos contaminantes volátiles presentes en la susodicha industria. Adicionalmente, se presenta una introducción general a la utilización de redes de neuronas (ANN) para sistemas ambientales, así como también al procedimiento que se debe seguir para aplicar este tipo de modelo. También se analiza si este modelo es adecuado para biorreactores que tratan gases residuales. Por último en este capítulo, se enumeran los objetivos y se explica el alcance y de esta tesis.

En el capítulo 2, se explora el tratamiento biológico de una mezcla gaseosa de H_2S, metanol y α-pineno a través de un sistema de biorreactor de dos etapas, consistente en un biofiltro percolador (BTF) como la primera etapa, seguido de un biofiltro (BF) como la segunda etapa, con el fin de estudiar el efecto de los parámetros de operación más importantes. El BTF se inoculó con una mezcla de un cultivo bacteriano autótrofo, con poder degradante para el H_2S y una levadura ácido tolerante, degradante de metanol (*Candida boidinii*) que se obtuvo a partir de trabajos anteriores sobre el co-tratamiento del H_2S y metanol en un BTF de bajo pH [8] . *Ophiostoma stenoceras sp*, un hongo bien conocido por colonizar la savia y la madera, se aisló de un previo BF existente, el cual había estado tratando vapores de α-pineno, se utilizó para inocular la segunda etapa BF. Los experimentos se realizaron en modo continuo en ambos biorreactores, variando distintos parámetros del proceso tales como caudal de gas, concentración de contaminantes y la tasa de recirculación del medio líquido, con el fin de realizar los siguientes estudios: (i) el efecto de la carga de los contaminantes, en el tiempo de residencia del lecho vacío (EBRTs), (ii) el efecto de la tasa de recirculación del medio líquido en el BTF (primera etapa), (iii) el efecto de sobrecagas puntuales de los contaminantes en la eliminación de cada uno de ellos y (iv) el efecto del cambio de operación a estado no estacionario, en los rendimientos de los BTF y BF. Los resultados fundamentales de este capítulo fueron los siguientes:

- La primera etapa (BTF) mostró una capacidad máxima de eliminación 45 g m^{-3} h^{-1} para el sulfuro de hidrógeno y de 894 g m^{-3} h^{-1} para el metanol. En la segunda etapa (BF), cuando el caudal de gas se aumentó dos veces, la capacidad máxima de eliminación (EC_{max}), del α-pineno, aumentó de 100 a 138 g m^{-3} h^{-1}.

- La estratificación en términos de biodegradación de contaminantes a lo largo de la altura del del lecho, se observó para ambas configuraciones de reactores. En el primer tercio de sección

del BTF se eliminó casi el 78% de metanol, mientras que el H_2S se eliminó de forma lineal durante los dos restantes tercios del lecho.

- El estudio del efecto de la tasa de recirculación de líquido mostró que, debido a las limitaciones de transferencia de masa, tasas altas de recirculación del líquido sometidas a altas y moderadamente altas cargas de contaminantes, podrían no favorecer una mejor eliminación simultánea de la mezcla gaseosa de H_2S, metanol y α - pineno.

- El aumento de la concentracisn del metanol (COV hidrσfilo) o el α-pineno (COV hidrófobo), en ell BTF, llevó a una bajada en la eficiencia de eliminación (EE) del H_2S de un 25%, sin embargo, un aumento gradual en la concentración H_2S, no pareció afectar la eliminación de los COV, tanto en el BTF como en el BF. Al ser un compuesto fácilmente biodegradable, el metanol también fue eliminado en la segunda etapa (BF), lo que podría haber sido posible gracias a la utilización preferente del metanol como fuente de carbono y energía por el *Ophiostoma sp*. presente en el BF originalmente.

- Con respecto a los experimentos de sobrecargas, se observó que cuando la sobrecarga aplicada fue inferior a su carga crítica, la eliminación de H_2S en el BTF fue afectada fuertemente mientras que la del metanol no se vio tan afectada. Durante altas sobrecargas, las eliminaciones de H_2S y de de metanol en el BTF fueron inferiores, mientras que altas eliminaciones (75%) de α - pineno tuvieron lugar, con una EC de 130,1 g m^{-3} h^{-1}. Esto muestra que el biorreactor en dos etapas fue sensible a los cambios en las cargas.

El enfoque del capítulo 3 fue determinar el rendimiento del reactor en dos etapas, en estado no estacionario, utilizando modelos de redes de neuronas (ANN). ANN se utilizó con el fin de predecir los perfiles de eficacia de eliminación (RE) de cada contaminante individual, es decir, metanol (RE_M), α-pineno (RE_P), y sulfuro de hidrógeno (RE_{HS}). La identificación de los

parámetros más importantes que afectan a la eliminación de cada contaminante se realizó mediante análisis de sensibilidad, y así mismo, también se identificaron los efectos de la interacción entre los tres contaminantes. Después de la optimización adecuada de los parámetros de red, se obtuvieron las siguientes topologías: 3-4-2 y 3-3-1, respectivamente, para el BTF y el BF. Los resultados del análisis de sensibilidad mostraron que el factor más crítico, que afectaba antagónicamente las RE_M y RE_{HS} en el BTF durante el estado transitorio, fue la concentración del α-pineno, mientras que la RE_P en el BF, fue sinérgicamente afectada por la concentración de sulfuro de hidrógeno.

El capítulo 4 muestra los resultados obtenidos a partir de nuestra idea original de desarrollar un BTF de una etapa altamente eficiente, mediante la inoculación con microorganismos que habían sido previamente testados para la eliminación de la mezcla de metanol, α-pineno y H2S. Por lo tanto, se realizó una evaluación del rendimiento del biorreactor en una etapa, mediante el estudio del efecto tiempo de residencia del lecho vacío (EBRT) en el rendimiento del BTF. También se describe comprensivamente, la dinámica de la eliminación de los contaminantes para diferentes secciones del BTF (estratificación sustrato) y se analiza en conjunto con los diferentes tipos de efectos de interacción (antagónicos o sinérgicos) entre los contaminantes y su patrón de eliminación en el BTF. Utilizando herramientas de biología molecular fueron realizados análisis de la comunidad microbiana en diferentes secciones del BTF después de una operación a largo plazo, con el fin de determinar la prevalencia o ausencia de las especies dominantes, con respecto al inóculo original, en el sistema.

Los resultados mostrados nos enseñan que la capacidad de eliminación ha mejorado con el tiempo de operación, llegando a 302, 175 y 191 $gm^{-3}h^{-1}$, para el metanol, el α-pineno y el H_2S, respectivamente. Los microorganismos degradadores del metanol y del H_2S fueron activos poco después de la puesta en marcha, mientras que el rendimiento de los microorganismos

degradadores del α-pineno mejoró lentamente debido a una lenta adaptación microbiana. Algunas de las bacterias inoculadas todavía se detectaron en el BTF aún después de ser operado a largo plazo. La distribución de las poblaciones microbianas del BTF se correlacionaron bien con el patrón de la estratificación de los perfiles de eficiencias de eliminación de los diferentes contaminantes.

En el capítulo 5, se realizó un modelado por redes de neuronas, basado en los resultados del biorreactor en una etapa, operado a largo plazo (resultados del Capítulo 4). Como continuación de nuestros esfuerzos para entender mejor el funcionamiento de dichos contaminantes en el BTF bajo diferentes condiciones de operación, este estudio se llevó a cabo con los siguientes objetivos: (i) identificar los efectos de la interacción entre los diferentes contaminantes a través del modelado con ANN, (ii) entender el patrón de interacción entre los compuestos orgánicos volátiles, es decir, metanol y α-pineno, y (iii) estudiar el efecto del cambio de operación a estado transitorio en el rendimiento del BTF.

Un modelo ANN de tres capas (5-8-3) fue desarrollado para predecir el rendimiento de un BTF usando concentraciones de entrada de sulfuro de hidrógeno (H), metanol (M) y α-pineno (P), UF y el tiempo de operación como parámetros de entrada. Los coeficientes de causalidad (CI) revelaron las relaciones entre los parámetros de funcionamiento y los eficiencias de eliminación de los contaminantes (REs), lo que puede ayudar en el diseño de biorreactores futuros. La RE de los tres contaminantes se vio afectada por el UF (IC -ve), mientras que el tiempo de funcionamiento del BTF sinérgicamente mejoró sus REs (+ ve CI). Los resultados de los tests de perturbación mostraron ECmax de 183, 239 y 76 $gm^{-3}h^{-1}$ correspondientes a cargas de entrada de 192, 260 y 302 $gm^{-3}h^{-1}$, respectivamente, para el sulfuro de hidrógeno, el metanol y el α-pineno.

La parte final de esta tesis, se presenta como el Capítulo 6. En dicho capítulo, se proporciona una comparativa entre los dos sistemas de biorreactores operados, (una y dos etapas), junto con sus resultados del modelado con ANN. Las capacidades de eliminación más altas (EC_{max}) obtenidas para el metanol, α-pineno y H_2S se compararon para ambas configuraciones. Nuevamente, hemos presentado los resultados importantes obtenidos durante el modelado ANN junto con estrategias propuestas, prácticamente demostrables, para desarrollar novedosos sistemas de control basados en el modelo ANN, con el fin monitorizar las variables de estado y el rendimiento del BTF o de cualquier otro sistema de tratamiento de gases residuales. Basándonos en nuestra experiencia, nuevas estrategias se han recomendado como una continuación de nuestras iniciativas de investigación, centrándose principalmente en el tratamiento de las emisiones volátiles de la industria de la pasta y el papel.

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SUMARIO

O problema da contaminación atmosférica é unha cuestión de primordial importancia e un dos máis urxentes problemas medioambientais que seguen sen solución en moitas partes do mundo. Estratexias e normativas para controlar a contaminación ambiental téñense centrado nos efectos dos contaminantes do aire e da auga sobre a saúde humana e o medio ambiente natural. Nos últimos cincuenta anos, con todo, os avances das ciencias médicas e ambientais levaron a unha mellor comprensión doutros efectos nocivos destes compostos. Os contaminantes normalmente presentes en actividades industriais, tales como benceno, tolueno, xileno, estireno, sulfuro de hidróxeno (H_2S), amoníaco (NH_3), diclorometano (DCM), hexano e contaminantes da auga, como fármacos, pesticidas, colorantes sintéticos, nitratos e fosfatos moitas veces poden entrar no medio ambiente natural a través de prácticas inadecuadas de manipulación e eliminación de residuos, tecnoloxías de tratamento ineficaces, fugas durante o almacenamiento e o transporte e residuos dos derivados do petróleo. O efecto potencial para a saúde causado por unha fuga accidental depende do tempo de exposición total da especie en cuestión e a concentración do contaminante liberado.

A produción de papel é unha industria florecente que conta no seu haber con preto de 5.000 plantas de pasta e papel no mundo enteiro, que producen uns 400 millóns de toneladas de papel ó ano [1], [2] [3]. A industria de pasta e papel xera grandes cantidades de residuos, tanto en correntes sólidas, así como en correntes líquidas e gasosas, a través dos seus diferentes procesos. As emisións atmosféricas procedentes de determinados procesos destas industrias, especialmente do proceso de Kraft, inclúen partículas e gases contaminantes. Estas emisións están xeralmente integradas por mesturas de compostos volátiles orgánicos e inorgánicos. Os compostos orgánicos volátiles (COV) máis representativos das industrias da pasta e o papel, inclúen alcois (sobre todo metanol e un pouco de etanol), terpenos e unha

certa cantidade de acetona [3]. Por outra banda, os compostos inorgánicos volátiles (CIV), integrados principalmente por compostos de xofre, tales como o sulfuro de hidróxeno (H_2S), o metilmercaptano, o sulfuro de dimetilo (DMS), o disulfuro de dimetilo (DMDS) e óxidos de xofre, tamén aparecen nas emisións procedentes da industria da pasta e do papel. Estes compostos inorgánicos volátiles son moi fedorentos e a súa purificación é un dos principais retos para estes tipos de industrias. Outros contaminantes nocivos, como dioxinas, furanos e outros compostos clorados volátiles, tales como o cloruro de metileno, cloroformo, cloruro de metilo, diclorometano, etc., entre outros, tamén aparecen nas emisións da industria de pasta e papel [4], [5]. O metanol é un subproduto do proceso de produción de celulosa e abrangue preto do 70% do total de emisións de produtos químicos tóxicos. Aínda que o metanol é moi hidrófilo, pode ser liberado á atmósfera a partir de varias fontes, como son os evaporadores, debido á natureza destes procesos, as temperaturas de operación relativamente elevadas e a baixa presión de vapor de metanol [6]. Os terpenos, que están naturalmente presentes na madeira, son un dos outros grandes grupos de compostos orgánicos volátiles emitidos polas industrias de papel e celulosa. O α-pineno, un COV hidrofóbo, é un monoterpeno naturalmente presente en produtos da madeira. A súa solubilidade na auga varía entre 2 e 22 mg L^{-1} a 25 ° C [7], e debido á súa natureza volátil, está comúnmente presente nas emisións de gases residuais da industria de pasta e papel.

Outro problema ambiental importante, que está frecuentemente asociado coa industria da pasta e o papel, é a xeración de grandes cantidades de augas residuais. Dende o punto de vista da valorización de residuos, unha das posibilidades do tratamento destas augas residuais é o uso dun dixestor anaerobio para a produción de biogás [3]. Con todo, hai que ter en conta que este biogás tamén contén unha cantidade significativa de contaminantes volátiles, como o sulfuro de hidróxeno. Polo tanto, sería absolutamente necesario outro proceso de depuración a

mayores, coa fin de mellorar a calidade do combustible. As distintas tecnoloxías de tratamento de efluentes gasosos descritos nesta tese (biofiltros e biofiltros percoladores) tamén poden ser aplicadas para a purificación de biogás, tendo en conta determinados axustes.

O sulfuro de hidróxeno, o metanol e α-pineno son contaminantes representativos dos compostos volátiles inorgánicos, orgánicos hidrófilos e orgánicos hidrófobos, respectivamente, xeralmente presentes nas emisións das industrias de pasta e papel. Entre as distintas técnicas de tratamento utilizadas para eliminar tales compostos presentes en correntes gasosas contaminadas, os tratamentos biolóxicos son unha das opcións máis versátiles e prometedoras, dado o grao de purificación obtida, así como polo seu baixo custo. A biodegradación explora as vantaxes inherentes dos microorganismos mediante a transformación de contaminantes peligrosos en productos finais inocuos.

No Capítulo 1, dase unha visión xeral dos problemas globais relacionados coas emisións atmosféricas. Así mesmo, expóñense as diferentes tecnoloxías que poden ser utilizadas para palialas. Por outra banda, introdúcense os procesos industriais de producción de pasta e papel e analízanse os contaminantes volátiles individuais da referida industria. Adicionalmente, preséntase unha introdución xeral ao uso de redes de neuronas (RNAs) para modelar sistemas ambientais, así como o procedemento a seguir para aplicar este tipo de modelo. Despois, examínase se este modelo é adecuado para o tratamento gases residuais con biorreactores. Por último neste capítulo, enuméranse os obxectivos e explícase o alcance desta tese.

No capítulo 2, o tratamento biolóxico dunha mestura gasosa de H_2S, metanol e α-pineno a través dun sistema de bioreactor de dúas etapas, composto dun biofiltro percolador (BTF) como a primeira etapa, seguido por un biofiltro (BF) coma a segunda etapa, coa fin de estudar o efecto dos parámetros operativos máis importantes. O BTF foi inoculado cunha mestura dun cultivo de bacterias autotróficas con poder para degradar o H_2S, e cunha lévedo ácido-

tolerante, capaz de degradar metanol (*Candida boidinii*) obtida a partir dun traballo anterior sobre o co-tratamento conxunto de H_2S e de metanol nun BTF operado a baixo pH [8]. *Stenoceras Ophiostoma sp*, un fungo ben coñecido por colonizar a saiba da madeira, foi illado a partir dun BF previamente existente tratando vapores de α-pineno, e foi usado para inocular a segunda etapa (BF). Os experimentos foron realizados en continuo para os dous biorreactores variando diferentes parámetros do proceso, tales como o caudal de gas, a concentración de contaminantes e a taxa de recirculación do medio líquido, coa fin de realizar os seguintes estudos: (i) o efecto da carga dos contaminantes presentes no tempo de residencia do leito baleiro (EBRT), (ii) o efecto da taxa de recirculación do medio líquido no BTF (primeira estapa), (iii) o efecto de sobrecargas puntuais dos contaminantes na eliminación de cada un deles, (iv) e o efecto de cambios na operación para o estado non-estacionario, nos rendementos dos BTF e BF. Os principais resultados deste capítulo foron:

- A primeira etapa (BTF) mostrou unha capacidade máxima de eliminación de 45 g m^{-3} h^{-1} para o sulfuro de hidróxeno e 894 g m^{-3} h^{-1} para o metanol. Na segunda etapa (BF), cando o caudal de gas foi aumentado dúas veces, a capacidade máxima de eliminación (EC_{max}) do α-pineno, aumentou de 100-138 g m^{-3} h^{-1}.

- A estratificación en termos de biodegradación dos contaminantes foi observada ó longo da altura do leito, para ámbalas opcións de reactores. No primeiro terzo de sección do BTF case o 78% de metanol foi eliminado, mentres co H_2S foi eliminado dun modo lineal nos restantes dous terzos do leito.

- O estudo do efecto da taxa de recirculación do medio líquido mostrou que, debido ás limitacións de transferencia de masa, a elevadas taxas de recirculación de líquido, baixo cargas elevadas e moderadamente elevadas de contaminantes, non promoven unha mellor eliminación simultánea da mestura gasosa de H_2S, metanol e α - pineno.

- O aumento na concentración do metanol (COV hidrófilo) ou do α-pineno (COV hidrófobo) no BTF, levou a unha diminución na eficiencia de eliminación (RE) do 25% de H_2S, con todo, un aumento gradual da concentración de H_2S non pareceu afectar á eliminación dos compostos orgánicos volátiles, tanto no BTF como no BF. Como o metanol é un composto facilmente biodegradable, tamén foi eliminado na segunda fase (BF), o que podería ser posible grazas á utilización preferente de metanol como fonte de carbono e enerxía por parte do *sp Ophiostoma*. orixinalmente presente no BF.

- En relación as experiencias con sobrecargas, observouse que cando a sobrecarga aplicada foi menor cá carga crítica, a eliminación do H_2S no BTF foi fortemente afectada, mentres que para o metanol non foi a tal punto afectada. Durante altas sobrecargas, as eliminacións do H_2S e do metanol no BTF foron máis baixos, mentres que elevadas eliminacións (75%) de α - pineno tiveron lugar, cunha capacidade de eliminación de 130,1 g m^{-3} h^{-1} . Este feito amosa co biorreactor de dúas etapas foi sensible a variacións nas cargas.

O enfoque no capítulo 3 foi o de determinar a eficiencia do reactor en dúas etapas, sometido a condicións de estado non estacionario, utilizando modelos de redes de neuronas (RNAs). Os modelos de redes de neuronas (RNAs) son utilizados, coa fin de prever os perfís de eficiencias de eliminación (RE) dos contaminantes individuais, é dicir, do metanol (RE_M), do α-pineno (RE_P), e do sulfuro de hidróxeno (RE_{HS}). A identificación dos parámetros máis importantes que afectan a eliminación de cada contaminante realizouse por análise de sensibilidade e, do mesmo xeito, tamén foron identificados os efectos de interacción entre os tres contaminantes. Despois da optimización adecuada dos parámetros de rede, obtivéronse as seguintes topoloxías: 3-4-2 para o BTF e 3-3-1 para o BF. Os resultados da análise de sensibilidade amosan que o factor máis crítico que afectaba antagonicamente á RE_M e á RE_{HS}

no BTF durante o estado de transición, foi a concentración do α-pineno, mentres ca RE_P no BF, foi sinérxicamente afectado pola concentración do sulfuro de hidróxeno.

O capítulo 4 mostra os resultados obtidos a partir da nosa idea orixinal de desenvolvemento dun BTF altamente eficiente nunca sola etapa, a través da inoculación con microorganismos que foran anteriormente utilizados con éxito na eliminación do metanol, do α-pineno e do H_2S. Polo tanto, unha avaliación do rendemento do biorreactor nunca etapa, mediante o estudo do tempo de residencia do leito baleiro (EBRT) no desempeño do BTF. Tamén se describe amplamente, a dinámica da eliminación de contaminantes nas diferentes seccións do BTF (estratificación do substrato) e analízase en conxunto cos diferentes tipos de efectos de interaccións (sinerxías ou antagonistas) entre os contaminantes e as súas eficiencias de eliminación no BTF. Utilizando ferramentas de bioloxía molecular foron realizadas análises da comunidade microbiana en diferentes seccións do BTF despois dunha operación a longo prazo, para determinar a prevalencia ou ausenza das especies dominantes orixinais. Os resultados presentados ensínannos que a capacidade de eliminación mellorou co tempo de actividade, chegando a 302, 175 e 191 g m^{-3} h^{-1}, para o metanol, o α-pineno e o H_2S, respectivamente. Os degradadores do metanol e do H_2S foron activos xa dende pouco tempo despois da inoculación, mentres que o rendemento dos degradadores de α-pineno mellorou lentamente debido á lenta adaptación microbiana. Algunhas das bacterias inoculadas aínda se detectaron no BTF, incluso tras o longo prazo operado. A distribución das poboacións microbianas no BTF estiveron ben correlacionadas co patrón da estratificación dos perfí de eficiencias de eliminación dos diferentes contaminantes.

No Capítulo 5, unha modelización por redes de neuronas foi efectuada a partir dos resultados do bioreactor de longa duración de operación, dunha etapa (resultados de Capítulo 4). Como unha continuación dos nosos esforzos para comprender mellor o funcionamento de ditos

contaminantes no BTF baixo diferentes condicións de operación, este estudo realizouse cos seguintes obxectivos: (i) identificar os efectos da interacción dos diferentes contaminantes a través da modelaxe con RNA, (ii) entender o nivel de interacción entre compostos orgánicos volátiles, é dicir, o metanol e o α-pineno, e (iii) para estudar o efecto do cambio de operación a estado transitorio no desempeño do BTF.

Un modelo de RNA de tres capas (5-8-3) foi desenrolado para prever o desempeño dun BTF usando as concentracións de entrada de sulfuro de hidróxeno (H), metanol (H) e α-pineno (P), o tempo operación e UF como parámetros de entrada. Os Coeficientes de Causalidade (CI) revelaron a relación entre os parámetros de funcionamento e as eficiencias de eliminación dos contaminantes (REs), feito que pode axudar na posible deseño de biorreatores no futuro. As eficiencias de eliminación dos tres contaminantes foron afectadas polo UF (CI-ve), mentres que o tempo de funcionamento do BTF sinerxícamente mellorou as súas REs (+ ve CI). Os resultados das probas de perturbacións mostraron capacidades máximas de eliminación de 183, 239 e 76 g m^{-3} h^{-1}, correspondentes a cargas de entrada de 192, 260 e 302 g m^{-3} h^{-1} respectivamente, para o sulfuro de hidróxeno, o metanol e o α-pineno.

A parte final desta tese é presentada como o capítulo 6. Neste capítulo, subministrase unha comparativa entre os dous sistemas de biorreatores operados (unha e dúas etapas), xunto cos seus resultados de modelaxe con RNA. As maiores capacidades de eliminación (EC_{max}) obtidas para o metanol, o α-pineno e o H_2S foron comparadas para ámbalas opcións. Unha vez máis, presentamos os resultados máis significativos obtidos durante a modelaxe con redes de neuronas artificiales, acompañado de estrategias propostas, practicamente demostrables, para desenvolver sistemas innovadores, baseados no modelo de redes de neuronas artificiales, coa fin de monitorizarr as variables de estado e o rendemento do BTF ou de calquera outro sistema de tratamento de gases residuais. En base a nosa experiencia, recomendáronse novas

estratexias coma unha continuación das nosas iniciativas de investigación, incidindo principalmente sobre o tratamento das emisións volátiles da industria de pasta e papel.

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Chapter 1

Introduction

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1.1 Background to emissions from the pulp and paper industry

The issue of air pollution has been a topic of great importance, and one of the most urgent environmental problems to be solved worldwide. Environmental pollution control strategies and regulations have focused on the acute effects of air and water pollutants on human health and natural environment. In the past fifty years, however, advances in medical and environmental sciences have led to a better understanding of other deleterious effects of these pollutants. Well known industrial air pollutants like benzene, toluene, xylene, styrene, hydrogen sulphide (H_2S), ammonia (NH_3), dichloromethane (DCM), hexane and water pollutants like pharmaceutical drugs, pesticides, synthetic dyes, nitrates and phosphates could frequently enter into the natural environment through improper handling and disposal practices, ineffective treatment procedures, leakage during storage and transportation and disposal of petroleum by-products. The potential health effect caused by an accidental release depends on the total exposure time of the species with the released chemical and its concentration level, usually expressed as ppm or gm^{-3}.

Paper production is a growing industry with about 5000 pulp and paper mills worldwide, producing nearly 400 million tons of paper annually [1], [2], [3]. The pulp and paper industry generates solid, liquid and gaseous waste streams from its various processes. The atmospheric emissions from pulp and paper making operations, especially from the Kraft's pulping process, include both particulate and gaseous pollutants. The gaseous emissions are usually a mixture of volatile organic and volatile inorganic compounds. Representative volatile organic compounds (VOCs) include alcohols (mainly methanol and some ethanol), terpenes and some amount of acetone [3]. The most concentrated emission sources are the non-condensable gases from the digester, brown stock washers and evaporator operations [4]. On the other

hand, volatile inorganic compounds (VICs), comprising mainly of sulphur compounds such as hydrogen sulphide (H_2S), methyl mercaptan, dimethyl sulphide (DMS), dimethyl disulphide (DMDS) and sulphur oxides are also emitted from the pulp and paper industry. These volatile sulphur compounds (VSCs) are extremely malodorous and their removal is one of the major challenges for this type of industry. Other hazardous pollutants such as dioxins and furans, and other volatile chlorinated compounds such as methylene chloride, chloroform, chloromethane, dichloromethane, etc, among others, are also emitted in pulp and paper industry emissions [5], [6].

Methanol is a normal by-product of the Kraft's pulping process and methanol accounts for ~70% of the total toxic chemical release. Although methanol is very hydrophilic, it can be released into the atmosphere from several sources such as evaporators and brown stock washers due to the nature of the processes, their relatively high temperatures and methanol's low vapour pressure [7]. Terpenes, which are naturally present in softwood, are another group of VOCs emitted from pulp and paper industries. α-Pinene, a hydrophobic VOC, is a natural mono-terpene present in wood products. Its water solubility varies between 2 and 22 mgL^{-1} at 25ºC [8], and due to its volatile nature, it is commonly present in waste gas emissions from the pulp and paper industry.

Another important environmental issue frequently associated with the pulp and paper industries is the generation of large quantities of wastewater. From a resource recovery view point, one of the possibilities for wastewater treatment would be the use of an anaerobic digester for biogas generation [3]. However, it is noteworthy to mention that the biogas would also contain volatile pollutants such as hydrogen sulphide as an impurity. Therefore, biogas upgradation is required in order to improve the fuel quality. The different biological waste gas treatment technologies described in

this thesis (biofilter and biotrickling filter) can also be applied for biogas upgradation, with some adjustments, for improving its effectiveness.

1.2 Technologies for waste gas treatment

The different technologies used for the treatment of gaseous emissions or waste gases can be classified into physical, chemical and biological. For the selection of an appropriate treatment technique, a number of considerations must be taken into account, such as the composition and property of the waste stream, its quantity and concentration, characteristics of the air or waste gas stream and the generation of by-products from the selected process. In this section, the different physico-chemical technologies used typically for waste gas treatment are briefly discussed. As the focus of this thesis is on the use of biological techniques (biotrickling filter and biofilter), important literature information in relation to their use in treating volatile organic compounds (VOCs) and volatile inorganic compounds (VICs) has been provided.

1.2.1 Physico-chemical techniques

1.2.1.1 Absorption

In absorption techniques for waste gases purification, the polluted gas stream is placed in contact with a continuously trickling liquid phase, the purpose being the mass transfer of the contaminant from the gas-phase to the liquid-phase [9]. The different absorption technologies use different types of absorbents, *viz.*, water scrubbing, organic physical scrubbing and chemical scrubbing [10]. The pollutants transferred to the liquid phase must be treated. The mass transfer depends on the partition coefficient, as well as temperature and pH. Efficient gas-liquid mass transfer can be accomplished by using packed or bubble columns, washing towers or venturi contactors [11].

Water is the most frequently used scrubbing absorbent for volatile pollutants with a high solubility and organic solvents such as silicone oil or polyethylene glycol are more adequate for high hydrophobic waste gases. In chemical scrubbing, absorption involves the formation of reversible chemical bonds between the pollutants and the solvent. Regeneration of the solvent, therefore, involves breaking of these bonds and correspondingly, a relatively high energy input [12].

The main disadvantage of this technique is the creation of a new waste stream, emerging from the transfer of pollutants from the gas phase to the liquid phase. Therefore, other strategies (a post-treatment step) should be applied in order to treat the pollutant, which in turn increases the investment and operating costs.

1.2.1.2 Adsorption

In adsorption systems, the gas-phase contaminants are retained in the surface of a solid-phase adsorbent. The adsorption mechanism can be of chemical or physical nature. In chemical adsorption, a chemical reaction between the contaminants and the solid adsorbent occurs and therefore solid-phase regeneration by desorption is difficult. On the other hand, in physical adsorption, contact is achieved through intermolecular forces [13]; this allows solid regeneration, usually by thermal treatment. Well known commercial adsorbents are activated carbon, zeolites, silica gel, and molecular sieves. Carbon activated adsorption provides a very good performance for the treatment of highly hydrophobic VOCs, with removals ranging from 90 to 99%. However, their affinities for VICs such as NH_3 or H_2S are not so strong. Carbon activated beds are exhausted quite soon, depending on the adsorbent nature and the characteristics of the waste gases, but usually ranges between 3 and 9 months. After this period, it has to be replaced and treated as a hazardous waste, thus

increasing the operational costs of the system. Regeneration can also be possible with pollutant recovery by desorption, either with steam or hot air [11].

1.2.1.3 Condensation

Condensation technologies involve the conversion of a gas or a vapour into a liquid, either by pressure increase or by lowering the temperature, although combination of both temperature and pressure variations is also possible. By pressurization of air the molecules are brought closer together, while lowering the temperature reduces the kinetics energy of the molecules [9]. This technique is useful to remove volatile compounds if the concentration of pollutants is very high and the mass flow rates are low. Contaminants with a high boiling point can be concentrated by simultaneous cycles of cooling and compression of gas.

1.2.1.4 Incineration

Incineration involves the complete combustion of the volatile pollutant at high temperatures. As an example, under optimal conditions, hydrocarbons are converted to CO_2 and water, although if combustion is not complete, it can release more toxic products than the original pollutant, such as dioxins, CO and nitrogen oxides. As the pollutant concentration would be relatively low, this technology requires high energy inputs in order to maintain the high temperatures necessaries for the correct oxidation. Depending on the type of catalyst used, incineration can be classified into two types [9]: thermal incineration, which takes place in most of the cases at temperatures ranging between 700 and 1400ºC, and catalytic incineration, in which the temperatures can be reduced up to 300 to 700ºC by introducing a catalyst in the combustion unit, such as metals (platinum, palladium, copper, etc.) or metal oxides (cobalt, manganese, iron, etc.). Incineration is a destructive technique and it does not allow the recovery of the contaminant.

1.2.1.5 Ultraviolet oxidation

During ultraviolet oxidation, the volatile pollutant is disintegrated by UV light releasing radicals, which then reacts with oxygen or other oxidants such as O_3, H_2O_2, OH, O- [13]. For the case of H_2S, equation 1.1 shows the breakdown of the H-S bond by UV light:

$$H_2S + h\nu \rightarrow HS^{\bullet} + H^{\bullet} \quad (1.1)$$

Similar to absorption, the pollutant has to be passed from the gas phase to a liquid solution. Then, the contaminated solution is passed through a chamber where it is exposed to intense UV radiation provided by UV lamps of appropriate wavelengths and intensity. Oxidation of pollutant can also be achieved by direct action of UV light in combination with O_3 and/or H_2O_2. The main factor governing the success of this technique is UV light transmission to the dissolved pollutants. However, this system poses some problems. Some VOCs such as trichloroethane (TCA) cannot be oxidized and moreover high turbidity of the water would cause interferences with light penetration. Besides, untreated pollutants may be vaporized and would need to be treated in an off-gas system. This technology can be improved by the use of a catalyst, wherein UV light is combined with a semiconductor and a photo catalyst (TiO_2, CdS, etc). The mechanism is based on the excitation of the electrons of the semi-conductor material, inducing areas with both an excess and a deficit of electrons [14]. Photocatalytic oxidation allows the oxidation of a wide variety of organic compounds (Table 1.1), and recently they have also been tested for treating inorganic pollutants in gas phase. However, as shown in this table, some of the degradation products are difficult to degrade than the parent compound and therefore they will require addition post-treatment steps.

Table 1.1: Photocatalytic oxidation products of gas-phase pollutants in photocatalytic reactors (adapted from [15])

Main pollutant	Degradation products
Trichloroethylene, Perchloroethylene	Methylene chloride, carbon tetrachloride, phosgene, CO_2 and dichloroaceyl chloride
Benzene	Phenol, hydroquinone, benzoquinone, and malonic acid
Toluene	Benzaldehyde, benzene, benzyl alcohol, formic acid, acetic acid, CO_2 and trace amounts of benzoic acid and phenol
Formaldehyde	Formic acid
α-Pinene	Pinocamphone, 3-hydroxyl - α-pinene, acetaldehyde, acetone, formic acid, acetic acid, glycolic acid, propionic acid, propanedioic acid, CO, and CO_2
2-Propanol	Acetone, mesityl oxide, CO_2 and H_2O

1.2.1.6 Membrane processes

Membrane processes are based on different rates of diffusion of compounds through a thin membrane. This separation technique is highly dependent on the type of membrane used. Many different membranes are commercially available, with different specifications, in order to permit or avoid the transport of specific compounds [10]. The driving force is the pressure difference on both sides of the membrane, *i.e.*, between the feed and permeate. A vacuum pump creating a lower pressure on one side of the membrane respective to the other enhances the separation process. There are two types of membrane systems, *i.e.*, with high pressure gas phase on both sides and with low pressure of adsorbent liquid on one side. In this case, the final products are a permeate containing most of the organic pollutants and a residual gas streams that still contains small quantities of the same pollutants, so complete removal cannot be achieved. The most important parameters for membrane design include the gas flow rate, the temperature and the pollutant concentrations [9].

1.2.2 Biological techniques

Although some examples of biological treatment for air pollutants can be found as early as in the 1920s [16], it is not up to the late 1970s when systems were designed with prior knowledge gained in the field of chemical engineering and biotechnology Biodegradation of VOCs has always been a promising and comprehendible technique for waste gas treatment. Gas phase biological reactions utilize microbial metabolic reactions to treat contaminated air [11], [17]. The major advantages of biological methods are that they are inexpensive, reliable and environmentally compatible. Furthermore, the pollutants are not merely transferred from one phase to another; instead they are completely mineralized to simple end products such as CO_2 and H_2O. In this section, details pertaining to the operation of bioprocesses such as a biofilter, a biotrickling filter, a continuous stirred tank bioreactor and a membrane bioreactor are discussed.

1.2.2.1 Biofilters

Biofiltration utilizes a support matrix for microbial growth to remove odors and contaminants from air streams. A typical biofilter (BF) consists of a packed bed containing microorganisms. It is a two step process consisting of the transfer of the compounds from the air phase to the water phase and oxidation of the absorbed compound by the microorganisms present in the BF. The dissolved contaminant is transported by diffusion and by advection in the air [11], [18]. When air flows around the particle there is continuous mass transfer between the gas phase and the biofilm (Figure 1.1).

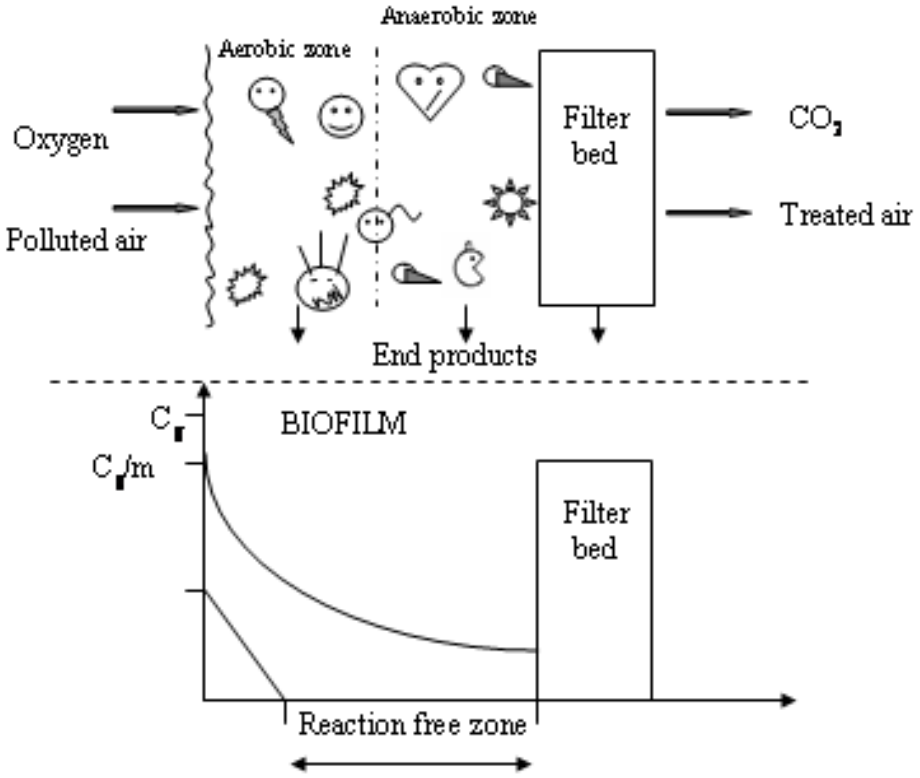

Figure 1.1: Schematic of pollutant removal mechanism in the biofilm attached to the filter bed of waste gas treatment systems (C_g is the gas phase pollutant concentration)

The solid support matrix consisting typically of compost, peat moss, wood chips and synthetic materials provides adequate nutrients required for the activity of the microorganisms. An ideal packed bed should have a long working life and offer low pressure drop for the gases to pass through. The humidified contaminated air is pumped through a distributor placed at the top or the bottom of the filter bed (Figure 1.2a). Besides, a nutrient solution comprising inorganic salts and trace elements is added periodically to the bioreactor to supply the nutrients required for microbial growth, and to maintain optimal moisture content in the filter bed (usually 40-60%). The contaminants in the air stream are absorbed and metabolized by the microbial flora. The treated air is discharged into the atmosphere through an outlet at either the

top or the bottom of the BF, depending on whether air is fed in either upflow or down flow mode. Most BFs that are in operation today can treat odors and VOCs effectively with efficiencies greater than 90%.

Conventional biofilters have some interesting advantages over other biological technologies. It is an eco-friendly and cost-effective technology with few operation problems. A drop in pH during the conversion of acidic compound such as hydrogen sulfide into sulfur or sulfate can seriously affect both the microbial population and the removal efficiency. In order to solve this problem, periodic adjustment of the pH should be done. The addition of inorganic materials such as ceramic, plastics, lava rock, or activated carbon adds more structural stability, reduce the pressure drops and increase the biofilter lifespan.

Typical examples for maximum elimination capacity (EC_{max}) envisioned in different bioreactor configurations under steady state conditions are given in Table 1.2.

1.2.2.2 Biotrickling filters

The schematic of a biotrickling filter (BTF) is shown in Figure 1.2b. The packing is generally made of chemically inert materials such as a plastic support, polyurethane foams, activated carbon, lava rock, pall rings, etc. that can be either arranged in a random or structured manner [19]. These materials offer no nutrients to the microorganisms. Hence, nutrient medium is continuously trickled from the top of the reactor. The liquid phase and gas phase flow can be fed co -or counter currently through the bed depending on the convenience of the user. The trickling solution contains inorganic and other trace nutrients for sustaining microbial activity in the biofilm. It can also act as a buffer, especially for compounds that are difficult to degrade or for compounds that generate more acidic metabolites [20].

The advantages of BTFs compared to BFs include; (i) better process control (ii) smaller footprints (iii) treatment of high concentration of VOCs, (iv) treatment of hot gases and acid producing contaminants and (v) good adaptation capacity of biomass [11], [9]. The factors affecting pollutant removal are, among others; (i) composition and concentration of the waste gas stream, (ii) structural configuration of the packing material, (iii) flow pattern, (iv) nutrient composition, (v) residence time, (vi) pH, and (vii) temperature. Biotrickling filters are more complex than biofilters. This is due to its better performance in handling acidic compounds like hydrogen sulfide, and its easiness in controlling the different physico-chemical operational parameters, *viz.*, pH, temperature and others.

1.2.2.3 Bioscrubbers

A typical bioscrubber consists of two reactors (Figure 1.2c). The first part is an absorption tower where pollutants are absorbed in a liquid phase followed by biodegradation in the second stage bioreactor. This bioreactor contains suspended activated sludge which is sufficiently aerated and much larger than the absorber. The effluent of this bioreactor is then re-circulated over the absorption tower in a co-or countercurrent mode to the flow of waste gas. Microbial activity is enhanced by adding sufficient nutrients in the reactor. This makes them flexible to handle fluctuating loads of waste gas streams [21], [22]. The main advantages of this technique are (i) better removal of reaction products by washing out (ii) no clogging problem and (iii) low occurrence of toxic metabolites in water phase.

The volatile compounds commonly removed in this system are phenol, NH_3, methanol, isopropyl alcohol, acetone, heptane and H_2S [22], [23]. However, this technique is only effective for pollutants having partition coefficient values less than 0.01 [24]. The mass transfer resistance of pollutant from gas phase to water phase

poses a major problem for hydrophobic VOCs. The energy consumption is high due to continuous liquid recycle and extra aeration which in turn increases the operating cost. Moreover, there are sufficient chances for the slowest growing microbial community to get washed out resulting in lesser removal of the target contaminant.

1.2.2.4 Continuous stirred tank bioreactors

Removal of air pollutants by means of diffusion through suspended growth bioreactors is often done in completely mixed type reactors (CSTB or continuous stirred tank bioreactors), with constant aeration (Figure 1.2d), where microbes are kept in suspension in a nutrient rich aqueous phase. However, CSTBs for waste gas treatment often use the gas phase pollutant as their sole carbon and energy source, preferably hydrophilic or slightly hydrophilic pollutants. As these systems are designed for aerobic biodegradation of the contaminants, mass transfer can be optimized for specific contaminants and both mass transfer and oxygen requirements would be the driving force for good reactor design [25]. The efficiency of the CSTB depends on the following factors: (i) the hydraulic retention time (HRT), (ii) concentration and characteristics of the gas phase pollutant, (iii) the presence of inhibitory metabolites within the system, and (iv) the gas hold up. The major challenge regarding its long term operation in industrial facilities is reducing biomass growth and disposal. A few methods have been suggested for reducing biomass accumulation in CSTBs; (i) increasing the mean cell residence time so that the requirement for maintenance energy increases, and/or (ii) decrease efficiency of energy generation for biomass growth by limiting nutrient supply. The advantages of this process include; better temperature and pH control, simple construction, good process control, adaptability to fit reactor configurations such as two stage systems, better control of different phases. CSTBs also facilitate the addition of an oil phase for

increasing pollutant solubility, easy maintenance and low operating costs. CSTBs have been tested under lab scale conditions for removing trichloroethylene (TCE) and dichloromethane (DCM), among others [26], [27].

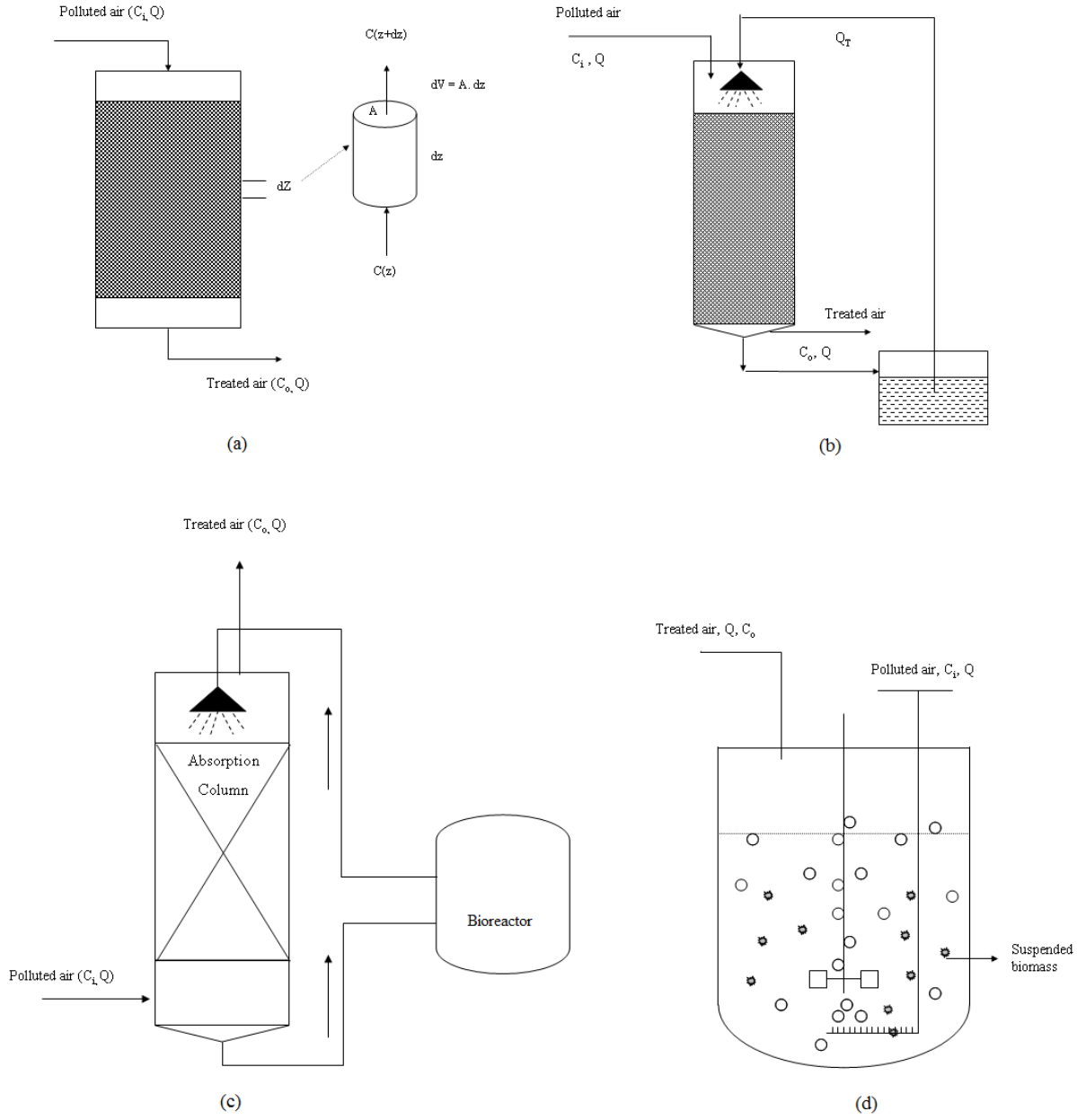

Figure 1.2: Schematic of different waste gas treatment systems, (a) biofilter, (b) biotrickling filter, (c) bioscrubber, and (d) continuous stirred tank bioreactor

Table 1.2: Typical gas phase pollutants treated in waste gas treatment systems and their corresponding EC values

Pollutant	Packing material	Microorganism	Reactor type	EC_{max}, $gm^{-3}h^{-1}$	References
Benzene	GAC	Mixed culture from wastewater treatment plant	BF	20.1	[28]
Toluene	Perlite	*Paecilomyces variotii*	BF	60	[29]
TEX	Perlite	2 bacteria + 1 fungi	BF	>120	[30]
Styrene	Perlite	*Sporothrix sp.*	BF	336	[31]
DCM	Lava rock	*Hyphomicrobium sp.*	BTF	160	[27]
HS-P-M	Pall rings + perlite	*Ophiostoma sp.,*+ autotrophic bacteria + *Candida boidinii*	BTF + BF	HS / 45 P / 138 M / 894	[32]
Toluene	Ceramic particles	*Bacillus cereus*	BTF	152	[33]
Styrene	Celite pellets	Mixed culture	BTF	62	[34]
Styrene	Ceramic monolith	*Sporothrix sp.*	MB	67.4	[35]
DCM		*Hyphomicrobium sp.*	CSTB	117	[27]

Note: GAC - granular activated carbon, TEX - toluene, ethyl benzene and xylene mixture, HS-P-M - mixture of H_2S+ α - pinene + methanol, DCM - dichloromethane, BF - biofilter, BTF - biotrickling filter, MB - monolith bioreactor, CSTB - continuous stirred tank bioreactor, EC_{max} - maximum elimination capacity

1.3 Microbial aspects of biofiltration

The elimination of organic substrates by microorganisms results from the fact that these organisms generally use organic compounds as their sole energy (catabolism) and carbon source (anabolism) [36].

$$VOC + O_2 \xrightarrow{microorganisms} CO_2 + H_2O + Heat + Biomass \quad (1.2)$$

A prior knowledge of the species that are present, their densities, their metabolic transformations and their interactions with the environment is useful to biofilter operation. Bacteria and fungi are the main groups of microorganisms used in most biological techniques. Bacteria present high growth and biodegradation rates, a high resistance to toxicity and have the capacity to biodegrade a great variety of compounds. However, most bacteria growing on aromatic VOCs are inhibited in acid environments [37] and they require high water activity. Typical bacteria include the following; *Pseudomonas putida*, *Coryneformic* bacteria, *Bacillus sp*., *Methylobacterium*, *Mycobacterium sp*., and *Pseudomonas fluorescens*, amongst others.

Concerning fungi, they can tolerate low pH environments (2.0-5.0), nutrients limitation and low humidity (which favors the biodegradation of hydrophobic pollutants) better than bacteria. Moreover, fungi form a filamentous network that would enhance the mass transfer between gaseous pollutant and biocatalyst. However, fungi seem to biodegrade a small range of substances compared to bacteria [38]. Among fungal cultures, the most extensively studied organism belongs to the genus *Exophiala*, although strains of *Scedosporium*, *Fusarium*, *Paecilomyces*, *Cladosporium*, *Cladophialophora*, *Pleurotus*, *Trametes*, *Bjerkandera* and *Phanerochaete* have also been detected in BFs or used to treat gas phase VOCs [38], [18], [23].

The biodegradation mechanisms/pathways of VICs such as H_2S or NH_3 are quite different than VOCs. VICs can be used as a source of energy by chemolithotrophic bacteria through oxidation of their inorganic reduced forms. In most of the cases, chemolithotrophs are autotrophic bacteria that have the capability to fix carbon dioxide and use it as a carbon source for microbial growth, although some of them can make use of other compound as a carbon source (heterotrophic bacteria). This group of microorganisms includes sulfur oxidizers, nitrifying bacteria, iron oxidizers, and hydrogen oxidizers. Among them, the sulfur oxidizing bacteria (SOB) has proved to be an excellent biocatalyst for the removal of malodorous sulfur compounds, especially hydrogen sulfide. The microbial pathways to oxidize inorganic compounds such as hydrogen sulphide can occur in quite different environments, depending on the bacterial nature and the available carbon sources. Table 1.3 shows some examples of different SOB and their requirements.

Under aerobic conditions, chemotrophs use oxygen as their electron acceptor, and hydrogen sulfide, thiosulfate or elemental sulfur as the electron donor, according to the following reactions [39], [40]:

$$H_2S + CO_2 + Nutrients + O_2 \rightarrow Cells + Nutrients + S / SO_4^{2-} \quad (1.3)$$

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \qquad \Delta G^0 = -169.35 \text{ kJ/mol} \quad (1.4)$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^{-2} + 2H^+ \qquad \Delta G^0 = -732.58 \text{ kJ/mol} \quad (1.5)$$

According to the above-mentioned equations, oxygen is the key parameter to control the level of final oxidation. In biogas streams, oxygen is present in small quantities and the main end-product would be elemental sulfur. Sulfate will be formed when sulfide is limited. Recently, several studies have reported the biological conversion of hydrogen sulfide using sulfur-utilizing chemolithoautotrophic denitrifiers. Among others, two species are well known, *Thiobacillus denitrificans* (autotroph) and *Thiomicrospira*

denitrificans (authotroph or heterotroph) that grow at neutral pH under aerobic or anoxic conditions. Under anoxic conditions, nitrate is used as an electron acceptor during the biological oxidation of sulfide to elemental sulfur or sulfate, according to the reaction shown below [41], [42];

$$H_2S + CO_2 + Nutrients + NO_3^- \xrightarrow{denitrifiers} Cells + S^0 / SO_4^{-2} + H_2O + NO_2^- / N_2 \qquad (1.6)$$

Table 1.3: Typical examples of sulfur oxidizing bacteria and their required conditions

Condition	***Thiobacillus thiooxidans***	***Thiobacillus novellus***	***Thiobacillus denitrificans***	***Thiomicrospira pelophila***
pH	2.0-3.5	7.0	6.8-7.4	6.0-8.0
Trophy	Obligate chemoautotroph	Mixotroph	Obligate Chemoautotroph	Obligate autotroph
Energy source	H_2S, polithionates, S	H_2S, MM, DMS, DMDS	Thiosulfate, tetrathionate, thiocyanate, sulfide, S	Sulfide, thiosulfate, S
Oxygen requirements	Strictly aerobe	Strictly aerobe	Facultative anaerobe	Strictly aerobe

1.4 Two stage bioreactors for waste gas treatment

Combination of two biological techniques can be used, especially when the waste gas contains mixtures of pollutants with different physico chemical characteristics or different biodegradation rates. In this case, the first stage biological reactor would be designed and operated in such a way that it would serve as the primary system responsible for removing some of the gas phase pollutants, while the second stage system would remove the non-treated pollutants from the first stage, as well as other specific pollutants present in gas phase (Figure 1.3).

In a BF, aimed at removing H_2S and VOCs from waste gases emitted from the head works and other facilities at POTWs, Cox et al. [43], observed EC of 13.8 $gm^{-3}h^{-1}$, while VOC removal was poor irrespective of the experimental conditions. About 25 to 35% of low concentrations of benzene, toluene and chlorobenzene (BTC) were removed, while other chlorinated VOCs could not be removed in the BTF. In that study,

the low VOC removal was attributed to the presence of inhibitory concentrations of sulphate in the recycle liquid and the possible accumulation of metabolites other than sulphate that inhibits VOC biodegradation. Under such condition and for situations like emissions from typical pulp and paper industries, a two stage bioreactor (Figure 1.3) appears to be more promising and a practically feasible option for the co treatment of H_2S and VOCs and other gaseous pollutant mixture, which has shown positive results in the recent past [44], [45], [46], [32].

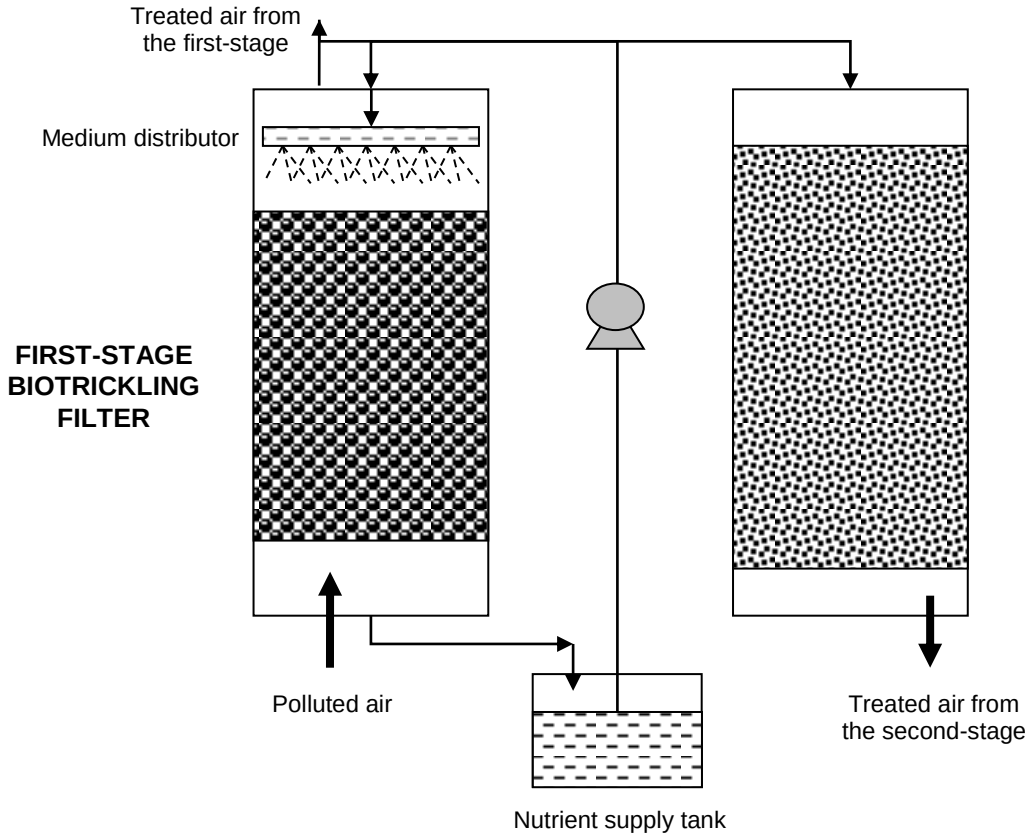

Figure 1.3: A two stage bioreactor for waste gas treatment

Chitwood and Devinny [44] evaluated the feasibility of using a two stage biofilter for the treatment of H_2S, air toxics and smog precursors. The 1st stage acid gas biofilter (AGB) packed with lava rock contained acidophilic autotrophic bacteria to remove H_2S, while the 2nd stage wood chip BF removed other air toxics that includes, methanol, acetone, methylene chloride, chloroform, toluene, xylene, ethyl benzene, methyl-tert-butyl ether (MTBE) and 2-methyl butane. However, they observed that the 1st stage AGB removed acetone and methanol completely, while other VOCs were intermittently removed depending on the concentrations, in addition to 99.6% removal of H_2S at an inlet loading rate (ILR) of 0.057 $gm^{-3}h^{-1}$. Manninen et al. [47] studied the biodegradation of acetone, methanol, methyl ethyl ketone (MEK), naphthalene, α-pinene and toluene in a coupled bioreactor that consists of a 1st stage liquid bioreactor and a 2nd stage BF. The coupled system yielded 97% overall VOC removal from initial start up to shutdown.

Ruokojarvi et al. [48] observed EC as high as 47.9 and 36.6 $gm^{-3}h^{-1}$ of H_2S and dimethyl sulphide (DMS) in a two stage BTF connected in series and inoculated with a microbial consortium enriched from wastewater treatment plant sludge. Similarly, Sercu et al. [45] showed that high ECs could be easily achieved in a two stage BTF for treating gas phase DMS and H_2S. The 1st and 2nd stage BTFs were inoculated with pure cultures of *Acidithibacillus thiooxidans* and *Hyphomicrobium VS*, and the maximum EC achieved were 83 $gH_2S\ m^{-3}h^{-1}$ in the 1st stage and 58 gDMS $m^{-3}h^{-1}$ in the 2nd stage, that predominantly removed DMS. In yet another study, the feasibility of using sequential biofilters for H_2S and a mixture of VOC vapors from wastewater treatment plant air was evaluated in laboratory scale and field studies [43]. At loading rate of 8.3 g $H_2S\ m^{-3}h^{-1}$ and 33 g MTBE $m^{-3}h^{-1}$, near complete removal of these pollutants were noticed. However in field trials, the removal efficiency profiles followed the order, H_2S > VOC

> chlorinated VOC. In a recent study, a hybrid bioreactor system consisting of a low pH BTF and a neutral pH biofilter contained within a single reactor column with different microbial population and two different pH zones was tested for removal of H_2S, methanol and α-pinene from polluted air. Though the hybrid reactor did not exhibit any synergistic effect in pollutant removal characteristics, even when fed with low concentrations of these pollutants, the results suggested the need for a two stage system for achieving high ECs. Low fungal growth in the BF section due to the only moderate tolerance of the fungus to acidification was considered as the major reason for such low EC values. The EC achieved from this study were 3.9, 4.3 and 1 $gm^{-3}h^{-1}$ for H_2S, methanol and α-pinene respectively [49].

1.5 Shock loads in bioreactors for waste gas treatment

The dynamic behavior of biofilters to sudden variations in operating conditions has received little attention, as most of the reported studies were carried out at steady state. It is worthy to mention here that variation in concentrations and gas flow rates are common to any industrial emission and it is a pre-requisite to simulate these conditions at the laboratory scale to know whether the biofilter can respond effectively to such changes. The occurrence of transient conditions in biofilters (or in any bioreactors for waste gas treatment) can be either regular or frequent. These type of shock loads are expected in process industries under the following conditions; overnight and weekend closures, plant maintenance, when higher rate of solvent is used in a particular process, and regular change in process operation encountered in the paint spraying industry, coating and chemical manufacturing industries. The response of the immobilized biomass, bacterial and fungal colonies, to shock loading conditions can be identified by monitoring their removal efficiency, or elimination capacity profiles, during and at the end of the shock load.

Figure 1.4 (simulated graphical representation) shows a typical shock loading profile in a waste gas treatment system (for example, a biofilter), where the onset of low and high shock loads is clearly visible. The corresponding fluctuations in the removal efficiency profiles are also illustrated in Figure 1.4. It is clearly evident that the removal efficiency values are higher at low shock loads than when higher shock loads were introduced to the biofilter, and the biofilter shows good resilience to restore to its original (high) performance when normal conditions are restored after 34 hours of continuous operation.

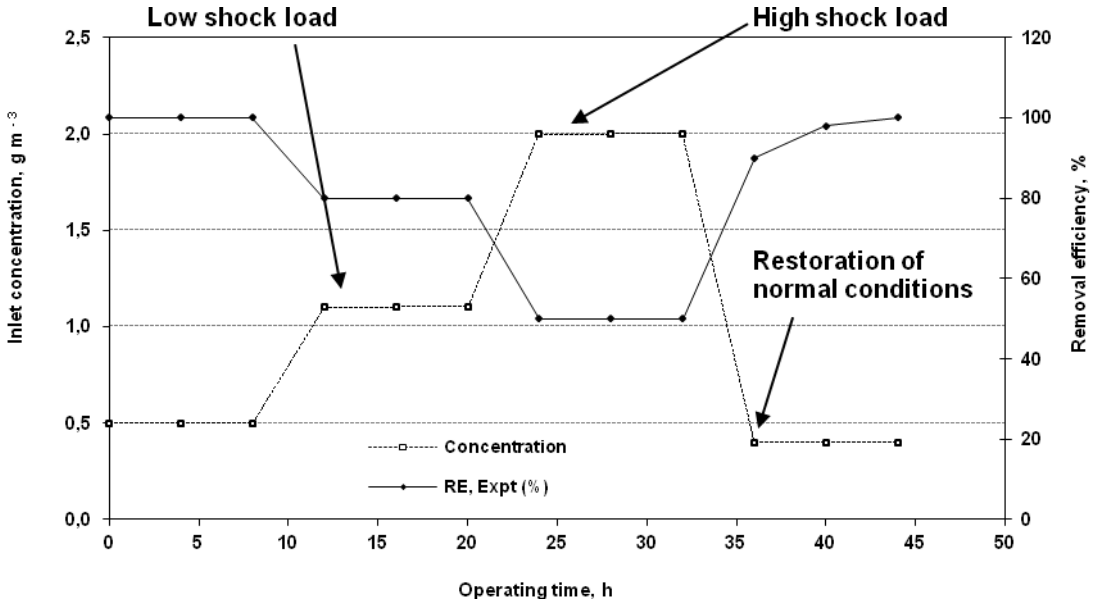

Figure 1.4: Simulated response of the biofilter to sudden variations in pollutant concentration, and corresponding pollutant removal efficiency profiles (region inside dotted brackets show the variations of shock load)

According to Wright [50], ``*microbial population in biofilters is related to the availability of substrates or nutrients, and has been shown to decrease by one or four orders of magnitude between the inlet and outlet, when systems are operated under nominal steady state conditions´´*. However, for cases involving large transient

operations, such as conditions where the bioreactor receives an instantaneous, yet severely high concentration levels of a particular pollutant, either the mass transfer capacity or the reaction capacity of the initial sections of the bed are exceeded and contaminants move into the latter sections where the microbial populations and reaction capacities are low and contaminant breakthrough may occur [51], [52], [18], [23]. Wright [50] outlined four effective, yet practically feasible strategies for industrial facilities, for managing transient loads in a biofilter system. These include; providing downstream polishing units, dampening variations in contaminant loading using sorbent material placed upstream (example: adsorption unit), supplemental feeding during extended periods of downtime, and maximizing reactor capacity.

Several lab-scale experimental results have shown that sudden fluctuations in loading rates (due to variation in both inlet concentration, and gas flow rates) either increased or decreased the removal profiles, but did not pose a threat or deteriorate (zero removal of the target pollutant) the microbial dynamics and performance of biological waste gas treatment systems, such as a biofilter, biotrickling filter, continuous stirred tank bioreactor (CSTB), and two liquid phase partitioning bioreactors (TLPPBs). Baltzis and Adroutsopoulou [53] studied shock loading effects in the biofilter containing peat/perlite as the filter medium for the treatment of ethanol and butanol and reported that the filter bed never failed completely under shock loading conditions. They further conclude that fluctuations in mass loading rates take a long time to decay the filter bed performance, and adsorption and desorption processes play an important role in the response to shock loadings. Arulneyam [54] investigated the performance of two biofilters treating methanol and ethanol vapors at two different upset modes, such as changes in flow rate and concentrations. The results reveal that the biofilm was quite

sensitive to changes in loading rates as seen from the removal patterns and the biofilm was able to recover quickly to the normal performance within two days.

Rene et al. [17] studied the transient behavior of the perlite biofilter by subjecting it to different types of shock loads, *i.e.*, short term shock load of 12 h and long term shock load of 10 d. Short term shock loads were studied at a flow rate of 0.15 m^3h^{-1}, in two stages, *viz.*, at a normal inlet loading rate (ILR) of approximately 60 $gm^{-3}h^{-1}$ and a shock load of 200 $gm^{-3}h^{-1}$ (low and medium loading rates, L-M), and at a normal ILR of 60 $gm^{-3}h^{-1}$ and a shock load of 450 $gm^{-3}h^{-1}$ (low and high loading rates, L-H). The results from that study indicated that the biofilter was able to maintain a high performance, close to 100%, when applying a medium shock load (L-M), however, when a higher, short term, shock load of 450 $gm^{-3}h^{-1}$ was applied, the removal efficiency dropped suddenly to 70% and then remained constant at such value during the shock load period of 12 h. Anew, the response of the biofilter was fast as seen from the immediate decrease in removal profile at high loads and the retrieval in performance (100%), when restoring low loads. In a biofilter handling hydrogen sulfide vapors, Barona et al. [55] investigated low and medium shock loads over 36 days of continuous operation. Their biofilter was subjected to an instant shock from 8 to 68 $gH_2S\ m^{-3}h^{-1}$ after a brief starvation period of 80 and 25 h, where the EC dropped from 68 to 48 $gH_2S\ m^{-3}h^{-1}$, and a restoration in the RE was reported when the original low loading rates were re-applied. Jin et al. [56] conducted long term shock loading experiments of one month, by subjecting a fungal biofilter to multiple medium and high shock loads of α-pinene and observed that the performance of the biofilter quickly recovered after every 4 h shock load, reaching EC values of 60 $gm^{-3}h^{-1}$ with removal efficiency greater than 90% over the 13 h period after the shock load.

1.6 Neural network modeling of waste gas treatment systems

Neural Networks are able to learn non linear static or dynamic behavior exclusively by measuring data. Since the knowledge of internal procedure is not necessary, the modeling can take place with minimum previous knowledge about the process through proper training of the network. The impetus of employing artificial neural networks (ANNs) to model dynamic biological waste gas treatment systems is due to their inherent advantage over other non linear modeling paradigms, that can be summarized as follows;

(i) usefulness in solving data intensive problems where the algorithm or rules to solve the problem are unknown [57], (ii) the ability to detect all possible interactions between predictor variables, (iii) less formal statistical training, (iv) ability to implicitly detect complex nonlinear relationships between dependent and independent variables, (v) ability to generalize and find relations in imperfect data as long as they do not have enough neurons to over fit data imperfections [58], and (vi) the availability of multiple training algorithms [59].

Besides, ANNs can be easily applied to solve seven categories of problems: pattern classification, clustering, function approximation, prediction, optimization, data retrieval and process control [60]. Livingstone et al. [61] nicely describe ANNs as ‘*’Data modeling with neural networks is certainly not ‘an answer to the maiden’s prayer’, but neural networks do offer a number of advantages over some of the more traditional methods of data modeling and should be viewed as an useful adjunct to these techniques*’’.

Hussain [62] reasons that ‘*the versatility in structure and application of neural networks enables them to be utilized in the middle ground between conventional model based approaches and black box approaches for solving many classes of problems*’.

1.6.1 Multilayer perceptron

A multilayer perceptron (MLP) belongs to the class of supervised feed-forward networks in which the processing elements are arranged in a multi-layered structure (Figure 1.5). The structure of MLPs consists of an input layer, one or more hidden layers and an output layer. The input from each processing element in the previous layer (χ_i) is multiplied by a connection weight (W_{ji}). These connection weights are adjustable and may be linked to the coefficients in statistical models. At each PE, the weighted input signals are summed and a bias value (θ_j) is added or subtracted. This combined input (I_j) is then passed through a non-linear transfer function ($f(.)$) to produce the output of the PE (y_j). The output of one PE provides the input to the PEs in the next layer. This process can be illustrated as follows;

$$I_j = \sum w_{ji} \chi_i + \theta_j \tag{1.7}$$

$$y_j = f(I_j) \tag{1.8}$$

The global ANN model framework illustrated in Figure 1.6 shows the different steps involved in the modeling process. More detailed information concerning the selection of network training parameters and methodology involved has been described adequately in Rene et al. [63].

1.6.2 Literature reports on neural modeling

Applying the concepts of ANNs to model waste gas treatment systems was initiated only recently, in the mid 2000's, when a BTF and BF were modelled for their performance [64], [65], [31], [63]. Table 1.4 summarizes the literatures pertaining to the use of neural models for different bioreactor configurations used to treat gas phase pollutants. Elías et al. [65] obtained start up, intermittent fluctuation, steady state and shut down data from a lab scale BF packed with pig manure and saw dust, handling H_2S vapors. Data division was done using cluster analysis in combination with a genetic

algorithm, and the data were divided as training (50%), testing (40%) and validation (10%). Inlet H_2S concentration and unit flow values (Q/V, h^{-1}) were used as the input to the model, for predicting the removal efficiency of the BF (RE, %). The best MLP was decided by trial and error, by testing nearly 10,000 different combinations of MLPs, and it was observed that a 2-2-1 network architecture was able to predict RE well with relatively high R^2 values (0.92). Results from sensitivity analysis showed the influence of flow rate in affecting the BF performance, and these findings were similar to the actual experimental data collected from the BF during 3 years of operation.

In another study, Rene et al. [31] modeled the performance of a BF (RE, %) using a back propagation algorithm for a reactor inoculated with a mixed culture taken from the wastewater sludge of a petrochemical refinery and treating gas phase styrene. A log-sigmoid transfer function was used with inlet styrene concentration and unit flow as the inputs, and the best network topology obtained through trial and error was found to be 2-4-1. During regular experiments, greater than 92% styrene removal was achievable for loading rates up to 250 $gm^{-3}h^{-1}$, and the critical load to the system was found to depend highly on the gas flow rate, *i.e.*, EBRT. The authors also carried out a sensitivity analysis, in terms of absolute average sensitivity (AAS), for the developed model to determine the most influencing input parameter for the model, The higher AAS value for unit flow suggested that the BF performance highly depended on the gas flow rate, and that the effects due to the pollutant, gas phase styrene, was only minimal.

Table 1.4: Summary of artificial neural network models developed for different waste-gas treatment systems

Pollutant	Type of neural network	Network parameters	Input parameters	Performance indicator	Data points	Network topology	Bioreactor configuration	R^2	Reference
H_2S	BP - conjugated gradient decent	η-0.01	UF, C_i	RE	194	2-2-1	BF	0.92	[65]
Toluene	Dynamic neural network observer	Sigmoid TF	CO_2, ΔP	EC	350		BF	1	[66]
Toluene	Dynamic neural network observer	Least mean square algorithm┼	ΔP	CO_2[1]	60		BF	0.9[2]	[67]
BTX	BP with gradient decent	η-0.4 α-0.9 T_c-10,000	C_i, Q, ILR, ΔP	a)- C_o b)- EC, RE	55	a)4-4-1 b)4-4-2	BTF	0.00011[3] 0.00186[3]	[64]
H_2S	BP with gradient decent	η-0.1 α-0.9 T_c-16,000	C_i, Q, ILR, ΔP	RE, EC	67	4-4-2	ICBF	0.9157	[68]
NH_3	BP with gradient decent	η-0.9 α-0.9 T_c-16,000	C_i, Q, ILR, ΔP	RE, EC	67	4-4-2	ICBF	0.9825	[69]
Styrene	BP with gradient decent	η-0.8 α-0.8 T_c-22,000	UF, C_i	RE	157	2-4-1	BF	0.973	[31]
DCM	BP with gradient decent	η-0.9 α-0.9 T_c-9,000	C_i, Q	RE	260	2-4-1	BF	0.944	[70]
Styrene	BP with gradient decent	η-0.75 α-0.8, 0.9 T_c-10,000 to 50,000	UF, C_i, G/L ratio, ΔP	RE	83 81 68	3-5-1 2-5-1 2-5-1 3-4-1	BF CSTB MB	>0.95 0.9667 0.8838	[63]

Note:

1) Elimination capacity (EC) was numerically reconstructed from this observer.
2) R^2 value was for EC *vs* CO_2 production profiles predicted from the network.
3) Sum squared error (SSE) values were reported by the authors, and two models (a and b) were developed in that study.
Pollutant: H_2S-Hydrogen sulphide, NH_3-Ammonia, BTX-Benzene, toluene and xylene, DCM-Dichloromethane.
Network parameters: η is the learning rate, α is the momentum term, T_c is the training count.
Input parameters: UF is unit flow, C_i and C_o are the inlet and exit pollutant concentrations, ILR is the inlet loading rate, G/L is the gas to liquid ratio, ΔP is the pressure drop.
Bioreactor configuration: BF-Biofilter, BTF-Biotrickling filter, ICBF-Immobilized cell biofilter, CSTB-Continuous stirred tank bioreactor, MB-Monolith bioreactor.
R^2 is the coefficient of regression during testing.
BP - Backpropagation algorithm.
┼-More details concerning this algorithm is given elsewhere [71]

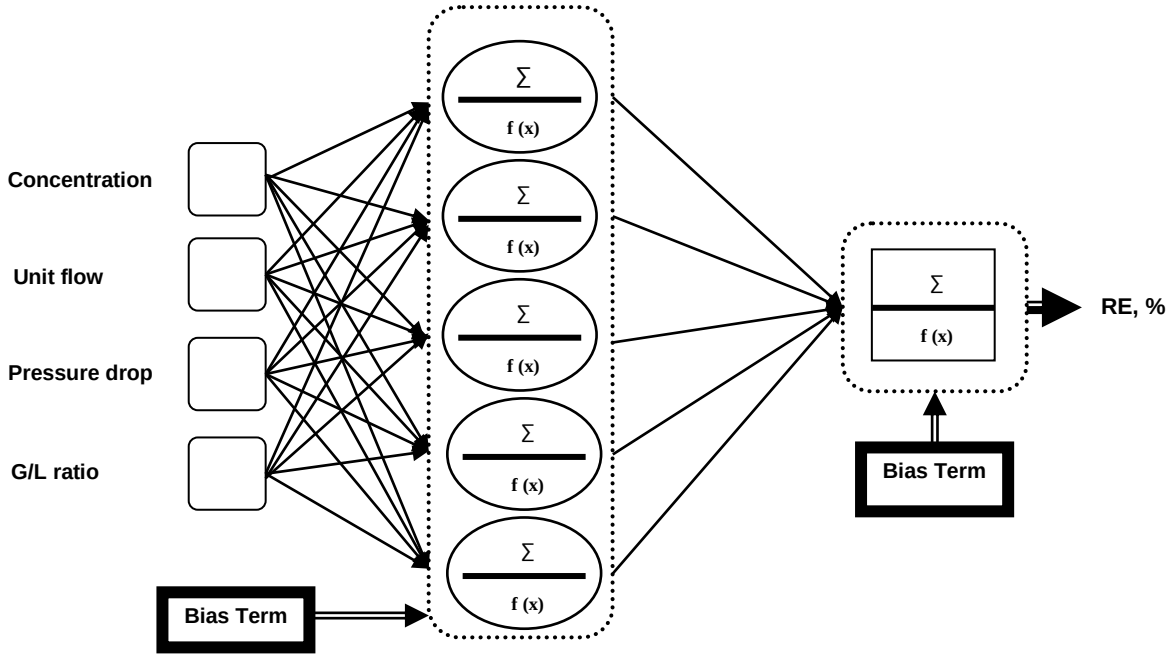

Figure 1.5: Structure of a multilayer perceptron (MLP) having 4 input parameters and one output parameter

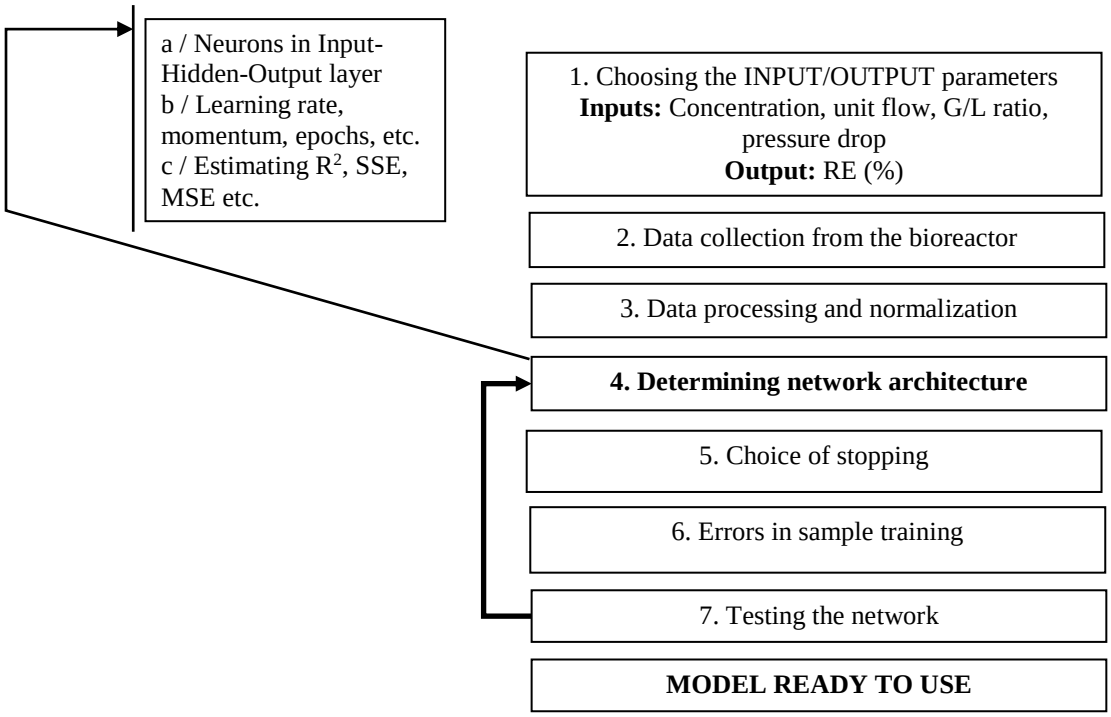

Figure 1.6: Steps involved in neural modeling of waste gas treatment systems

1.7 Objectives of this research

The main objective of this research was to compare the removal of a mixture of volatile compounds of different nature, *viz*., methanol, hydrogen sulphide and α-pinene using one and two-stage bioreactor configurations.

The specific objectives of this research were to;

- Assess the performance of a two-stage bioreactor (first stage biotrickling filter and a second stage biofilter) for the treatment of a gaseous mixture of hydrogen sulphide, methanol and α-pinene under steady and transient-state operations
- Demonstrate the performance of a one-stage biotrickling filter for the removal of a mixture a gaseous mixture of hydrogen sulphide, methanol and α-pinene under steady and transient-state operations
- Perform microbial community analysis in the one-stage biotrickling filter and relate the microbial community distribution to the removal of individual pollutants
- Understand the interactions between the VOC and VIC pollutants in the mixture under the influence of stable and fluctuating pollutant loading rates
- Formulate artificial neural network (ANN) based models to describe the performance of the two and one stage bioreactor configurations
- Compare the performances of two bioreactor configurations and suggest future research perspectives, in terms of practically applying these bioreactors for industrial situations

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Chapter 2

Steady- and transient-state operation of a two-stage bioreactor for the treatment of a gaseous mixture of hydrogen sulphide, methanol and α-pinene

The modified version of this chapter was published as:

Rene, E.R., López, M.E., Veiga, M.C., Kennes, C. (2010) Steady- and transient-state operation of a two-stage bioreactor for the treatment of a gaseous mixture of hydrogen sulphide, methanol and α-pinene. Journal of Chemical Technology and Biotechnology, 85(3), 336-348.

ABSTRACT

A two - stage bioreactor, comprising a biotrickling filter (BTF) as the first - stage and a biofilter (BF) as the second - stage, operated under steady - and transient - state conditions, was tested to remove gas - phase hydrogen sulphide, methanol and α - pinene. Hydrogen sulphide and methanol were removed in the first - stage, while α - pinene, was removed predominantly in the second - stage fungal BF. The effect of the liquid trickling rate was evaluated in the BTF, while concentration dependent synergistic and antagonistic interactions in both the reactors were understood by varying the concentration of one pollutant, and by maintaining 100% removal of other pollutants. Increasing the liquid trickling rate decreased methanol removal significantly, from >93% to 40%. Increasing the concentration of hydrogen sulphide from low to high loading rates did not affect the removal of VOCs, however the reverse occurred. Under all the tested conditions, α - pinene removal in the second stage biofilter still remained higher than 80%. The results show the maximum elimination capacities achievable for this complex ternary mixture, under a wide range of operating conditions.

KEYWORDS: Two - stage bioreactor, biotrickling filter, biofilter, liquid trickling rate, hydrogen sulphide, VOC, shock loads

2.1 INTRODUCTION

The acclivitous rise in the emission levels of toxic pollutants from the pulp and paper industry is a major health concern. Reduced sulphur compounds as hydrogen sulphide, methyl mercaptans, dimethyl sulphide and dimethyl disulphide are emitted from the sulphate process when sodium sulphide reacts with lignin [1]. On the other hand, a typical pulp and paper industry would also emit substantial amounts of volatile organic compounds (VOCs) such as methanol, terpenes, alcohols, phenols, ketones and formaldehyde. Hydrogen sulphide (H_2S), methanol (CH_3OH) and α - pinene ($C_{10}H_{16}$) are major representative air pollutants in such industries [2]. Exposure to respiratory irritants such as H_2S among pulp mill workers has shown to increase obstructive lung disorders, prevalence of respiratory symptoms, occupational asthma, reactive airways dysfunction syndrome (RADS) and increased risky for ischemic heart disease [3-5]. Accidental exposure to methanol through either inhalation or ingestion could result in headache, dizziness, gastric disturbances, visual disturbance, conjunctivitis and severe neurological damage [6]. α - pinene is released not only during the mechanical treatment of wood, but also during the storage of saw dust and shavings [7,8]. It is an irritant to the skin, eyes and mucous membranes and can easily penetrate the different barriers of the body, the gastro intestinal track and intact skin [9].

Microbial purification of mixture of waste gases such as hydrogen sulphide, methanol and α - pinene appears to be the most economical and efficient option for emissions of low pollutant concentrations, at moderately high flow rates. Biotrickling filters (BTFs) and biofilters (BFs) are two typical bioreactor configurations that are characterized by the use of packed beds with attached biomass [10]. The application of BTF and BF have been extended to several industrial facilities, as they appear to be reliable and cost - effective compared to physico - chemical gas treatment technologies [11-13]. Earlier

our research group had developed a series of studies, in order to implement bioreactor technologies, specifically using BTF and BF, for the treatment of off - gas emissions containing formaldehyde, methanol, dimethyl ether [14], α – pinene [2], hydrogen sulphide [15], and hydrogen sulphide and methanol [16]. Most of the previously reported works have focused mainly on the biofiltration of mixtures of VOCs or mixtures of reduced sulphur compounds [17-19]. Recently, there are however, only a few reports that pertain to the co - treatment of H_2S and a VOC using either BTF or BF [16, 20-22]. One of the most commonly reported problems during the co - treatment of H_2S and VOC is that the pH of the biofilm would drop when H_2S is converted to sulphuric acid, which conversely inhibits the biological activity in the BF and subsequent degradation steps. These include, acid attack to the organic media, channelling in some site specific areas and filter bed compaction.

In BTFs, the trickling liquid, usually a well - defined nutrient medium, acts as a main agent for oxygen and substrate transport from the gas - phase to the biofilm [23]. As a consequence of increased pollutant transfer limitations from the gas - phase to the biofilm, as a result of the thicker liquid layer than in BFs, removal efficiencies in BTF do sometimes not reach 100%, even at low inlet loads, thereby affecting the maximum EC that can be reached [14]. However, this depends on the characteristics of the incoming gaseous stream, whether hydrophilic or hydrophobic. For BTFs treating mixtures of H_2S and other VOCs, the continuous re - circulation of the trickling liquid phase easily eliminates the sulphuric acid produced during the biodegradation step, and helps to control the physiological conditions in the liquid phase such as nutrient supply to the attached biomass, contaminant absorption, removal of metabolites and toxic by - products and biofilm moistening [15]. The flow rate of the re - circulation liquid or the liquid trickling rate, a major hydrodynamic parameter in trickle beds, has also shown to

strongly affect the performance of BTFs, and is very critical for full utilization of the filter bed capacity [24].

The aim of the present research was to study the biological treatment of gaseous mixture of H_2S, methanol and α - pinene in a two - stage bioreactor system, consisting of a 1st stage BTF followed by the 2nd stage BF, and understand the effect of the most important operational parameters. Experiments were carried in continuous mode, in the BTF and BF, by changing the process parameters such as gas flow rate, pollutant concentration and liquid trickling rate, in order to undertake the following studies; (i) dependency of pollutant loading rate on the gas flow rate, i.e., the empty bed residence times (EBRTs), (ii) effect of liquid trickling rate in the 1st stage BTF, (iii) effect of increasing pollutant peak load on the removal of other pollutants present in mixture and (iv) effect of transient - state operating conditions on the performance of BTF and BF.

2.2 MATERIALS AND METHODS

2.2.1 Microorganisms and media composition

The BTF was inoculated with a mixture of autotrophic H_2S - degrading culture and an acid - tolerant methanol degrading yeast (*Candida boidinii*) that was obtained from our previous work on the co - treatment of H_2S and methanol in a low - pH BTF [16]. A *Ophiostoma stenoceras* sp., a well known sap - wood colonizing fungus, isolated from a biofilter efficiently degrading α - pinene was used to inoculate the 2nd stage BF [2]. The composition of the mineral salt medium used in the BTF, was (in g L^{-1} of de - ionized water); KH_2PO_4: 2; K_2HPO_4: 2; NH_4Cl: 0.4; $MgCl_2 \cdot 6H_2O$: 0.2; $FeSO_4 \cdot 7H_2O$: 0.01. The medium used in the fungal BF had the following composition (g L^{-1}); K_2HPO_4: 0.5, $MgSO_4 \cdot 7H_2O$: 0.1, KH_2PO_4: 4.5, NH_4Cl: 2, and 2 mL trace elements and vitamin solutions [15]. The BF bed's moisture content was maintained constant by periodic addition (once every 3 d) of fresh mineral salt medium (pH - 5.9) from the top.

2.2.2 Experimental setup and operation

The two - stage bioreactor comprising a BTF and a BF is shown in Figure 2.1. The first stage is a 2.78 L BTF, constructed using glass, 75 mm in diameter and 700 mm in height. The active height of the packed column, filled with polypropylene pall rings, was 640 mm. The pall ring bed had an initial porosity of 91% and a specific surface area of 350 m^{2} m^{-3}. The BF stage consisted of a cylindrical glass column with an inner diameter of 100 mm and a total height of 700 mm. The length of the BF bed was 600 mm, leading to a working volume of approximately 4.88 L. In the BF, irregular grains of perlite with a mean diameter of 4.5 mm were mixed with 50 % (weight) of the same polypropylene pall rings as used in the former BTF. The bioreactors were provided with four equidistant gas sampling ports, located along the reactor at 50 (outlet), 250, 450, and 650 (inlet) mm from the bottom. Two filter material sampling ports were uniformly distributed on the other side of the column. All fittings, connections and tubing's were made of either glass or Teflon.

A compressed air stream was split into three flows. H_2S was generated by passing the major portion of the air stream over a H_2SO_4 solution into which a solution of Na_2S was dripped. Different gas phase H_2S concentrations were obtained by changing the Na_2S concentration and/or dripping rate. The other two minor air streams were bubbled through flasks containing either liquid methanol or α - pinene separately. The three streams were combined in a mixing chamber, and fed to the bottom of the BTF column in a counter - current flow mode (Figure 2.1). The aqueous mineral medium described above was continuously recirculated over the packed bed using a peristaltic pump (323E/D, Watson - Marlow Ltd, Falmouth Cornwall, England). During start - up and for experiments undertaken to ascertain the maximum elimination capacity, the liquid trickling rate was held constant at 50 mL min^{-1}, besides varying its flow rate between

50 - 150 mL min $^{-1}$ for certain experiments, depending on the study condition. The exit air from the top of the BTF was later fed through the fungal BF in a downflow mode. The two - stage bioreactor's performance was estimated by calculating the elimination capacity of the filter bed and removal efficiency of the corresponding pollutant at different inlet loading rates, according to equations defined elsewhere [24].

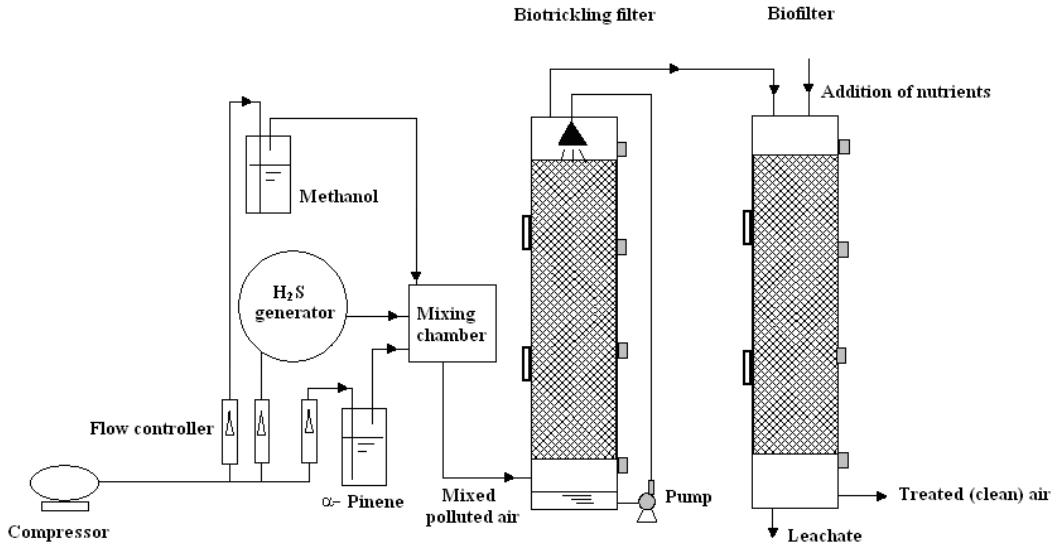


Figure 2.1: Schematic of the two - stage, BTF and BF connected in series

2.2.3 Analytical methods

Hydrogen sulphide concentration was determined using a hand held sensor (Dräger Sensor XSEC H_2S HC6809180). Inlet and outlet gas - phase concentrations of methanol and α - pinene were measured via gas chromatographic analysis using a Hewlett - Packard 5890 series II GC. The GC was equipped with a flame ionization detector (FID). The following flow rates were used; H_2: 30 mL min $^{-1}$, air: 300 mL min $^{-1}$. The GC was equipped with a 50 m TRACER column (TR - WAX, ID: 0.32 mm, film thickness: 1.2 μm) and helium was used as the carrier gas (flow rate: 2.0 mL min $^{-1}$). The temperatures at the GC injection, oven and detection ports were 150, 150 and 150 °C respectively. Similarly, CO_2 concentrations were measured using another Hewlett - Packard 5890 GC fitted with a thermal conductivity detector (TCD). The CO_2

concentrations were determined at an injection temperature of 90 ^{o}C, an oven temperature of 25 ^{o}C and using a TCD at 100 ^{o}C (Jin et al., 2007). pH was measured with a Crison pH - meter 507, using a combined glass electrode. A glass U - tube water manometer was used to measure the pressure drop across the filter bed height. At different time intervals, packing samples were gently removed from the upper and lower port of the 2nd stage BF. Dry biomass weight was measured by placing, around 2 g of perlite sample with biomass in an oven at 90 ^{o}C for 12 h until reaching constant weight. After drying, moisture content (MC) in the packing material was determined by measuring the weight loss. The dried samples were later placed in a muffle furnace at 550 ^{o}C for 2 h, and the dry biomass content was determined by measuring the weight loss. After each biomass sampling, the same quantity of fresh perlite grains was added to compensate for the withdrawn samples. Pall ring and perlite samples, immobilized with biomass and exposed to methanol, H_2S and α - pinene vapours were prepared for observations under a scanning electron microscope (SEM). Examinations were performed with a JOEL JSM - 6400 SEM working at a voltage of 20 kV and a working distance of 15 mm, and with Oxford Instruments EDX equipment, and quantitative elemental composition analysis, to confirm the accumulation of crystalline - sulphur particles, was done with the same equipment. Before the SEM analysis, the samples were dried for 24 h, placed on a metallic stub and covered with gold by means of a Balzers SCD - 004 sputter coater.

2.3 RESULTS AND DISCUSSIONS

2.3.1 Start - up of the bioreactors

The first - stage BTF and second - stage BF were acclimated with low concentrations of mixture of H_2S, methanol and α - pinene at a flow rate of 0.12 $m^3 h^{-1}$, that corresponds to an EBRT of 83.4 s in the 1st stage BTF and 146.4 s in the 2nd stage BF. The inlet

loading rates during the start - up were as follows: 1.5 - 2.8 g H_2S m^{-3} h^{-1}, 28.9 - 205.1 g $_{methanol}$ m^{-3} h^{-1} and 0.7 - 3.9 g $_{\alpha\text{ - pinene}}$ m^{-3} h^{-1}. The removal efficiency of H_2S and methanol in the BTF improved slowly reaching an EC of 1.9 g m^{-3} h^{-1} for H_2S and 197 g m^{-3} h^{-1} for methanol. The much higher EC reached for methanol than H_2S was presumably due to the much faster growth and activity of the heterotrophic *Candida boidinii* strain. The nutrient medium was changed once every 4 d or when its pH dropped below 2.7. On the other hand, the BF (2^{nd} stage), though fed with low concentrations of α - pinene (< 0.2 g m^{-3}), showed steady and increasing removal performance, where nearly 100% of the incoming α - pinene was removed at the end of 28^{th} d, corresponding to an EC of 3.9 g m^{-3} h^{-1}. After this start - up period (28 d), both the BTF and BF were ready to be tested for their performance under different operating conditions according to the operational schedule shown in Table 2.1.

Table 2.1: Operational schedule of the two – stage bioreactor

Nature of study	Range of inlet loading rates, g m^{-3} h^{-1}			Operation time
	H_2S^1	Methanol[1]	α – pinene[2]	
1. Acclimation	1.5 – 2.8	28 – 205	0.7 – 3.9	28 d
2. Effect of pollutant load on RE and EC	0.6 – 45	28 – 1260	0.7 – 161	132 d
3. Effect of liquid tricking rate	28 – 48	308 – 489	69 – 126	20 d
4. Effect of increasing concentrations	4 – 20	37 – 775	3 – 36	23 d
5. Effect of transient loads				
- Long – term shock loads	10 – 38	60 – 254	11 – 70	66 h
- Short – term shock loads	8 – 106	95 – 1220	17 – 176	12 h

Note: 1, 2 – Pollutant loading rates to the BTF, BF respectively

2.3.2 Effect of inlet loading rate on the elimination capacity and removal efficiency

The effect of H_2S, methanol and α - pinene load on the removal efficiency of these compounds in the BTF and BF was evaluated at different gas flow rates (0.12 to 1 m^3 h^{-1}), for 132 d, corresponding to EBRTs varying between 83.4 and 10 s in the 1^{st} stage BTF and 146.4 and 17.6 s in the 2^{nd} stage BF (Table 2.2). It was observed that the maximum EC (EC_{max}) achieved at different EBRT, for each pollutant in either the BTF or BF, was highly dependent on the inlet loading rate (ILR). The removal efficiencies of

each pollutant in each step of operation, corresponding to different EBRTs, depended not only on the concentration of individual pollutant, but also on the concentrations of other pollutant in the mixture, suggesting interaction effects could play a major role in determining the removal of a given compound in the mixture, as also shown in later experiments. As seen from Table 2.2, the EC_{max} of methanol decreased from 894 g m^{-3} h^{-1} to 695 g m^{-3} h^{-1}, when α - pinene load was increased from 61 to 245 g m^{-3} h^{-1}, in the first - stage BTF, which occurred due to a decrease in the EBRT from 41.7 to 20 s, as well as the combined effect of the hydrophobic and hydrophilic VOC concentrations. On the other hand, the critical H_2S and methanol load in the BTF, dominantly removing these two pollutants, decreased with an increase in the gas flow rate. For instance, at an EBRT of 83.4 s in the BTF, the critical H_2S load to achieve > 90% removal was 11 g m^{-3} h^{-1}, while for the same pollutant, at an EBRT of 27.8 s, the critical load decreased to 7.9 g m^{-3} h^{-1}. A maximum EC of 45 g H_2S m^{-3} h^{-1} was achieved with 70% removal in the BTF. Similarly, the critical methanol loads to reach > 90% removal decreased from 497 to 186 g m^{-3} h^{-1}, when the gas flow rate was increased from 0.36 (27.8 s) to 1 m^3 h^{-1} (10 s). For a load of almost 1200 g m^{-3} h^{-1}, the maximum methanol EC decreased when decreasing the EBRT from 41.7 to 20 and 10 s (Table 2.2). However, this dependency of critical load on the gas flow rate was not clearly evident in the second stage BF, where α - pinene was predominantly removed by the *Ophiostoma* sp., followed by the removal of residual methanol and H_2S entering from the 1st stage BTF. Batch experiments with attached microbes taken from the perlite, from different ports along the bed height, confirmed that the heterotrophic microbial population in the BF and the predominantly available *Ophiostoma* sp. was able to remove both methanol and mixtures of methanol and α - pinene in aqueous phase (data not shown). The maximum EC achieved in the BF, for each step of operation, for α - pinene was a strong function

of the inlet loading rate. The high EC achieved in the BF, 138 g $m^{-3} h^{-1}$, for a hydrophobic VOC, α - pinene, was plausible due to the inoculation of that reactor with the fungus *Ophiostoma stenoceras.* It was later confirmed through SEM analysis results and by means of periodically examining the perlite particle under an optical microscope, that the second stage BF showed a predominant presence of the original fungus. Besides, the maximum EC of hydrogen sulphide and methanol in the BTF were 16.8 g $m^{-3} h^{-1}$ and 315 g $m^{-3} h^{-1}$ respectively. It has been shown earlier that fungal dominant systems could offer contaminant removal rates greater than those observed from bacterial systems [2]. For biofiltration of hydrophobic compounds, like α - pinene, fungal growth is preferred over bacterial growth owing to their ability to degrade the substrates under extreme operating conditions regardless of pH and water content fluctuations, and limiting nutrient concentrations [25].

Table 2.2: Maximum elimination capacity in the first - stage BTF and second stage BF

	Hydrogen sulphide		Methanol		α – pinene	
EBRT (s)	ILR_{max}	EC_{max}	ILR_{max}	EC_{max}	ILR_{max}	EC_{max}
First – stage BTF						
83.4	5.7	4.5	294	282	13.3	5.8
41.7	18.4	13.9	1145	894	61.8	21.4
27.8	25	15.1	553	439	150.7	8.2
20	72	33.2	1260	695	244.5	35
10	93.5	45	1139	613	248.5	18.1
Second – stage BF						
146.7	0.68	0.68	7.16	7.16	4.9	4.8
73.2	3.5	1.98	142.8	84.1	33.7	30.5
48.8	6.16	2.54	64.9	40.9	82.7	44.6
35.2	23.8	8.2	321.7	315.9	138.7	100.7
17.6	34.2	16.8	411.2	161.9	161.1	138.1

Note: ILR_{max} and EC_{max} are in g $m^{-3} h^{-1}$

2.3.3 Sulphur accumulation in the filter bed

Pall rings with attached biomass from the BTF were collected after 44 d of continuous operation and subjected to SEM and elemental composition analysis. As seen from the SEM photograph in Figure 2.2, the rod - shaped particles formed on the surface of the

pall rings was mainly condensed crystal - like elemental sulphur, which was also confirmed by elemental analysis as well as by the change in colour (colourless to pale yellow in less than 6 h and to dark yellow in less than 24 h) of the nutrient medium collected in the reservoir of the recirculation liquid. The sulphur content in the attached biomass, on the 44th d of our experiment was about 60% (wt basis), in a condition where nearly 80% of the incoming H_2S vapour was removed at an inlet loading rate of 6.1 g m $^{-3}$ h $^{-1}$. On the same day, methanol removal efficiency was about 96% at an inlet loading rate of 146 g m $^{-3}$ h $^{-1}$. Sulphur formation during the partial oxidation of sulphide instead of the complete oxidation to sulphate, as shown in Eqs. (1) and (2), could be due to oxygen limitation caused by preferential utilization of methanol by the acid tolerant yeast, because of its good biodegradability [16].

$$2\,HS^- + O_2 \rightarrow 2S^o + 2\,OH^- \quad (1)$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2\,H^+ \quad (2)$$

Similar observation has been reported extensively in the literature, and this presents environmental implications as elemental sulphur can be easily removed by sedimentation. During biodegradation, the incomplete oxidation of H_2S is generally reflected by high values of SO_3^{2-} and S^{2-}. The accumulation of elemental sulphur or ammonium sulphate have also been observed in biofilters, packed with wood chips and granular activated carbon, treating H_2S and NH_3 as single compounds [26]. Such periodic accumulation led to a rapid decrease in the performance of those systems, from 99% to 75% and 30%, respectively. Elias et al. [27], showed that at a loading rate of 45 g H_2S m $^{-3}$ h $^{-1}$, the conversion products in biofilters were mainly sulphur (82%), followed by sulphates and thiosulphates (<18%). Buisman et al. [28] reported that, at sulphide concentrations below 20 mg L $^{-1}$, the oxygen concentration should be kept sufficiently low, below 1 mg L $^{-1}$, to limit sulphur oxidation to sulphate. The

accumulation of sulphur in the packing material of a BTF, as well as in the re-circulation liquid has shown to decrease the removal efficiency of H_2S, additionally causing operational problems such as blockage of pores and channeling [15]. However, in this study, as the recirculation liquid was changed once every 4 d or, when the pH dropped to values below 2.7, it was presumed that consistent accumulation of sulphur and other metabolic end - products was minimized, thereby reducing some major operational problems.

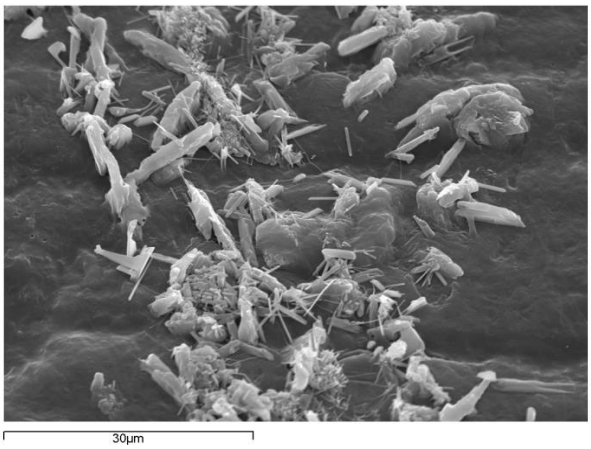
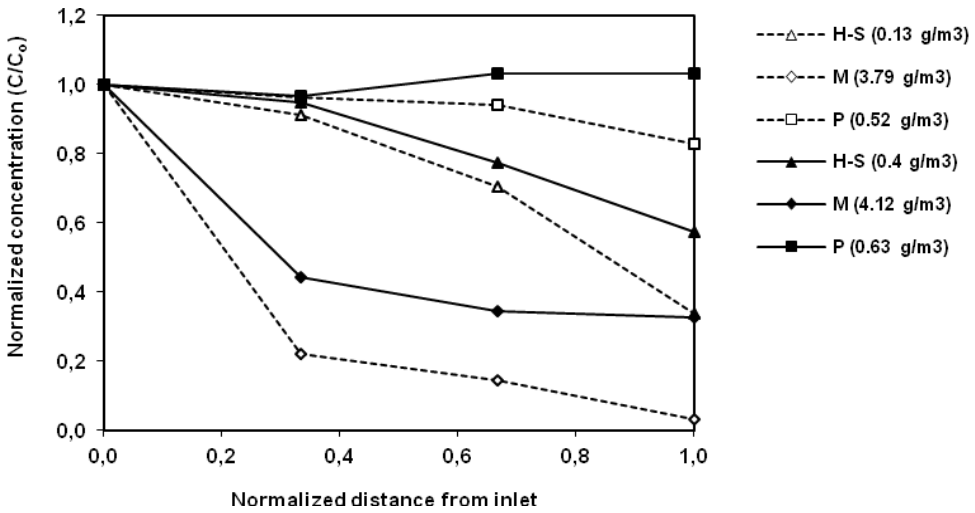


Figure 2.2: SEM image showing the accumulation of elemental sulphur crystals on the pall rings

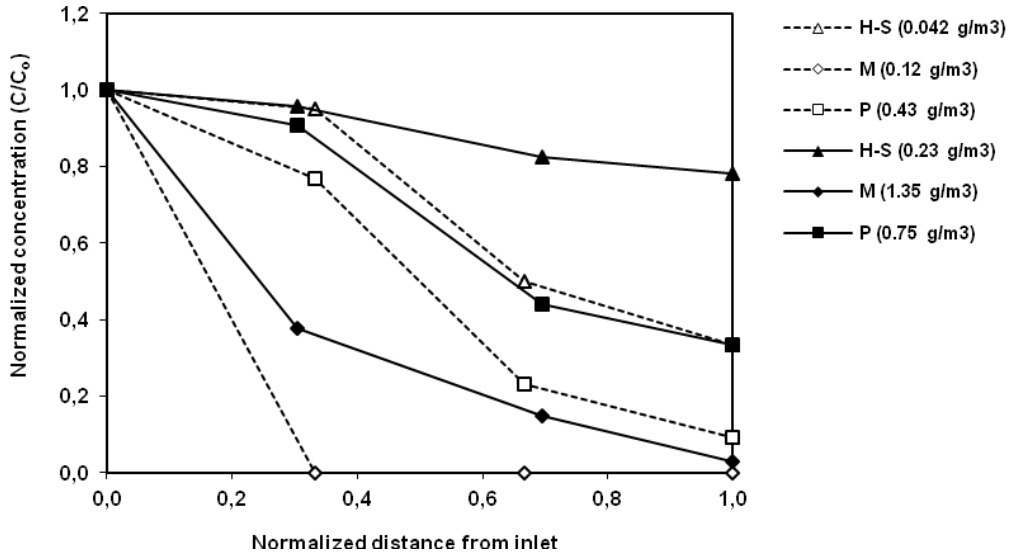
2.3.4 Substrate stratification along the bed height of the BTF and BF

In order to understand the dynamics of pollutant removal within the BTF and BF, their concentration profiles were measured at different heights in the column. Figure 2.3 a and b shows the normalized concentration profiles of H_2S, methanol and α - pinene along the length of the BTF and BF, measured on the 57^{th} and 126^{th} d of operation, when gas flow rates were 0.24 and 1 $m^3 h^{-1}$ respectively (EBRT: in BTF - 83.4, 10 s ; in BF - 146.7, 17.6 s). From Figure 2.3 a, it is evident that for different flow rates and at methanol concentrations of 3.70 and 4.12 g m^{-3}, the first one - third section of the filter bed (BTF) removed most of the alcohol (nearly 78% and 56%, respectively). On the

other hand, H_2S was predominantly removed linearly over the next two - third section of the filter bed, suggesting that methanol was biodegraded before H_2S. The first one - third section of the filter bed was only able to remove <10% H_2S, while the second and third section removed more than 50% of H_2S under the tested condition.



(a)



(b)

Figure 2.3: Normalized concentration profile along bioreactor bed height at different flow rates, (a) BTF and (b) BF

[- - - dotted line: 0.24 $m^3 h^{-1}$; ── dashed line: 1 $m^3 h^{-1}$; H-S: Hydrogen sulphide, M: Methanol and P: α – pinene]

As expected, removal of α - pinene did not occur in the BTF. Therefore, it could be envisaged that, the acid - tolerant, heterotrophic, yeast *Candida boidinii* colonized predominantly in the inlet section of the filter bed, while the autotrophic H_2S degraders prevailed in the later two sections of the column. An obvious explanation for this is that the fast growing heterotrophic methanol - degrading culture overgrows the slower H_2S - degrading organisms, at neutral to slightly acidic - pH, close to the inlet of the BTF. Conversely, a slow pH decline takes place in the lower part of the reactor as a result of H_2S removal. The pH of the leachate reaches a minimum value of 2.7 at the outlet of the BTF, which becomes inhibitory for the methanol - degraders overgrown by the H_2S - degraders in the bottom section of the reactor. A similar behaviour was observed in another study on the removal of H_2S and methanol in a BTF. In that study, more than 75% of methanol was degraded in the first one - third section of the column, while H_2S, at low concentrations, was removed at a constant rate over the bed height [16].

For the 2nd stage BF, expected to remove α - pinene linearly over the bed height by *Ophiostoma sp*., clear stratification in terms of methanol and α - pinene removal was noticed (Figure 2.3 b). At gas flow rates of 0.24 and 1 $m^3 h^{-1}$, corresponding to EBRTs of 73.2 and 17.6 s in the BF, methanol was removed in the first one - third section of the column, while the other sections predominantly removed α - pinene. When low concentrations of methanol (0.12 g m^{-3}) entered the BF, nearly 100% was removed in the first - section of the filter bed, while more than 60% methanol was also removed in the first - section when methanol concentrations were high (1.35 g m^{-3}). The other two sections contributed to more than 80% of the α - pinene removed in the BF, irrespective of their concentrations in gas phase (0.43 - 0.75 g m^{-3}). At low concentrations (0.042 g m^{-3}), nearly 60% of the non - treated H_2S entering into the BF from the 1st stage BTF was removed in the second and third section of the column, suggesting the presence of

H_2S degraders that would have developed in the BF. Presumably, air from BTF carrying methanol - and H_2S - degraders, reached the inlet of the 2nd stage BF. The fast, heterotrophic, methanol - degraders colonized the inlet section of that reactor, while H_2S - degraders colonized deeper sections of the system.

Biomass concentration, measured as dry biomass weight per g of perlite is shown in Figure 2.4. During the start - up step, biomass concentration was initially low (0.9 g g^{-1} perlite) and this value then gradually increased up to a maximum of 1.6 g g^{-1} perlite over a period of 102 d. However, a minor increase in these values was noticed when the EBRT was decreased beyond 48.8 s after 102 d, where the pollutant load to the two - phase bioreactor, both BTF and BF, was linearly increased to observe the maximum EC. The moisture content was also monitored periodically by collecting known amounts of samples, taken 2 d after medium addition, from the two sampling ports (Figure 2.5). It was found that, the moisture levels across the biofilter height varied somewhat depending on the gas flow rate, but remained within an optimal moisture range, i.e., 53 - 64%, for biofilters [10]. The lowest moisture content (MC) was found at the highest gas flow rate of 1 m^3 h^{-1}, while the highest MC was attained at a gas flow rate of 0.12 m^3 h^{-1}.

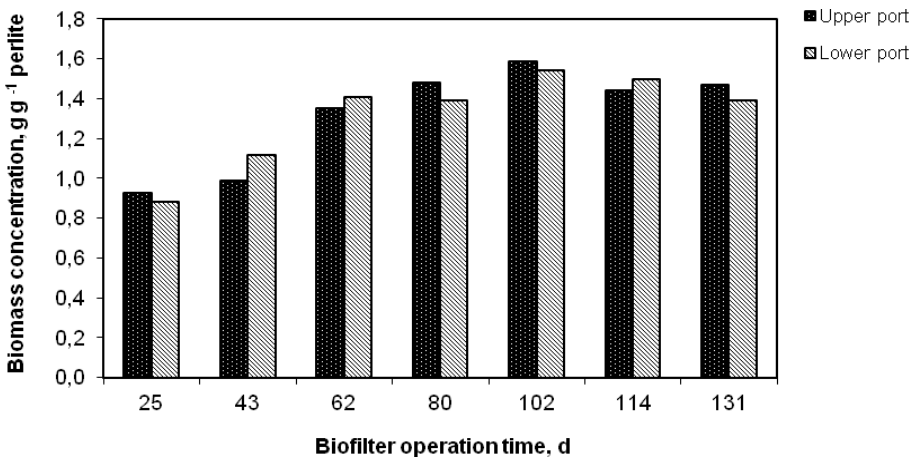


Figure 2.4: Variation of biomass concentration in the second phase BF

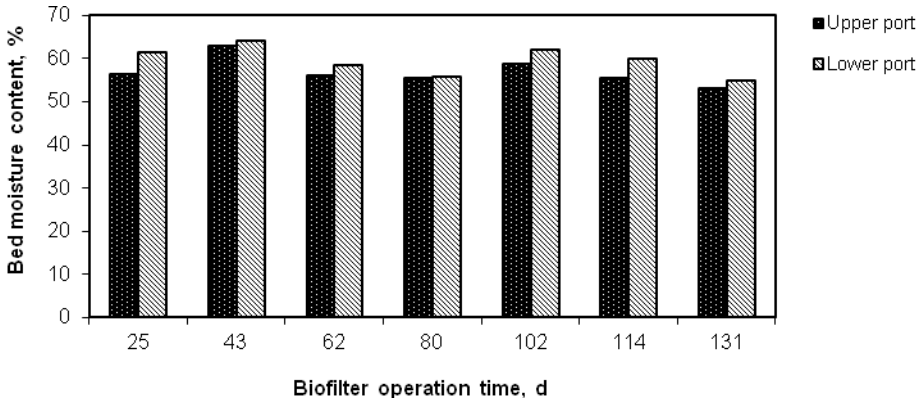


Figure 2.5: Variation of bed moisture content in the second phase BF

2.3.5 Effect of the liquid trickling rate

In order to understand the effect of the liquid trickling rate on the removal of H_2S, methanol and α - pinene in the BTF and BF, experiments were carried out at constant gas flow rate (0.5 $m^3 h^{-1}$) corresponding to EBRTs of 20 s in the BTF and 35.2 s in the BF, respectively. The liquid trickling rate or the liquid recirculation rate was varied in 4 steps at equal intervals of 25 mL min^{-1}, from 50 mL min^{-1} to 150 mL min^{-1}, while the corresponding loading rates to the BTF ranged from 28 - 48 g H_2S $m^3 h^{-1}$, 308 - 489 g $_{methanol}$ $m^{-3} h^{-1}$ and 121 - 247 g $_{\alpha\text{ - pinene}}$ $m^{-3} h^{-1}$. At each of the aforementioned trickling rates, experiments were carried out for 4 - 5 d. The nutrient medium was changed at the end of every step - change in the liquid trickling rate to remove the acidic metabolites formed (pH ~ 2.7) and start each experiment under the same conditions. Only a few data have been published in the literature on the influence of that parameter [24], with sometimes different conclusions, showing the importance of aspects as the type of pollutant or the range of liquid flow rate. The results from this study are shown in Figure 2.6 a - c.

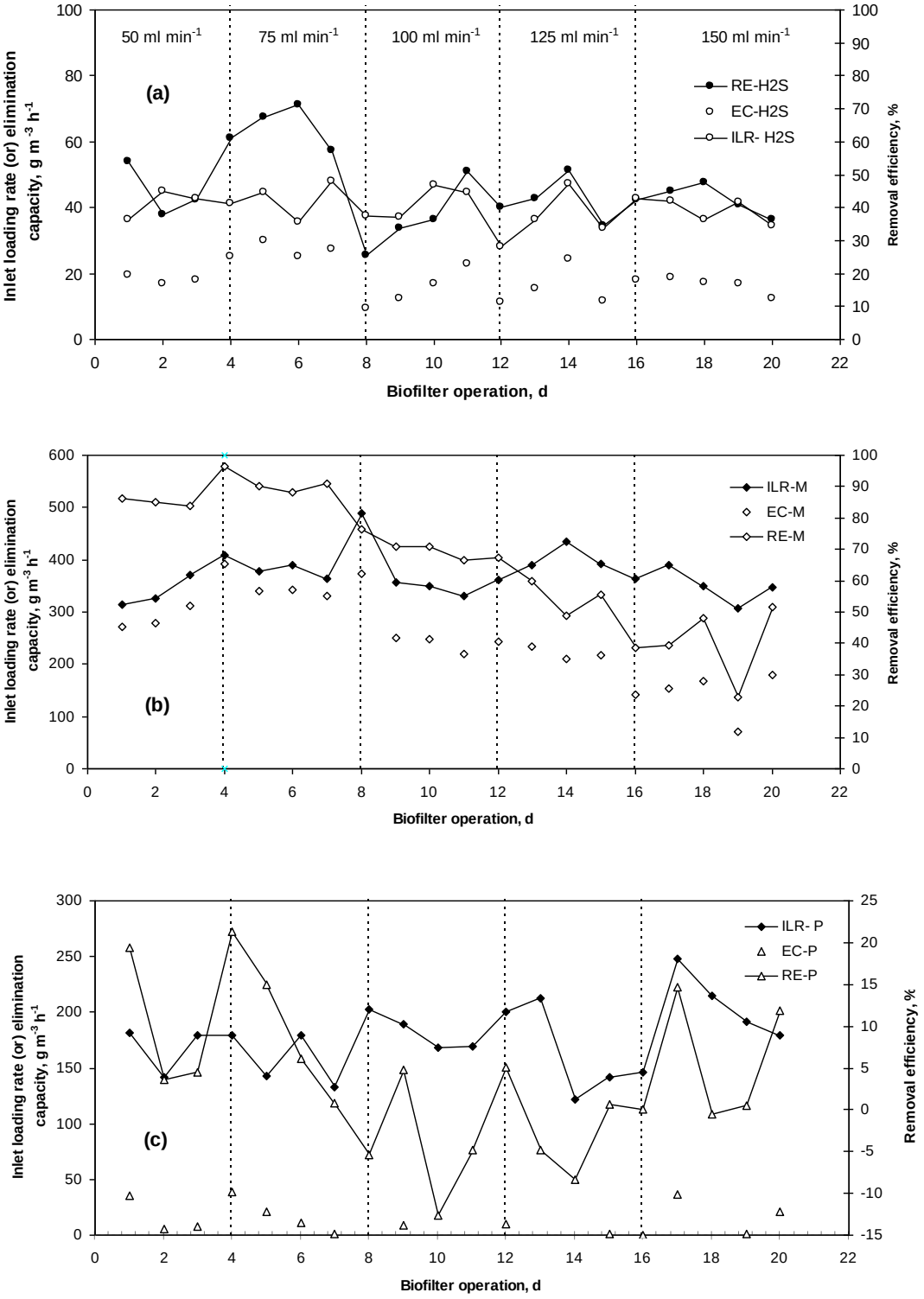


Figure 2.6: Effect of liquid trickling rate on the removal efficiency of (a) hydrogen sulphide (b) methanol and (c) α – pinene in BTF

In the BTF, at a liquid trickling rate of 50 mL min^{-1}, and for an ILR up to 40 g H_2S m^{-3} h^{-1}, the removal of H_2S was about 40%. However, though this value of RE seemed to increase slightly at a higher liquid trickling rate of 75 mL min^{-1}, it can be considered that it actually remained almost constant, considering the somewhat fluctuating behaviour of the inlet load (36 - 51% removal). On the other hand, stepwise increase in the liquid trickling rate from 50 - 150 mL min^{-1} showed a clear decreasing trend in the removal profile for methanol. Initially, even at methanol loading rates greater than 350 g m^{-3} h^{-1}, high RE (> 95%) were noticed at 75 mL min^{-1}, nevertheless, at ILR of 407 g m^{-3} h^{-1} and at a liquid trickling rate of 150 mL min^{-1}, the removal efficiency dropped significantly, to 22%. The influence of the liquid trickling rate on the BTF performance has been reported in the literature. Liquid flow rates have shown to have higher impact on the removal of the pollutant at higher inlet loads, compared to lower ones, such as for H_2S observed in this study [24]. At near constant loads, the high removal of methanol at 75 mL min^{-1} and the subsequent decrease in removal at high liquid trickling rates, suggests that high liquid trickling rates and moderate pollutant loading rates may not favour better removal of gaseous mixtures of H_2S and methanol. Under operational conditions such as batch recirculation modes with continuous recycle of medium, although liquid residence time per - pass decreased with increase in liquid trickling rate, the number of passes increased [29]. Hence, during all the 20 d of operation in this study, irrespective of the liquid flow, the overall liquid residence time inside the BTF remained the same over the duration of the experiment. Changes in liquid trickling rate did not appear to have any effect on the removal of α - pinene in the 1^{st} stage BTF. Under all the tested conditions, α - pinene removal was less, and in some instance even slightly negative due to improper residence times of that pollutant in the BTF, and this can be attributed to the low solubility of α - pinene in the liquid phase,

that eventually shows that mass transfer resistance was present in the trickling liquid (Figure 2.6 c). Another explanation for observing negative RE profile for α - pinene is given in a later section. Some possible explanation for reduction in methanol removal, a hydrophilic VOC, at high liquid trickling rates and high pollutant loads are given herein; (i) an increase in the thickness of the liquid phase at higher liquid flow rate causes mass transfer limitation, due to high methanol concentrations, between gas - phase and the liquid / biofilm phase [15], (ii) high liquid flow rates could cause liquid channeling in the centre region of the column, which in - turn affects the liquid - gas - biomass contact, (iii) the high gas velocity (0.5 $m^{3} h^{-1}$) used in this study could have affected methanol removal, in addition to the liquid trickling rate, as it has been reported that, at high gas flow rates, the external mass transfer resistance becomes negligible, but transfer from the liquid to the biofilm becomes limiting [30], and (iv) changes in flow pattern at high liquid trickling rates, as the liquid trickling rate increases, the rivulets will grow in size and an enlargement of the existing channels or the formation of additional channel would occur. However, in order to ascertain the exact reason and to find a proper trickling rate that ensures higher removal at high pollutant loads, more studies on the hydrodynamic aspects that uses critical factors such as property of support matrix, amount of biomass present, bed void fraction, pressure drop, liquid hold - up, liquid distribution, partial wetting and stagnant water, would be needed. In the BF, for ILR up to 88 g $m^{-3} h^{-1}$, > 95% of α - pinene was removed, irrespective of the loading rate of H_2S and methanol, reaching maximum EC as high as 83.4 g $m^{-3} h^{-1}$. Methanol loading rate to the BF varied between 69 - 126 g $m^{-3} h^{-1}$ depending on its removal in the 1st stage BTF, and the BF was able to maintain high RE for this compound (83 - 86%).

2.3.6 Effect of high concentrations of one pollutant on the removal of mixtures

In general, multi - component gas - phase mixtures having different biodegradation rates and characteristics tend to show interactive effects, i.e. the presence of one pollutant can increase or decrease the removal of the other pollutant in biological systems. In order to understand the synergistic and antagonistic interactions during the removal of H_2S, methanol and α - pinene, experiments were conducted for 23 d, by varying the concentration of one pollutant from low to high values at a constant gas flow rate of 0.24 $m^3 h^{-1}$, EBRT - 41.7 s in the BTF and 73.2 s in the BF, and by maintaining the concentrations of the other pollutants constant so as to achieve near 100% removal (Figure 2.7 and 2.8). The reduction in removal performance of the individual pollutant, due to the presence of other pollutant was then calculated from the original 100% removal achieved at constant, yet low loading rates. On days 1 - 9, in the BTF, the concentration of H_2S was increased from 0.05 - 0.23 g m^{-3} (i.e., loading rate of 4.8 - 20.4 g H_2S $m^{-3} h^{-1}$), while the loading of methanol and α - pinene were kept constant at 50 g $m^{-3} h^{-1}$ and 12 g $m^{-3} h^{-1}$, respectively. The removal of methanol in the BTF was >98%, and the RE of H_2S dropped from 100% to 71%, while as usual, α - pinene removal in the BTF was not significant (Figure 2.7 a - b). In the next step (days 10 - 18), an increase in α - pinene concentrations from 0.11 to 0.73 g m^{-3} (i.e., loading rate of 9.7 to 63.3 g $m^{-3} h^{-1}$) rapidly decreased the removal of H_2S by 23% and slowly decreased methanol removal by 10% in the BTF, when their loading rates were 8 and 42 g $m^{-3} h^{-1}$. However, due to an increase in the concentration of α - pinene in the 1st stage BTF, the α - pinene load to the 2nd stage BF also increased from 3 to 35 g $m^{-3} h^{-1}$, and its removal decreased by about 15% in that reactor (Figure 2.8). In the BF, H_2S and methanol ECs were 1.2 and 3.8 g $m^{-3} h^{-1}$ respectively, and these values were low, as most of the H_2S and methanol were removed in the 1st stage BTF. On days 19 - 23,

when methanol concentration was increased stepwise from 1.4 to 9 g m^{-3}, corresponding to loading rates as high as 775 g m^{-3} h^{-1} to the BTF, its removal in the BTF decreased from 95% to 71%, the removal of H_2S decreased by 25% and α - pinene removal was non - altered. A maximum EC of 554 g m^{-3} h^{-1} was noticed for methanol in the BTF. However, in the BF, the remaining non - treated methanol caused an increase in the inlet load from 3 - 125 g methanol m^{-3} h^{-1}, where the RE of methanol also decreased from 88 to 78%. An increase in the concentration of methanol in the 2nd stage BF also caused an average decrease in the removal of α - pinene of in that reactor 14% (Figure 2.8). In other words, the *Ophiostoma* sp. had preferential utilization property for methanol biodegradation in some zones of the biofilter. In a compost biofilter, fed with equal proportions of gas - phase methanol and ethanol, the presence of ethanol decreased methanol removal by 32%, while ethanol removal was also reduced by 30% [31]. This phenomenon, mutual inhibition, was later explained by the presence of two different groups of microorganisms, namely methanol utilizers and ethanol utilizers, while the methanol utilizers showed the ability to switch to ethanol utilization in the presence of ethanol, the ethanol utilizers appeared to be inhibited by the presence of methanol.

Overall, increasing the H_2S concentrations from low to high values, did not affect the removal of VOC in both the reactor configurations, however increasing the concentration of either methanol or α - pinene reduced the removal of H_2S by almost 25% in the BTF. Increasing the concentration of methanol in the BTF, indirectly also had an effect on α - pinene and methanol removal in the 2nd stage BF. An increase in the α - pinene concentrations from low to high values, did not significantly decrease methanol removal (10%) in the 1st and 2nd stage bioreactors, however H_2S removal was affected strongly in the 1st stage BTF, and α - pinene removal decreased slightly in the

2nd stage BF, depending on the loading rate. In a two - stage biofilter, BTF followed by BF, for the treatment of a gaseous mixture of formaldehyde and methanol, RE as high as 88% and 72% in the 1st stage BTF followed by >95% removal of both the compounds in the 2nd stage BF was observed.[14] However, no cross - inhibition effects were reported in that work. In a biofilter packed with inert glass beads, the removal of methanol in the presence and absence of H_2S was found to be more stable than H_2S biofiltration alone, reaching EC as high as 480 g m^{-3} h^{-1} [21]. No mutual cross - inhibition occurred during biofiltration of H_2S and toluene in two BTFs operated in parallel at pH 7 or 4.5 was noticed [20]. This was attributed to the possible presence of two different types of microbes within the BTF, viz., autotrophic microorganisms for H_2S degradation and heterotrophic microorganisms for toluene degradation. Apparently, these behaviours are clearly different from the results observed in our study and some of the other literature. During the co - treatment of methanol and H_2S, the presence of methanol significantly affected the removal of H_2S, while the removal of methanol was not affected by the presence of H_2S, despite low - pH values.[16] Greater than 90% removal of H_2S in a two - stage BF, with a maximum EC of 1.46 g m^{-3} h^{-1}, in the first - stage acid - gas biofilter and moderate removal (73%) in the second - stage BF, has been reported during the treatment of H_2S and a wide range of VOCs present in the waste gas [32]. The low pH might have caused poor VOC removal in some of the studies using mixtures of H_2S and VOC. Jeong et al. [33] studied the removal of ethanol, acetaldehyde and toluene in a single - and two - stage biofilters and envisaged that the two - stage BF indeed improved the performance with no cross - inhibition patterns occurring amongst pollutants. Mohseni and Allen [34] studied the removal pattern of gas - phase methanol and α - pinene in a biofilter packed with a mixture of wood - chips and spent mushroom compost. The presence of pinene did not affect

methanol removal, which indicated that α - pinene did not interfere with the activity of the methanol degrading microorganisms, however maximum EC of α - pinene depended highly on the concentration of the incoming vapour and a value of 45 g α - pinene m^{-3} h^{-1} was observed when methanol was not present in the air stream. Jianwei et al. [35] attributed multi - substrate inhibition or cross - substrate interactions effects to low ECs of H_2S, ethyl mercaptans, ammonia, styrene and butyric acid (1.7 - 3.1 g m^{-3} h^{-1}) in low and neutral - pH biofilters.

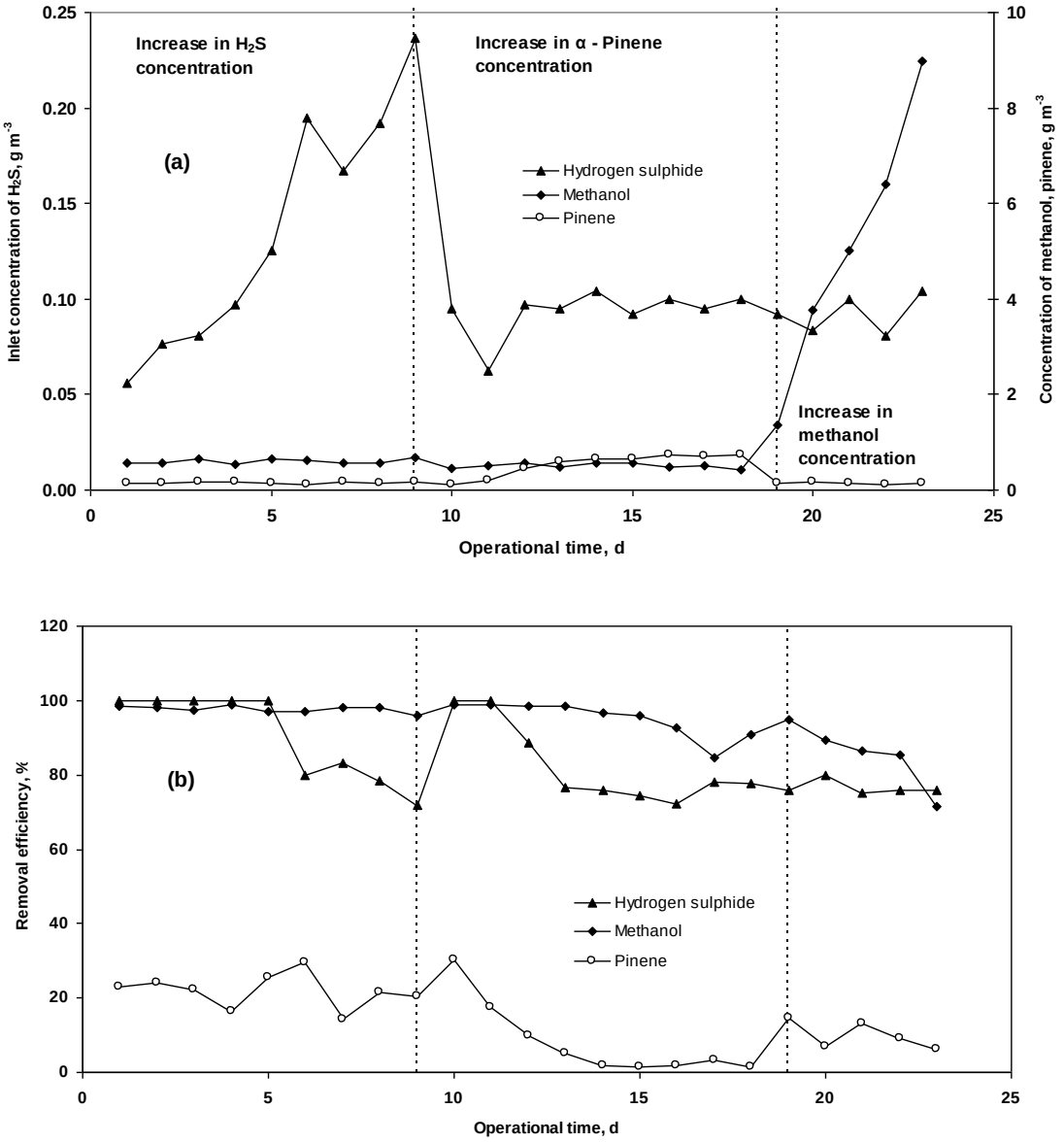


Figure 2.7: Effect of changing pollutant concentration on the removal efficiency of hydrogen sulphide, methanol and α – pinene in BTF, (a) concentration profile, (b) removal efficiency

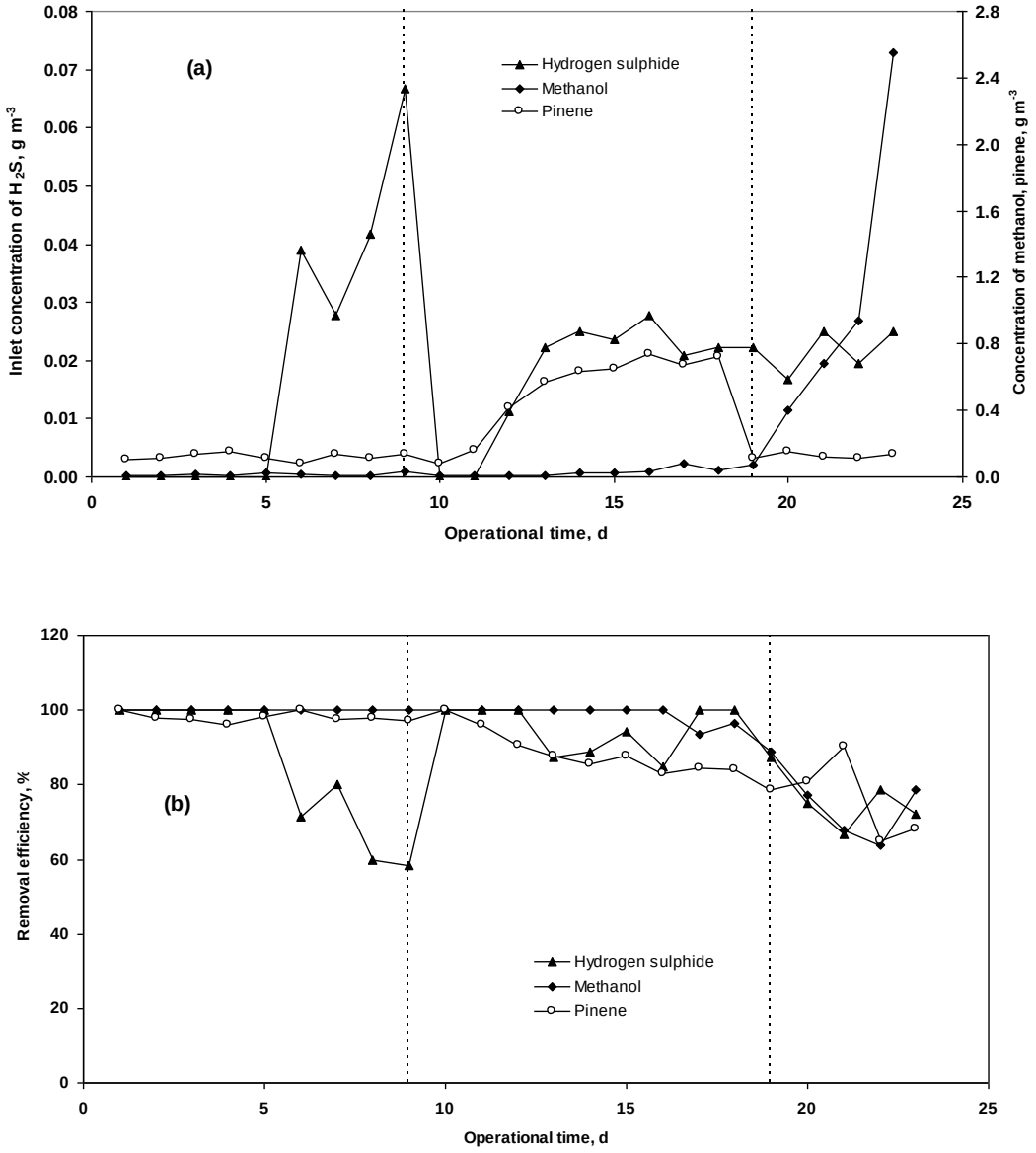


Figure 2.8: Effect of changing pollutant concentration on the removal efficiency of hydrogen sulphide, methanol and α – pinene in BF, (a) concentration profile, (b) removal efficiency

2.3.7 Effect of transient loads on bioreactor performance

The effect of transient - state conditions, such as shock loads, imparted on biofilters in practical situations was stimulated in two steps, viz., as long - term shock loads (66 h - experiment, low to medium loads) and short - term shock loads (12 h - experiment, low to high loads), by increasing the concentration of all three compounds, H_2S, methanol and α - pinene, during the applied shocks.

2.3.7.1 Long - term shock loads

In this study, the gas flow rate was set to the maximum, 1 $m^3 h^{-1}$, and experiments were carried out for 66 h, that includes a shock load period of 52 h for the BTF and BF. Initially for 8 h, the loading rates of H_2S, methanol and α - pinene were maintained low at 10, 60 and 18 g $m^{-3} h^{-1}$, respectively. The bioreactors were subjected to shock loads from the 8th h and the concentrations of pollutants were measured after 12 h, allowing the BTF and BF to respond to the shock load. Figure 2.9 shows the shock loading and pollutant removal pattern observed in the BTF. As can be noticed, the removals of H_2S decreased from 100% to as low as 50%, at a shock load of 38 g $m^{-3} h^{-1}$, while methanol removal decreased slightly by 30%, when the load was 250 g $m^{-3} h^{-1}$. However no removal of α - pinene was noticed in the BTF. Barona et al. [36] investigated the response of a biofilter to abrupt changes in flow rate and concentration and showed that an increase in concentration of H_2S from low to high levels (0.59 g m^{-3}) reduced the RE significantly. When the concentration was decreased to 0.07 g m^{-3} the biofilter performance fully recovered to 100% efficiency. The fraction of the non - treated H_2S and methanol, as well as the incoming pinene vapours induced a shock load to the 2nd stage BF, where the EBRT of the pollutants were 17.6 s (Figure 2.10). Though the ILR of H_2S and methanol were low in the BF (< 9.9 and < 41.9 g $m^{-3} h^{-1}$), the α - pinene loads increased from 11 to 70 g $m^{-3} h^{-1}$. It was observed that the removal of α -

pinene in the BF was not affected much by this medium shock load, dropping the RE by just 10%.

2.3.7.2 Short - term shock loads

During this experimental step, the BTF and BF were submitted to short - term high shock loads for 8 h. The concentrations of individual pollutants were increased from low values to very high values during the shock loading step, that corresponds to increases from 8.5 to 106 g H_2S m^{-3} h^{-1}, 95 to 1220 g methanol m^{-3} h^{-1} and 30 to 305 g α - pinene m^{-3} h^{-1}, respectively. Earlier, the BTF and BF were adjusted to receive low loads of H_2S, methanol and α - pinene overnight, and measurements were taken the next day for 2 h initially at these low loads, before subjecting both the bioreactors to the shock loads as shown in Figures 2.11 and 2.12. It was observed that the high shock loads instantaneously and severely affected the removal of both H_2S and methanol in the BTF, though nearly 100% removal was noticed for all the pollutants before the shock load. From the 3rd h, H_2S removal was just 31%, when the H_2S load was 106 g m^{-3} h^{-1}, while at a loading rate of 1220 g methanol m^{-3} h^{-1}, methanol removal decreased by 50% initially and occasionally reached as low as 33%. On the other hand, as observed during the previous shock loading study (Figure 2.9), α - pinene was not removed in the 1st stage BTF during the shock load, irrespective of the applied load, whether medium or high. Instead, just after the shock load, when the concentrations were brought down to previously applied low values, α - pinene concentrations were even somewhat higher, by a margin of 0.03 to 0.12 g m^{-3}, in the outlet of the 1st stage BTF than the inlet section, giving rise to short, transient, negative removal profiles as shown in Figures 2.10 and 2.12, a phenomenon that was also noticed earlier (Figure 2.6 c).

It has been reported that organic pollutants tend to adsorb to the surface of the solid surfaces, packing material and biomass related compounds, and also partially absorb into the liquid film present over the packing material. In such cases, the pollutant would be retained for a somewhat longer period in the BTF than the mean residence time of the pollutant. Similarly, Mendoza et al. [37] observed through tracer studies that, in a biofilter operated at a calculated EBRT of 56 s, the mean residence time of styrene were 185 s during start - up, while during the second year of continuous biofilter operation, that value increased 5.35 fold. The lower volatility and higher density of styrene, as well as heavy biomass growth during the experimental period was considered as the main reason for such a major change in the residence time of the pollutant.

However, as a result of this high shock load, and the lower removal of both H_2S and methanol in the BTF, the 2nd stage BF received loads of 42.4, 414 and 176 g m^{-3} h^{-1} of H_2S, methanol and α - pinene, respectively (Figure 2.12). H_2S and methanol removal efficiencies were lower, about 8.5% and 25%, while high removals (75%) of α - pinene were maintained in the BTF giving rise to a maximum EC of 130.1 g m^{-3} h^{-1}. Besides, H_2S and methanol EC in the BF were 8.6 and 101.7 g m^{-3} h^{-1}, respectively. The consistent high performance of the 2nd stage BF during shock loads is not surprising, as results from our previous study have shown the ability of the *Ophiostoma sp.* to withstand periodic shock loads of gas - phase pinene, for more than one month of transient - state operations, where EC and RE were found to be 60 g m^{-3} h^{-1} and >90% respectively.[2] Moreover, the presence of filamentous fungi as *Ophiostoma stenoceras* in the BF offers some advantages for the treatment of hydrophobic compounds such as α - pinene. Fungi develop hyphea which provide a large surface area in contact with the gas phase so that a direct efficient mass transfer from the gas phase to the biofilm phase is

possible. This allows a faster uptake of hydrophobic compounds (α - pinene), than in flat aqueous bacterial biofilms [10].

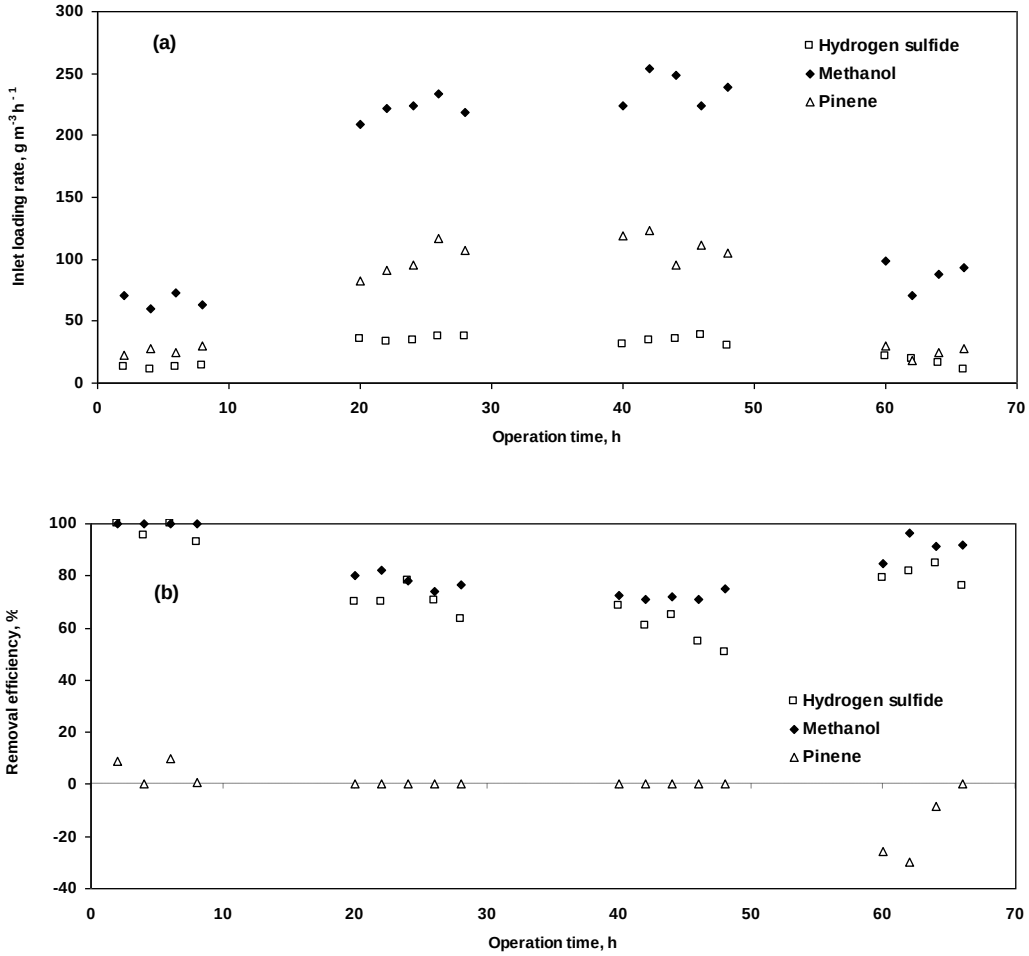


Figure 2.9: Effect of long – term, low to medium shock loads on the first – stage BTF (a) inlet loading rate and (b) removal efficiency

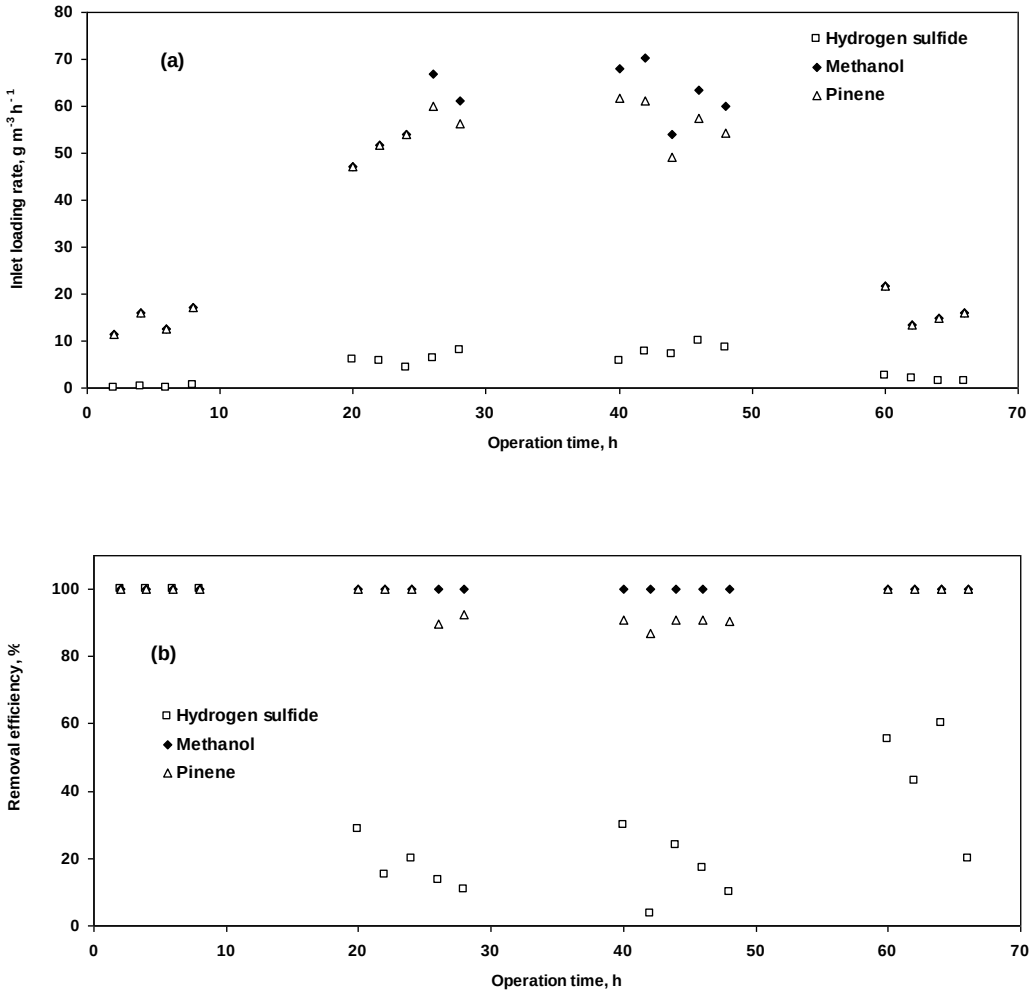


Figure 2.10: Effect of long – term, low to medium shock loads on the second – stage BF (a) inlet loading rate and (b) removal efficiency

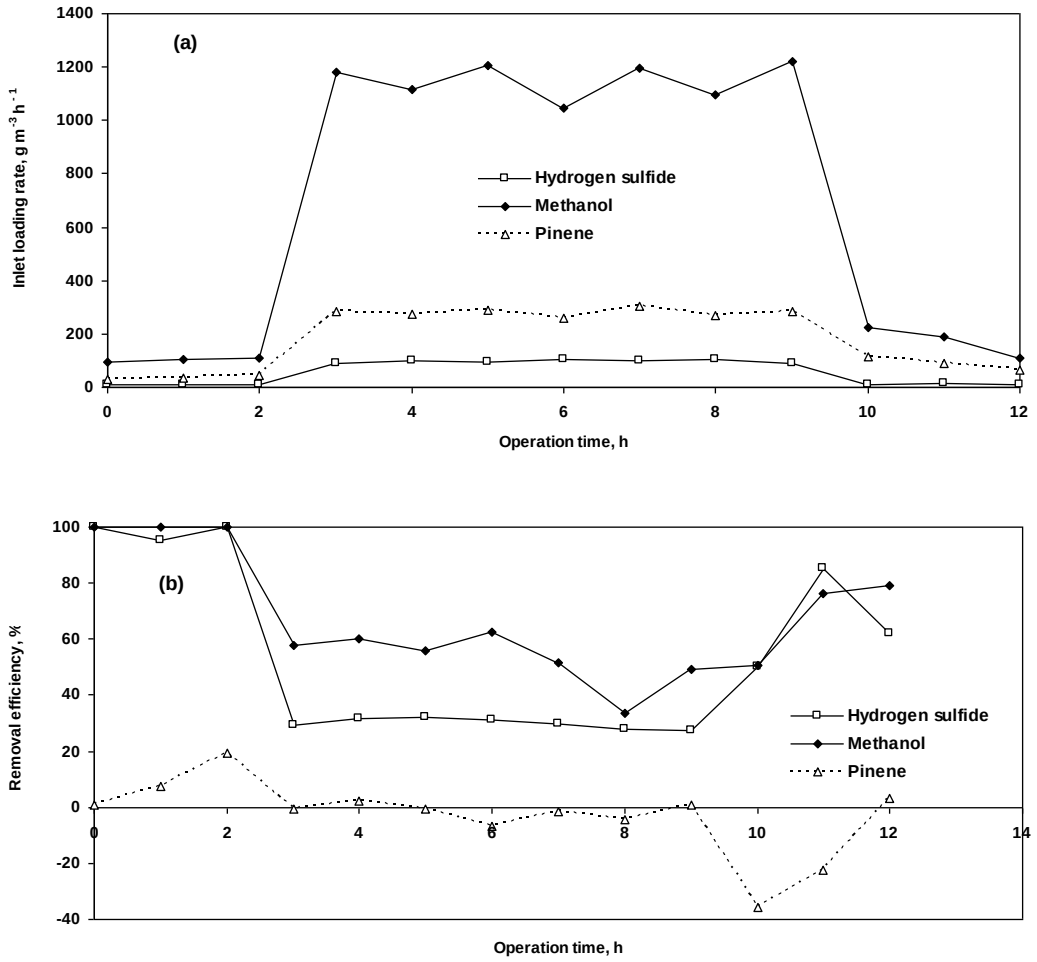


Figure 2.11: Effect of short – term, low to high shock loads on the first – stage BF (a) inlet loading rate and (b) removal efficiency

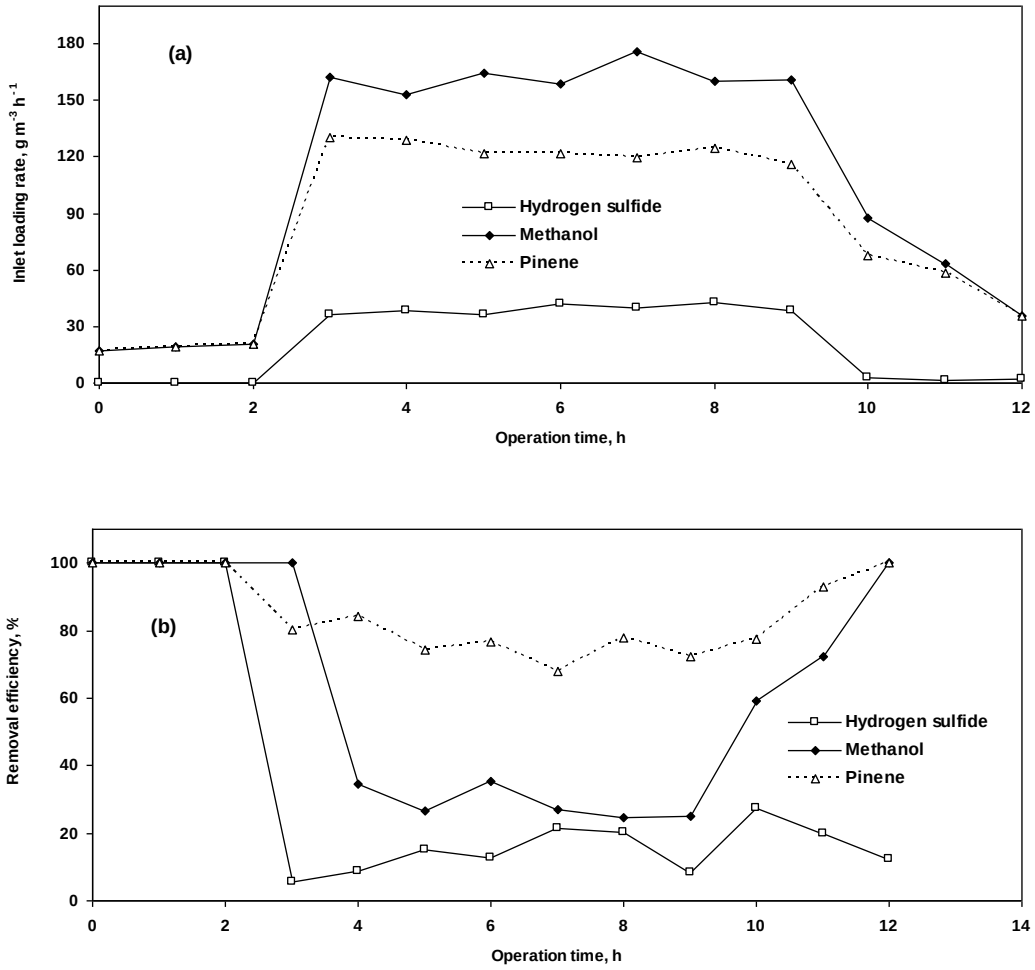


Figure 2.12: Effect of short – term, low to high shock loads on the second – stage BF (a) inlet loading rate and (b) removal efficiency

2.4 CONCLUSIONS

Biological treatment of a complex gas - phase mixture of hydrogen sulphide, methanol and α - pinene has shown promising results in a two - stage bioreactor system, composed of a first - stage BTF inoculated with autotrophic H_2S degraders and an acid - tolerant yeast (*Candida boidinii*) and a second - stage BF inoculated with the fungus *Ophiostoma stenoceras*, at different inlet loading rates and process conditions.

- The first - stage BTF showed a maximum elimination capacities of 45 g m^{-3} h^{-1} for hydrogen sulphide and 894 g m^{-3} h^{-1} for methanol. In the second - stage BF, when the gas flow rate was increased two - fold, the EC_{max} due to α - pinene

removal increased from 100 to 138 g m^{-3} h^{-1} at an ILR of 127 and 161 g m^{-3} h^{-1}.

- Stratification in terms of biodegradation of pollutants along the bed height was observed in both reactor configurations. The first one - third section of the BTF was able to remove nearly 78% of methanol, while H_2S was removed linearly over the next two - sections of the filter bed.

- The effect of the liquid recirculation rate on pollutant removal characteristics in the BTF was understood by changing the liquid trickling rate from 50 to 150 mL min^{-1}. The results showed that, due to mass transfer limitations, high liquid trickling rates and moderately high pollutant loading rates might not favour better, simultaneous removal of gaseous mixture of H_2S, methanol and α - pinene.

- Increasing the concentration of the hydrophilic VOC, methanol, or the hydrophobic VOC, α - pinene to the BTF, lead to decline in the RE of H_2S by about 25%, however, a stepwise increase in H_2S concentration did not appear to affect the removal of VOC in both the BTF and BF. Being an easily biodegradable compound, methanol was also removed in the second - stage BF, which could have been possible due to the preferential utilization of methanol as carbon and energy source by the original *Ophiostoma* sp. in the BF.

- The commonly reported practical problems in continuous bioreactor operation such as prevalence of unexpected shock loads, either medium and / or high loads, were simulated in the present study. H_2S removal was affected strongly in the BTF, while methanol removals were not affected much, when the applied shock load was less than their critical load. During high shock loads, H_2S and methanol removal was less in the BTF, while high removals (75%) of α - pinene was

maintained with an EC of 130.1 g m^{-3} h^{-1}. This shows that the two - phase bioreactor system was sensitive to changes in loading rates.

- The results from this study provide sufficient information on the antagonistic and synergistic effects occurring during the biological treatment of a complex gaseous mixture containing organic, inorganic, hydrophilic and hydrophobic pollutants.

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Chapter 3

Modeling the removal of volatile pollutants under transient conditions in a two-stage bioreactor using artificial neural networks

The modified version of this chapter has been submitted for publication:

López, M.E., Rene, E.R., Veiga, M.C., Kennes, C. (2015) Modeling the removal of volatile pollutants under transient conditions in a two-stage bioreactor using artificial neural networks. Journal of Hazardous Materials (*Submitted*).

ABSTRACT

A two-stage biological waste-gas treatment system consisting of a first-stage biotrickling filter (BTF) and second-stage biofilter (BF) was tested for the removal of gas-phase methanol, α-pinene and hydrogen sulphide mixture. The bioreactors were tested with two types of shock loads, *i.e.*, long-term (66h) low to medium concentration loads, and short-term (12h) low to high concentration loads. Methanol and hydrogen sulphide were removed in the BTF, reaching maximum elimination capacities (EC_{max}) of 684, and 33.1 $gm^{-3}h^{-1}$, respectively. α-pinene was removed better in the second-stage BF with an EC_{max} of 130.1 $gm^{-1}h^{-1}$. Their performances were modelled using two multi-layer perceptrons (MLPs) that employed the error backpropagation with momentum algorithm, in order to predict the removal efficiencies (RE, %) of methanol (RE_M), α-pinene (RE_P) and hydrogen sulphide (RE_{HS}), respectively. It was observed that, a MLP with the topology 3-4-2 was able to predict RE_M and RE_{HS} in the BTF, while a topology of 3-3-1 was able to approximate RE_P in the BF. The results show that artificial neural network (ANN) based models can effectively be used to model the transient-state performance of bioprocesses treating gas-phase pollutants.

KEYWORDS*:* Artificial neural networks, biofilter, biotrickling filter, two-stage bioreactor, transient-state performance

3.1 INTRODUCTION

The deleterious short-term acute and long-term chronic effects of a wide variety of air pollutants have been well documented in several reports, and major air pollution episodes have shown their effect on human health and environment. Point source emissions from petrochemical and refinery complexes, incinerators, painting works, pulp and paper industry, pharmaceutical industry and electrical power generators, among others, have to be controlled and curtailed in order to improve air quality. Thus, research pertaining to the development of suitable, eco-efficient and cost-effective air pollution control technologies has gained interest. Besides, regulations on controlling air pollutants have been issued worldwide, and this has further compelled process industries to adopt suitable remediation techniques to prevent unwanted air pollutants from entering the environment. For example, according to the Directive on Ambient Air Quality (DAAQ) and Cleaner Air for Europe (Clean Air for Europe-CAFE programme), the total volatile organic compound (VOC) limit was set at 35 g total organic compound m^{-3} gasoline loaded [1].

Although there are different physical, chemical, and biological techniques for air pollution control, the pertinence of applying a particular treatment process depends on the composition and amount of pollutants present in the waste-gas [2]. Biofilters (BF) and biotrickling filters (BTF) can be used in industrial situations as a single-stage or stand-alone system, and are considered to be technically best suited for the removal of relatively low concentrations of pollutants, over a rather wide range of gas-flow rates, *i.e.*, empty bed residence times (EBRT) [3-7]. However, for the (bio)treatment of mixture of pollutants such as methanol, α-pinene and hydrogen sulphide, representative volatile hydrophilic, hydrophobic and inorganic gas-phase pollutants emitted from the pulp and paper industry, a combination of a BTF and a BF (two-stage process) was

recently tested under steady and transient-state conditions [8, 9]. In that study, during steady-state conditions, the first-stage BTF inoculated with hydrogen sulphide utilizing autotrophic bacteria and the yeast *Candida boidinii* was able to handle the prevailing low-pH conditions caused by the conversion of hydrogen sulphide to sulphuric acid and both methanol and hydrogen sulphide were removed effectively with high elimination capacities (EC_{max}= 894.4 and 45.1 $gm^{-1}h^{-1}$). Subsequently, in the second-stage BF inoculated with the fungus *Ophiostoma stenoceras*, α-pinene was removed with an EC_{max} of 138.1 $gm^{-3}h^{-1}$, which is a similar efficiency as reached during the fungal biodegradation of α-pinene as single pollutant in a BF [10].

Although till date there are several experimental studies that have demonstrated the steady-state performance of different waste-gas treatment systems, their dynamic behaviour to sudden variations in operating conditions has received only little attention from researchers [6, 8, 11-14]. From a practical view-point, sudden variations in concentrations and/or gas-flow rates (shock loads) are common to any industrial emission, and by simulating these loading patterns under laboratory conditions, one would easily understand the effectiveness and operational limits of the waste-gas treatment system [15, 16]. During transient operation, if the waste-gas treatment system receives exceedingly high pollutant loads, either the mass transfer capacity or the reaction capacity of the initial sections of the bed are exceeded and pollutants move into the later sections where microbial populations and reaction capacities are low and contaminant breakthrough could easily occur [17]. Jin et al. [18] performed shock load experiments of one month, by subjecting a fungal BF inoculated with *O. stenoceras* to multiple medium and high shock loads of α-pinene. It was observed that the performance of the BF quickly recovered after every 4h shock load, reaching EC values of 60 $gm^{-3}h^{-1}$ with removal efficiency (RE) >90% over the 13h period after the shock

load. According to Wright [17], it is important to characterize transient response and minimize contaminant breakthrough in BTF and BF because of the following reasons: (i) the actual operating conditions should be monitored continuously and linked to the treatment efficiency, (ii) transient operations are inherent to waste-gas characteristics and thus cannot be avoided, and (iii) the microbial activity could be limited (substrate inhibition) in biological treatment systems leading to a drastic reduction in performance when pre-shock conditions are restored.

3.2 ARTIFICIAL NEURAL NETWORKS FOR MODELING TRANSIENT-STATE OPERATIONS

Contaminant transport in fixed-bed waste gas treatment systems such as BTF and BF occurs by the continuous transfer of pollutants from the gas-phase to the biofilm phase, and the following phenomenological steps are involved: absorption, adsorption, diffusion, and biodegradation [19-21]. Most of the conventional mathematical models proposed in the literature were derived to represent steady-state behaviour, and not derived to accommodate transient-state operations [19, 20, 22-24].

Artificial neural networks (ANNs) possess the inherent capability to learn '*by example*' wherein an actual measured set of input and output variables are presented to determine the rules that regularizes the relationship between the variables [24-27]. A recently published ANN modeling study has shown that there is good prospect to model waste gas treatment systems such as a BF, a continuous stirred tank bioreactors and a monolith bioreactor using ANNs, due to its process complexity, dynamic behaviour and persistence of uncertainty due to changing pollutant loads and microbial characteristics [27]. In a typical ANN topology, the neurons in different layers of a multi-layer perceptron (MLP) are interconnected to form a network of nodes mimicking the biological structure of a human brain. The number of neurons in the input layer usually

depends on the number of input variables. The number of neurons in the hidden layer depends on the complexity of the problem presented to the network and the size of inputs, while the number of neurons in the output layer depends on the number of performance monitoring variables chosen for a particular study. The input signals flow through a gain or weight called synaptic weight, whose objective function is analogous to that of the synaptic junction in a biological neuron [26-28]. The weights (W_{ji}) can be positive or negative corresponding to the acceleration or inhibition of the flow of electrical signals in a biological cell. The summing node accumulates all the input weighted signals, adds a bias signal and then passes to the output through the activation function, which is usually non-linear in nature [27-29]. The commonly used activation function $f(x)$ for prediction purposes is the sigmoid transfer function which can be represented as follows;

$$f(x) = \frac{1}{1+e^{-x}} \tag{3.1}$$

Training of neural networks can be performed using the most commonly used error backpropagation with momentum algorithm that uses a gradient descent procedure to minimize the objective function [30]. The goal of this training process is to minimize the sum-squared error in the overall training pattern. The weight update for the t^{th} epoch between nodes i and j can be given by;

$$W_{ij}(t) = W_{ij}(t-1) - \eta \frac{\partial E}{\partial W_{ij}} + \alpha \Delta W_{ij}(t-1) \tag{3.2}$$

Where, $\frac{\partial E}{\partial W_{ij}}$ is a gradient of error with respect to weight, η is the learning rate, and α is the momentum term.

Although ANNs have found widespread applications in modeling bioremediation [31] and wastewater treatment systems [32-35]; the ANN concept was tested only recently to

model waste-gas treatment systems [7, 27, 36-38]. Elías et al. [37] modeled the performance of a lab-scale BF packed with pig manure and saw dust, handling H_2S vapours. The authors divided the large data set, as training (50%), testing (40%), and validation (10%) sets, respectively, using a combination of cluster analysis and genetic algorithm. The inlet H_2S concentration and unit flow (gas-flow rate/volume, h^{-1}) values tested in the BF were used as inputs to the model, while the RE of the BF was used as the output. The best MLP was chosen after evaluating 10,000 different combinations of MLPs, and it was reported that a 2-2-1 MLP was able to predict the RE well with high correlation coefficients (R^2 = 0.92). Ravi et al. [7] used a MLP to predict the performance of a compost BF handling dichloromethane vapors. The authors performed long-term experiments, at gas-flow rates of 0.024-0.144 m^3h^{-1}, with dichloromethane concentrations varying between 0.1 and 1.1 gm^{-3}. It was reported that the RE profiles were a strong function of the inlet loading rate (ILR), *i.e.*, less removal at high ILRs and vice versa, and an EC_{max} of 20 $gm^{-3}h^{-1}$ was reported. On modeling this data set with ANNs, the authors reported that a 2-4-1 neural architecture was optimum to predict the RE profiles of the BF with high R^2 values (0.9321). Zamir et al. [39] reported the ANN modeling results of a compost BF treating *n*-hexane vapours by varying the operating temperature of the BF between 30 and 45ºC. The BF was inoculated with a non-identified fungal consortium and operated under intermittent loading conditions (10 h aeration d^{-1}). Besides achieving an EC_{max} of 491 $gm^{-3}h^{-1}$, at 35ºC, the authors also formulated a 2-10-1 ANN to predict the RE profiles using ILR and operating temperature as the inputs. Although high R^2 (0.914) was observed during training, the training/generalization pattern of the network was affected when the RE of the BF dropped significantly, from 100% at 35ºC to <50% during its operation at 45ºC.

The main aim of this study was to model and analyze the results of transient-state performance of a previously described two-stage waste-gas treatment system [8, 9], and predict the RE profiles of individual pollutants, *i.e.*, methanol (RE_M), α-pinene (RE_P), and hydrogen sulphide (RE_{HS}), using ANNs. Sensitivity analysis was carried out to envisage the most important parameter affecting the removal of each pollutant in this system, and the interaction effects between pollutants were identified. The practical implications of this modeling work have also been stated.

3.3 MATERIALS AND METHODS

3.3.1 Media composition and microorganisms

The mineral salt medium used in the first-stage BTF had the following composition (in gL^{-1} of de-ionized water); KH_2PO_4: 2, K_2HPO_4: 2, NH_4Cl: 0.4, $MgCl_2 \cdot 6H_2O$: 0.2, and $FeSO_4 \cdot 7H_2O$: 0.01. The medium used in the second-stage fungal BF had the following composition (gL^{-1}); K_2HPO_4: 0.5, $MgSO_4 \cdot 7H_2O$: 0.1, KH_2PO_4: 4.5, NH_4Cl: 2, and 2 mL trace elements and vitamin solutions [8, 9]. The first-stage BF was inoculated with autotrophic hydrogen sulphide degrading culture and an acid tolerant methanol degrading yeast (*C. boidinii*), while the fungus *O. stenoceras* was the dominant strain in the second-stage BF.

3.3.2 Experimental setup and operation

The following configurations of bioreactors were used in this study; glass column BTF: diameter-75 mm and height-700 mm (Working volume-2.78L); glass column BF: diameter-100 mm and height-700 mm (Working volume-4.88L). The BTF was packed with pall-rings (porosity-91% and specific surface area-350 m^2m^{-3}), while the BF was packed with a composite mixture of pall-rings and perlite (mean diameter-4.5 mm). To generate the desired levels of gas-phase pollutants, compressed air stream was split into three flows *viz.*, as one major and two minor streams. Hydrogen sulphide was generated

by passing the major portion of the air stream over a H_2SO_4 solution into which a solution of Na_2S was dripped. The desired values of gas-phase hydrogen sulphide concentrations were obtained by changing either the Na_2S concentration and/or the dripping rate. The two minor streams were bubbled through troughs containing liquid methanol and α-pinene, respectively. The waste-gas containing a mixture of methanol, α-pinene, and hydrogen sulphide was passed first through the BTF in upflow mode, counter-current to the trickling liquid, where methanol and hydrogen sulphide were removed. The outlet of the BTF was connected in series to the second-stage fungal BF, operated in downflow mode, to remove α-pinene vapours. During continuous steady-state experiments, it was observed that some of the non-treated methanol and hydrogen sulphide vapours from the first-stage BTF were also removed in the latter system [8, 9]. Four equidistant gas sampling ports and two filter material sampling ports were provided along the depth of the column.

During shock load studies, gas samples were collected from the inlet and outlet port of the two bioreactors and subjected to gas chromatographic analysis. The performance of the individual bioreactor to remove gas-phase methanol, α-pinene, and hydrogen sulphide were ascertained by periodically monitoring the EC and RE profiles, determined by the following equations (Eqs. 3.3 and 3.4):

Elimination capacity:

$$EC = \frac{Q \times (C_i - C_o)}{V}, \left[gm^{-3}h^{-1}\right] \quad (3.3)$$

Removal efficiency:

$$RE = \frac{(C_i - C_o)}{C_i}, [\%] \quad (3.4)$$

Where, Q is the gas flow rate (m^3h^{-1}), V is the volume of the filter bed (m^3), and C_i and C_o is the inlet and outlet pollutant concentrations (gm^{-3}), respectively.

3.3.3 Analytical methods

Hydrogen sulphide concentrations (0-1000 ppm) were determined using a hand held sensor (Dräger Sensor XSEC H_2S HC6809180). Gas-phase methanol and α-pinene concentrations were measured *via* gas chromatographic analysis using a Hewlett-Packard 5890 series II GC, fitted with a flame ionization detector (FID). The following flow rates were used; H_2: 30 mL min^{-1}, air: 300 mL min^{-1}. A 50 m TRACER column (TR-WAX, ID: 0.32 mm, film thickness: 1.2 μm) and helium (2.0 mL min^{-1}) were used in the GC. The temperatures at the GC injection, oven and detection ports were 150, 150 and 250 °C, respectively.

3.4 ANN MODEL DEVELOPMENT

Two MLPs (input-hidden-output layer) were formulated to predict the RE of different pollutants in the BTF and the BF, respectively, using inlet concentrations of methanol (C_M), α-pinene (C_P), and hydrogen sulphide (C_{HS}) as the input parameters. Although one model could be developed for the whole system under consideration (two-stage bioprocess), it could not be then used in cases where either the BTF or the BFr, is used as a stand alone bioprocess to eliminate methanol and hydrogen sulphide (BTF) and α-pinene (BF) from gas-phase. Anew, as envisaged in our study, as the first-stage BTF removed most of the methanol and hydrogen sulphide entering the system, the model developed for the BTF had only two outputs, namely RE_M and RE_{HS}. On the other hand, the model developed for the BF used only one output, *i.e.*, RE_P, because that bioreactor predominantly removed α-pinene vapours [8, 9]. The schematic of these two MLPs is illustrated in Figure 3.1. The experimental data points were normalized and scaled to the range of 0 to 1. The sigmoid transfer function was used in the hidden layer, while a linear transfer function was used in the output layer. The dataset (100%) was divided into two sets, as training (N_{Tr}: 58%), and testing sets (N_{Te}: 42%). Table 3.1 describes the

basic statistical information about the training and test data sets, for the BTF and the BF, respectively. The training data set was randomly chosen in order to represent the minimum and the maximum values from the experimental conditions, *i.e.*, the pre-shock, shock and post-shock loading patterns. N_{Te} were kept aside during training, and the performance of the trained network was intermittently assessed to avoid over-training of the network. More details concerning the selection of data points and internal network parameters have been described elsewhere [26-28].

Table 3.1: Basic statistics of the training and test data set

(a) Model for the first-stage BTF						
	Training data (N_{Tr}=18)			Test data (N_{Te}=13)		
	Mean	Mininmum	Maximum	Mean	Mininmum	Maximum
C_M	1.069	0.167	3.391	1.043	0.176	3.349
C_P	0.3308	0.0505	0.792	0.311	0.067	0.848
C_{HS}	0.1120	0.026	0.287	0.105	0.0236	0.296
RE_M	74.92	33.71	100	80.37	51.67	100
RE_{HS}	63.41	27.17	100	70.86	29.79	100
(b) Model for the second-stage BF						
	Training data (N_{Tr}=18)			Test data (N_{Te}=13)		
	Mean	Mininmum	Maximum	Mean	Mininmum	Maximum
C_M	0.4334	0.000	2.020	0.378	0.000	1.608
C_P	0.338	0.0568	0.792	0.319	0.0606	0.859
C_{HS}	0.0579	0.000	0.207	0.053	0.000	0.204
RE_P	91.97	72.14	100.00	90.79	67.97	100.00

Weight corrections between interconnected neurons were modified using the error backpropagation algorithm with gradient descent [28, 30]. The best values of network parameters, *viz*., training count (T_c), number of neurons in the hidden layer (N_H), learning rate (η), momentum term (α), and epoch size (ε), were selected by trial and error [7, 27, 38, 39]. These values are shown in Table 3.2. More information concerning the effect of these network parameters and neural network modeling can be found elsewhere [27, 28, 36-39]. ANN training, testing and sensitivity analysis were performed using the multivariable statistical and neural network modeling software, NNMODEL (Version 1.4, Neural Fusion, NY). Details pertaining to the application of

ANNs for evaluating the performance of a BF has been elaborated and discussed in recent publications [27, 38].

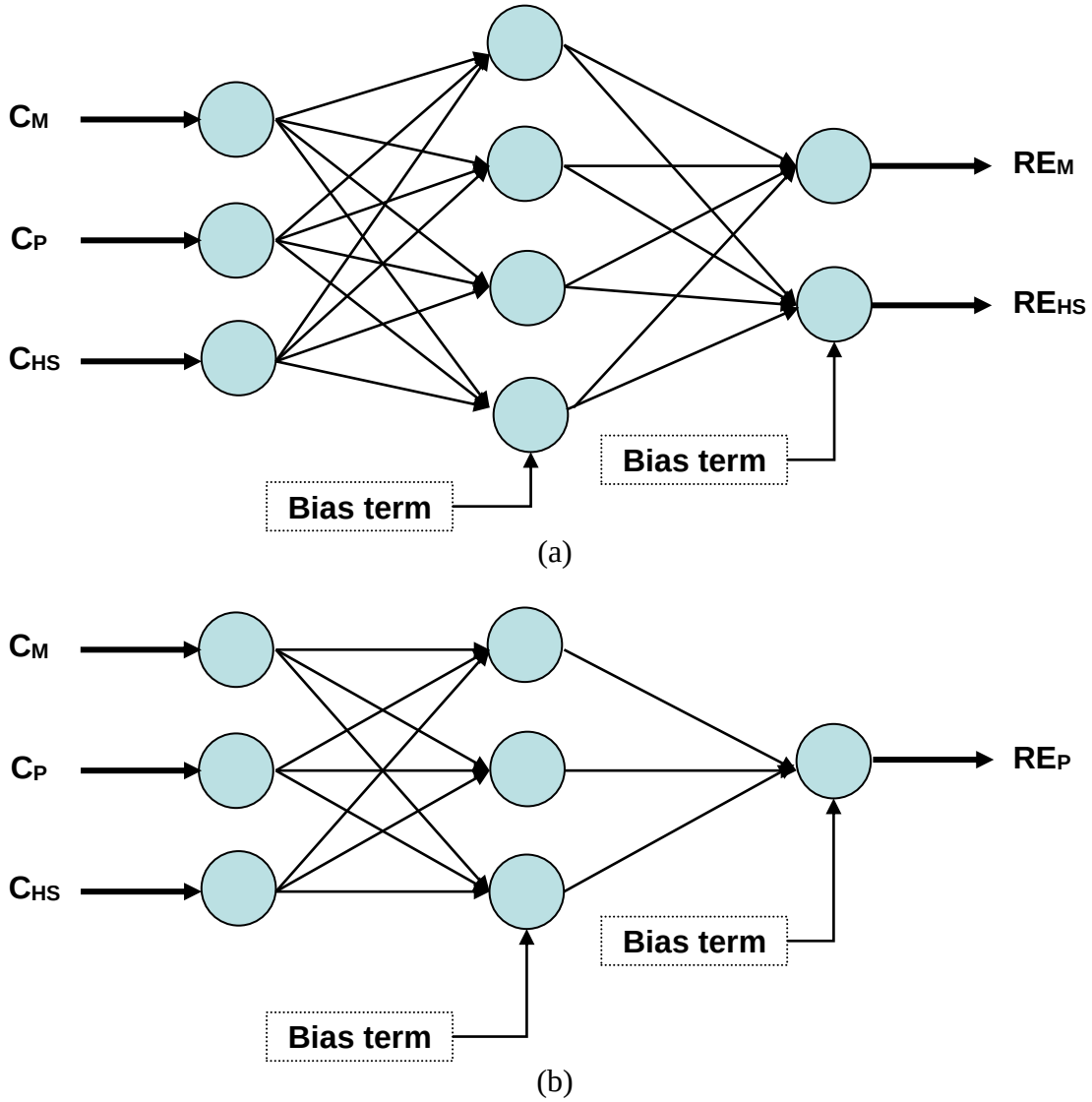

Figure 3.1: Schematic of the multi-layer perceptron model for; (a) first-stage BTF, and (b) second-stage BF (C_M-Concentration of methanol, C_P-Concentration of α-pinene, and C_{HS}-Concentration of hydrogen sulphide; Unit-gm^{-3}).

Table 3.2: Best values of network parameters and other variables during model training

Parameter	Model for BTF	Model for BF
	Best value	Best value
Training count, T_c	5,000	15,000
Learning rate, η	0.7	0.75
Momentum term, α	0.5	0.8
Error of training	0.0001	0.0001
Epoch size, ε	18	18
Neurons in input layer, N_I	3	3
Neurons in hidden layer, N_H	4	3
Neurons in output later, N_O	2	1
Network topology	3-4-2	3-3-1
Sum squared error	0.00626	0.00034
Size of training data, N_{Tr}	18	18
Size of test data, N_{Te}	13	13

3.5 RESULTS AND DISCUSSION

3.5.1 Performance of BTF and BF during transient-state operations

Transient-state experiments were conducted in the two bioreactors in the form of long-term and short-term shock loads at a constant gas-flow rate of $1 m^3h^{-1}$. The ILRs of methanol, α-pinene, and hydrogen sulphide were thus varied from low to medium (66h), and low to high (12h) values during the shock loading step, and the performance was evaluated by monitoring the RE and EC profiles for each bioreactor [3]. When the BTF was subjected to medium shock loads (38 $g_{\text{hydrogen sulfide}}\, m^{-3}h^{-1}$), the RE_{HS} decreased from 100% to 50%, while RE_M decreased from 100 to ~30% when the load was >250 $g_{\text{methanol}}m^{-3}h^{-1}$. During this step, the second-stage BF experienced α-pinene loads of about 70 $gm^{-3}h^{-1}$, and high RE_P were noticed (90%). The EC profiles of individual pollutants observed in the BTF and the BF, respectively, are plotted in Figure 3.2 as a function of the ILR.

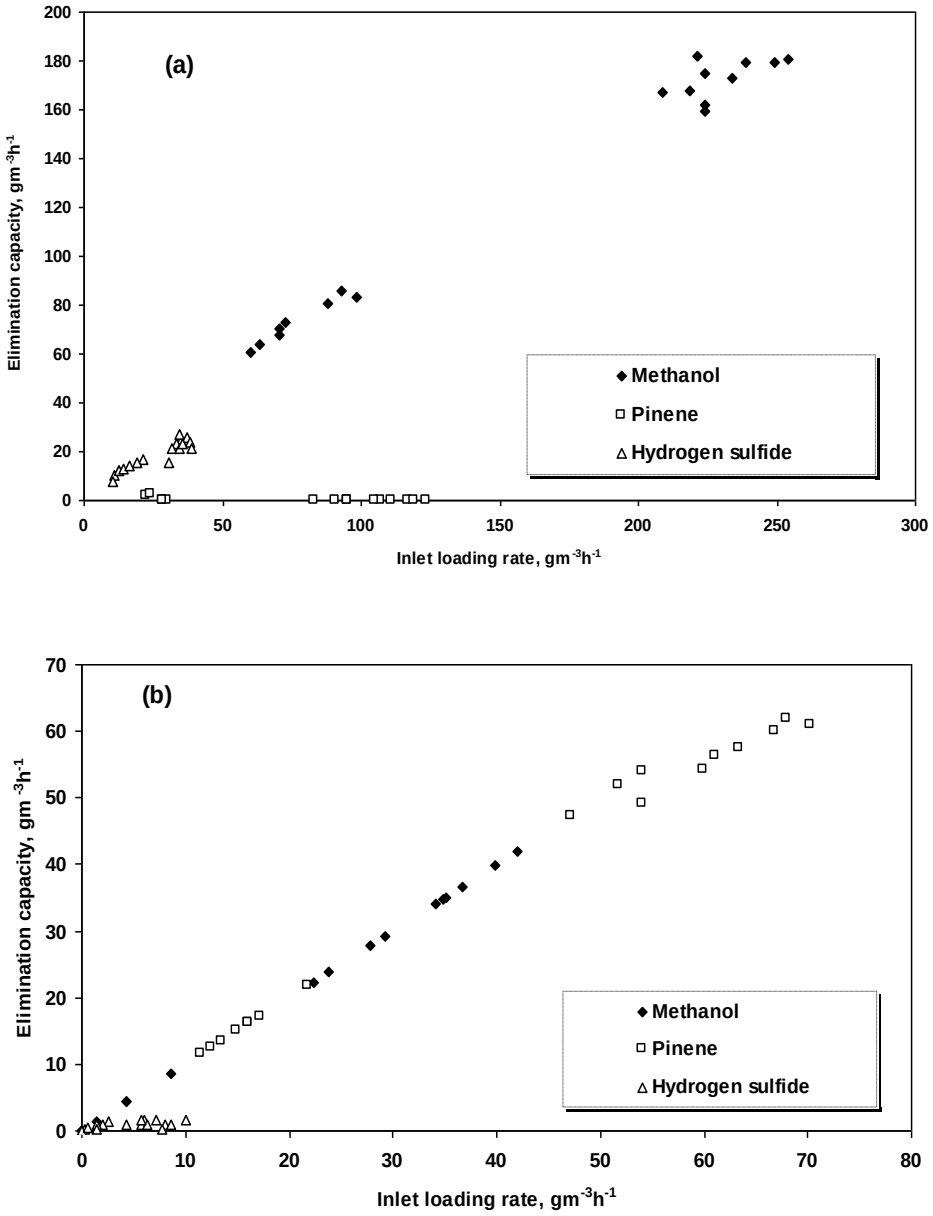

Figure 3.2: Effect of ILR on the EC of: (a) first-stage BTF, and (b) second-stage BF, during long-term low to medium shock loads.

During short-term low to high concentration shock loads, the ILRs were increased as follows; 8.5 to 106 $g_{hydrogen\ sulphide}$ $m^{-3}h^{-1}$, 95 to 1220 $g_{methanol}$ $m^{-3}h^{-1}$, and 30 to 305 $g_{\alpha\text{-}pinene}$ $m^{-3}h^{-1}$. It was observed that RE_M and RE_{HS} dropped significantly in the BTF, reaching ~50 and 31%, respectively. The non-treated methanol and hydrogen sulphide thus imparted a shock load of 414 and 42.4 $gm^{-3}h^{-1}$ to the second-stage BF, in addition

to the already entering high loads of α-pinene (176 $gm^{-3}h^{-1}$). The second-stage BF was able to achieve only low RE_M and RE_{HS} (8.5% and 25%), while high RE_P (75%) were maintained in the BF giving rise to an EC_{max} of 130.1 $g_{\alpha\text{-pinene}}$ $m^{-3}h^{-1}$ (Figure 3.3). The EC_{max} for methanol and hydrogen sulphide in the first-stage BTF were 684, and 33.1 $gm^{-3}h^{-1}$, respectively.

3.5.2 ANN modeling

The first step of this modeling task was to identify a suitable network topology for the two MLPs through proper optimization of the network parameters [28, 29, 34, 39]. In order to achieve this, the T_c and N_H were varied from 1,000 to 20,000, and 3 to 6, respectively, by keeping the η and α at their default values of 0.5. After assigning the T_c as 5,000 and 15,000, and N_H as 4 and 3 for the models developed for, respectively, the BTF and the BF (Figure 3.1), the best values for η and α were estimated by changing their values from 0.1 to 0.9. The optimized values of network parameters for both the models are shown in Table 3.2. The best network topology for the first-stage BTF, and the second-stage BF, were found to be 3-4-2 and 3-3-1, respectively.

The measured and model fitted profiles of RE for the individual pollutants, during model training and testing are shown in Figures 3.4 and 3.5, respectively. As seen from these figures, the transient-state ANN model developed for the BTF and the BF showed high R^2 values during both training and testing. The BTF model gave R^2 values of 0.8955 and 0.9725 for methanol, and 0.9206 and 0.9457 for hydrogen sulphide, respectively, during training and testing.

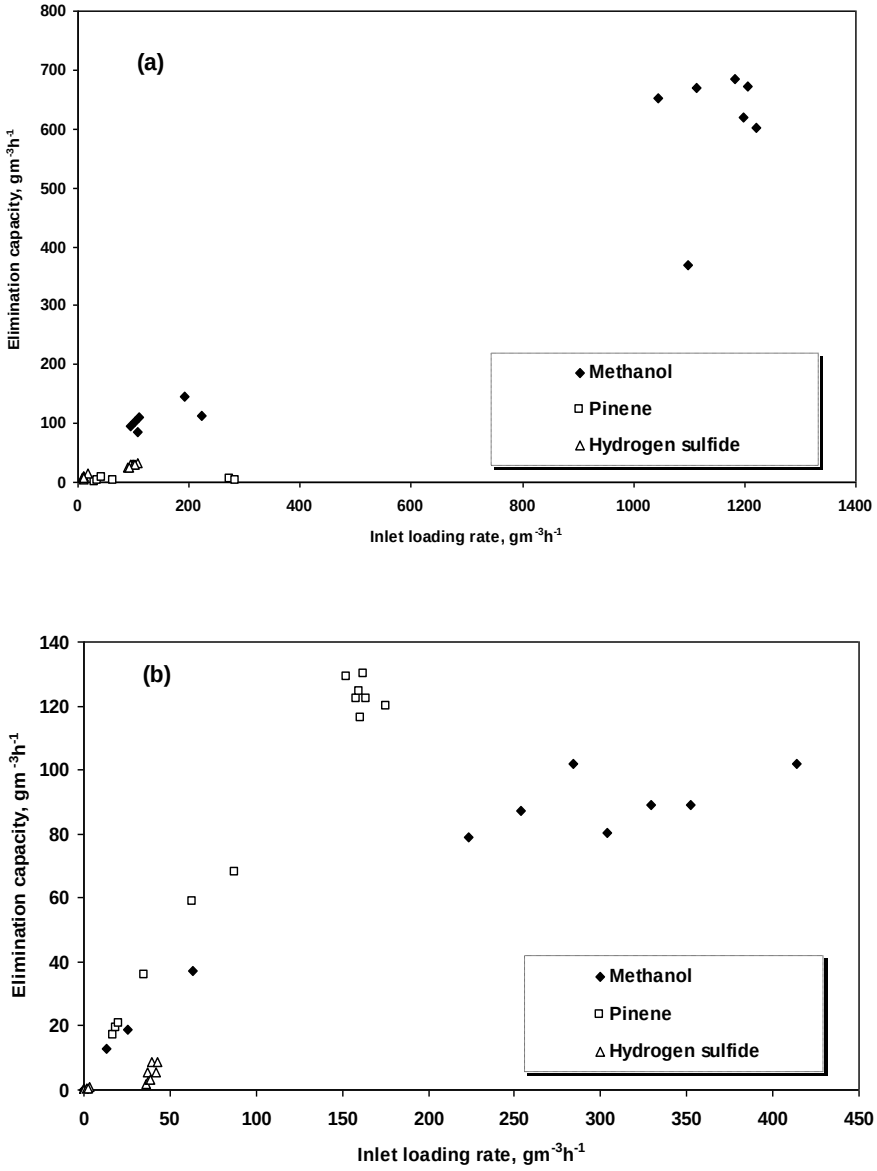

Figure 3.3: Effect of ILR on the EC of; (a) first-stage BTF, and (b) second-stage BF, during short-term low to high shock loads.

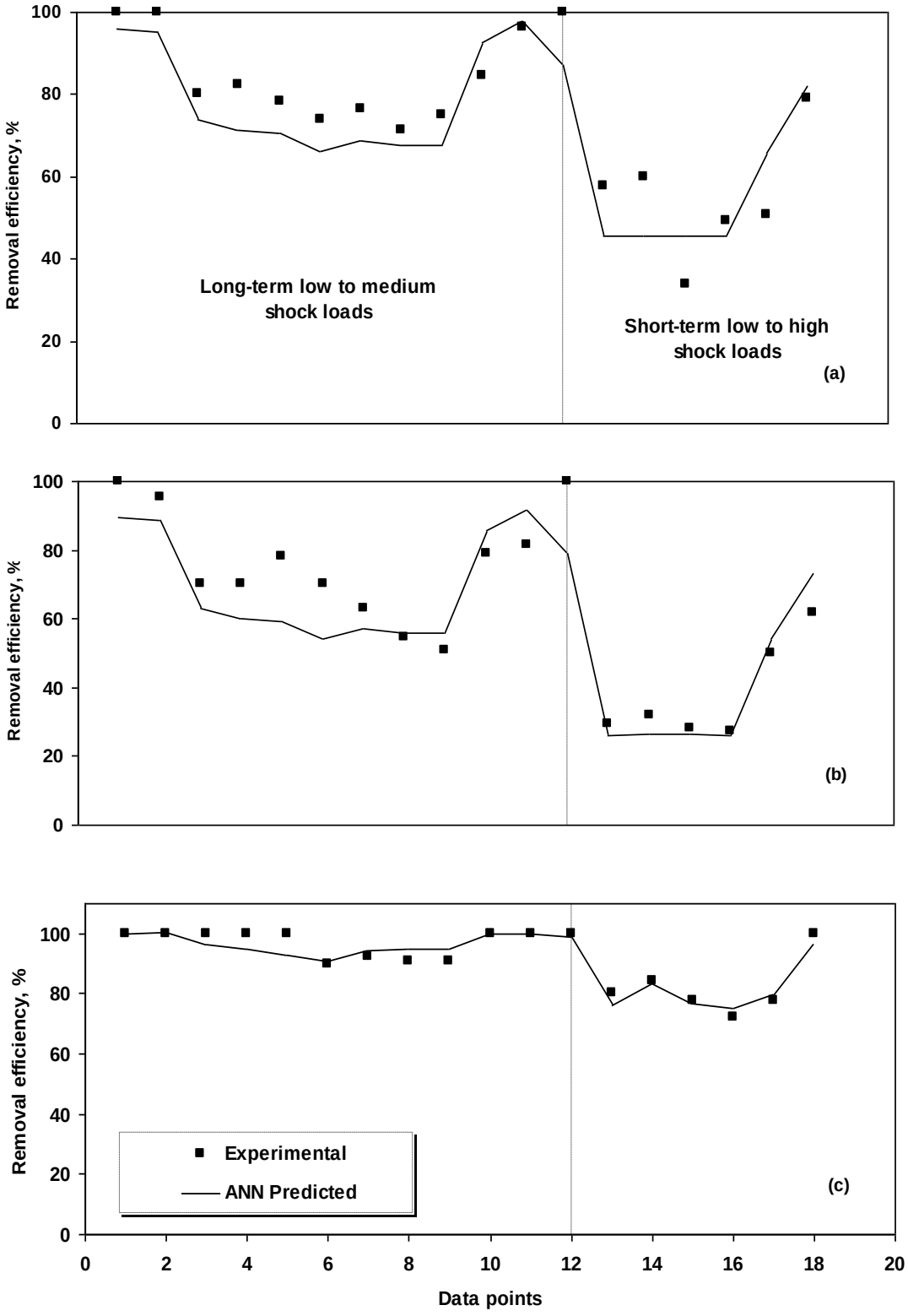

Figure 3.4: Experimental and ANN model predicted profiles of RE in the training data set; (a) methanol, (b) hydrogen sulphide, and (c) α-pinene.

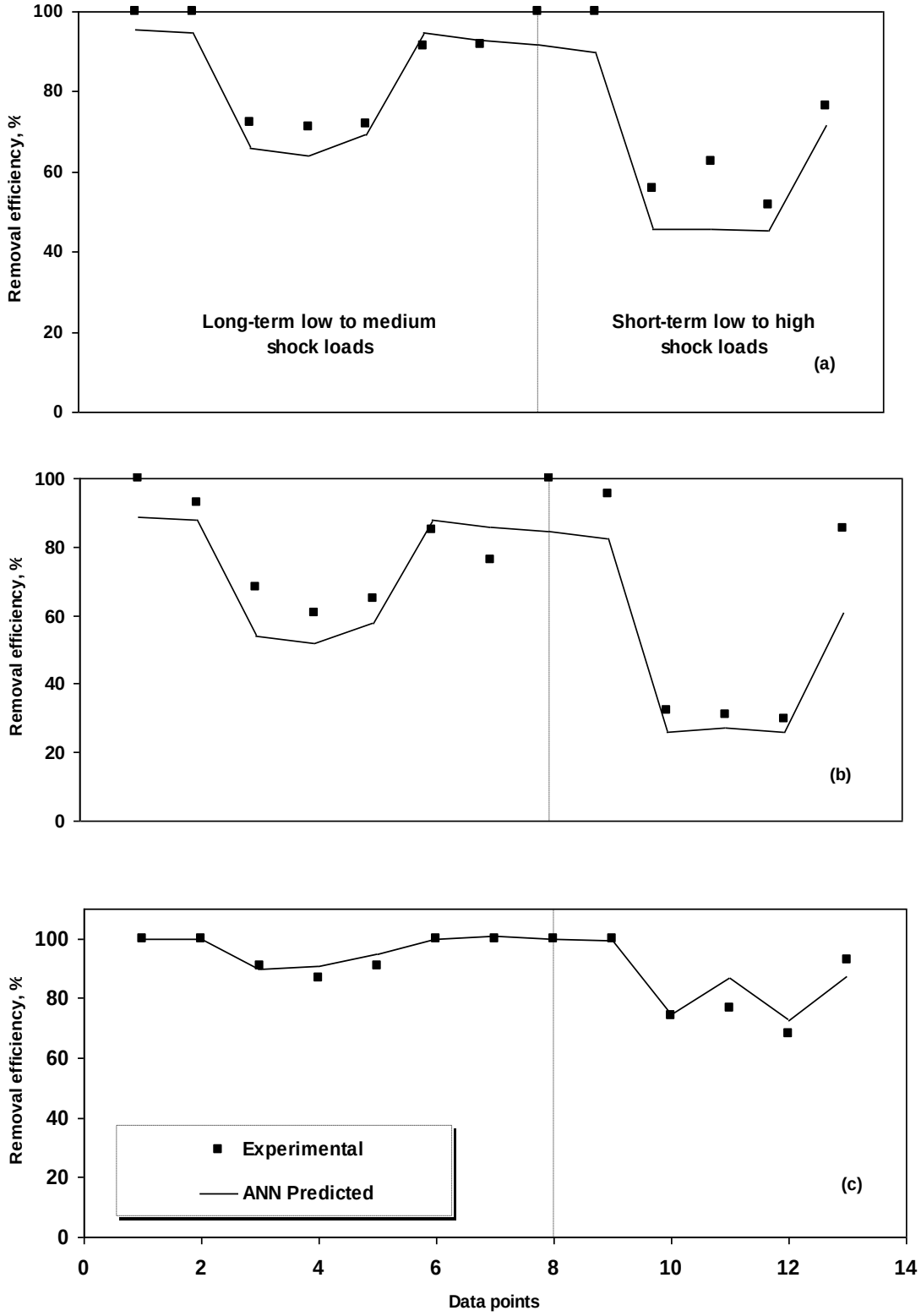

Figure 3.5: Experimental and ANN model predicted profiles of RE in the test data set; (a) methanol, (b) hydrogen sulphide, and (c) α-pinene.

On the other hand, R^2 values of 0.9486 and 0.9540 were obtained for the BF model during training and testing. Thus, overall, only <10% of the total deviations could not be mapped by these models during the training process. However, some of these deviations in the BTF model can be attributed to the fluctuating values of RE_{HS} during the long-term low to medium shock loading step. At this stage of operation, during pre-shock conditions, nearly complete RE_{HS} was noticed at an inlet loading rate of 10 $gm^{-3}h^{-1}$, and when the shock load was introduced (38 $gm^{-3}h^{-1}$) the RE_{HS} fluctuated between 80 and 50%, even when C_{HS} was maintained constant at ~0.3 gm^{-3} to the first-stage BTF. The fluctuating pollutant removal profiles that are usually governed by the activity of the microorganisms in the bioreactor are not interpreted by a neural network during training, unless a process based model is integrated with a neural network model. Thus, any unannounced variations in RE profiles can beset the ANNs learning capacity, eventually leading to a decline in performance of the model [39].

After obtaining the best network topology for the two models (3-4-2 and 3-3-1), the connection weights and bias term were obtained for the interconnections between different neurons in different layers of the MLP (Table 3.3). According to Garson [40], the connection weights W_{ih} and W_{ho} determine which input neuron dominates the contribution to a hidden neuron, while the sign (+, –) suggests the nature of correlation between an input to a neuron and the output from the neuron. Sensitivity analysis was performed in order to estimate the strength and magnitude of relationships prevailing between the output variables (RE_M, R_{HS}, and RE_P) and the input variables (C_M, C_{HS} and C_P) [7, 27, 37-39].

Table 3.3: Connection weights between the input - hidden layer (W_{ih}), and hidden - output layer (W_{ho}) of the developed ANN models

(a) Model for the first-stage BTF							
Model inputs	Input-hidden layer (W_{ih})				Hidden-output layer (W_{ho})		
	HID-1	HID-2	HID-3	HID-4		RE_M	RE_{HS}
C_M	2.307	-1.991	1.737	-6.272	HID-1	-1.661	-1.468
C_P	3.681	-4.522	0.999	-9.856	HID-2	1.790	2.570
C_{HS}	-0.330	0.047	0.275	3.132	HID-3	0.977	-0.149
Bias term	0.005	0.462	-0.735	4.722	HID-4	5.250	5.354
					Bias term	0.704	0.920

(b) Model for the second-stage BF					
Model inputs	Input-hidden layer (W_{ih})			Hidden-output layer (W_{ho})	
	HID-1	HID-2	HID-3		RE_P
C_M	0.802	-0.377	-0.710	HID-1	-2.062
C_P	-0.647	-1.342	-4.044	HID-2	0.406
C_{HS}	-3.234	1.663	9.452	HID-3	3.421
Bias term	0.637	-0.612	0.075	Bias term	-0.098

Table 3.4: Sensitivity analysis of model inputs

Model inputs	BTF				BF	
	RE_M		RE_{HS}		RE_P	
	AAS	AS	AAS	AS	AAS	AS
C_M	0.2437	-0.2416	0.2624	-0.2624	0.0915	-0.0915
C_P	0.5870	-0.5870	0.5847	-0.5847	0.3320	-0.3320
C_{HS}	0.1692	+0.1692	0.1528	+0.1528	0.5764	-0.5764

Note: AAS-Absolute average sensitivity, AS-Average sensitivity

For waste-gas treatment systems handling mixtures of gas-phase pollutants, it has been reported that small changes in the inlet concentration of one pollutant could have a significant impact on overall reactor performance and synergistic and/-or antagonistic interactions can be expected [19, 20]. Sensitivity analysis in the form of absolute average sensitivity (AAS) and average sensitivity (AS) values were computed to determine the most influential input parameter affecting the output of the ANN models [27, 38]. If the direction of the change in the output variable is always the same then both these sensitivity values would be identical. The results of sensitivity analysis for the first-stage BTF and second-stage BF models are shown in Table 3.4. It can be inferred from this table that, the RE_M in the BTF was affected more, in an antagonistic

way (AS=-0.5870), by the presence of α-pinene, a hydrophilic VOC, than by its own concentration, C_G (AS=-0.2416). Regarding RE_{HS}, both C_M and C_P affected RE_{HS} in the first-stage BTF during transient-state operations. Nevertheless, the presence of hydrogen sulphide did not affect the RE_M, an easily biodegradable hydrophilic VOC, in the biotrickling filter (AS=+0.1692). These results are in strong agreement with a previous study, where it was shown that the presence of methanol significantly affected the RE_{HS}, but the RE_M was not affected by the presence of hydrogen sulphide [41]. The authors reported an EC_{max} of 236 $gm^{-3}h^{-1}$ for methanol, and 6.4 $gm^{-3}h^{-1}$ for hydrogen sulphide, respectively, and occasionally the pH dropped to very low values. During steady-state operation in the first-stage BTF, it was shown that when increasing either C_M or C_P while maintaining the C_{HS} at constant values, the RE_{HS} reduced by almost 25%, but the reverse did not occur [8]. However, in the case of the second-stage BFr, both C_M and C_P negatively affected RE_P, and the presence of hydrogen sulphide synergistically affected the BF performance (AS=+0.5762) despite a drop in the pH of that bioreactor from 5.9 to 3.5 during steady-state operations [8, 9]. The drop in pH values can be attributed to the formation of hydrogen chloride during α-pinene biodegradation, as the mineral medium used contained ammonium chloride as the nitrogen source. On the other hand, the non-treated hydrogen sulphide entering the fungal BF from the first-stage BTF was also partially removed in the BF [8]. Thus, during its biodegradation, it could also have interacted with the different chemical species present in the mineral medium to produce sulphuric acid as one of its main end-product, thereby contributing to a decline in the pH values. Despite a drop in the operating pH of the BF, the RE_P values were found to be significantly high both during long-term and short-term shock loads. This can be explained by the dominant presence of the fungus *O. stenoceras* in the BF, and its ability to degrade α-pinene vapours under

fluctuating conditions of pH and water content [42]. Moreover, recent research suggests that fungal species such as *Cladosporium sphaerospermum, Penicillium brevicompactum, Exophiala jeanselmei, Fusarium oxysporum, Fusarium nygamai, Talaromyces flavus,* and *Fonsecaea pedrosi* can degrade a wide variety of VOCs (*n*-butyl acetate, methyl ethyl ketone, methyl propyl ketone and toluene), at rates equal to or greater than those observed in bacterial systems even under no pollutant loading (starvation) conditions [43].

3.5.3 Practical implications

Neural networks have recently found application to predict the performance of lab-scale waste-gas treatment systems such as BF and BTF [7, 27, 36-39], though no serious effort has been made so far by plant managers to implement this technique for real-time systems. Some salient features of neural networks include the following: adaptive nature, ability to perform data analysis and recognize patterns, ability to deal with highly non-linear data, and high processing speeds. In industrial wastewater treatment plants (WWTPs), ANNs have successfully been implemented for fault detection and diagnosis, plant and instrument monitoring, dynamic forecasting and robust process control [44]. However, for waste-gas applications, ANN based models can provide adequate information on the different safe operational regimes of the bioreactor, in terms of inlet concentrations of the different pollutants, to reach high REs. These regimes can be represented by two-dimensional contour plots as shown in Figure 3.6. This figure shows the response of the second-stage BF (RE_P) as a function of methanol and α-pinene concentrations during transient-state operations. It is evident that, to achieve more than 99% RE_P, the BF should be fed with <1.8 g methanol m^{-3}, and <0.3 g α-pinene m^{-3}. However, for increasing concentrations of α-pinene (>0.3 g m^{-3}), the RE_P can decrease significantly in the second-stage BF to values as low as 39%. Besides

identifying the safe operating regimes for the system under consideration, the ANN model also provides data on the most important factor that is likely to affect the removal of methanol, α-pinene and hydrogen sulphide in the two-stage system, in the form of a sensitivity analysis report (Table 3.4).

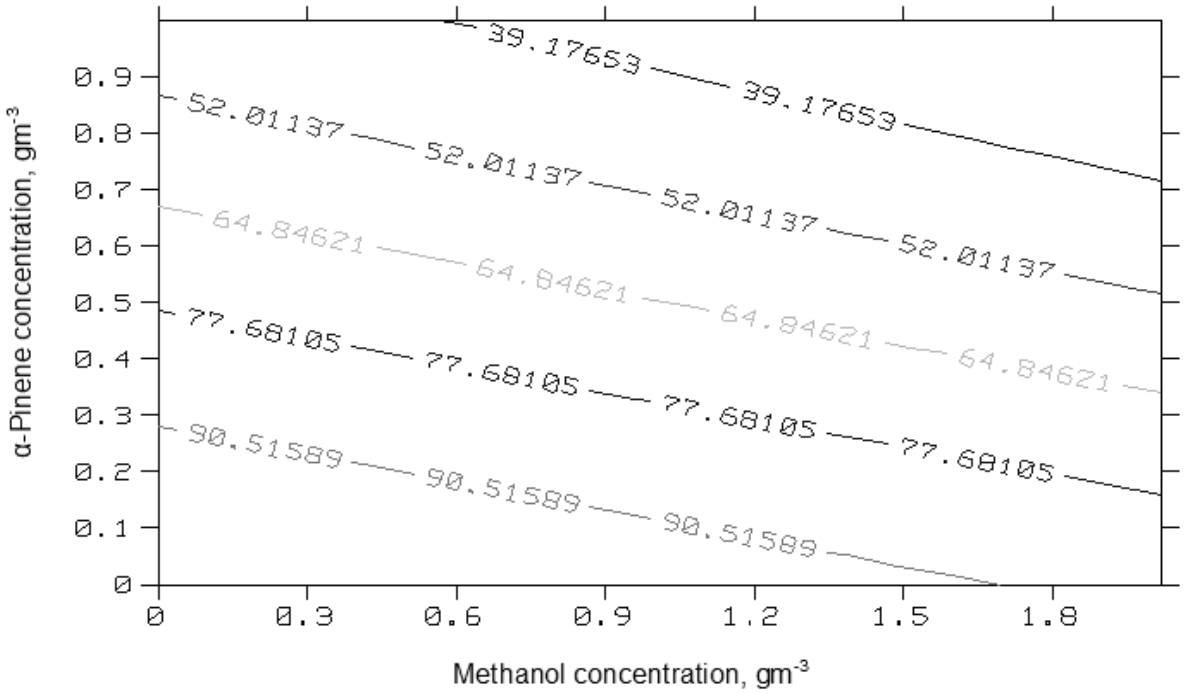

Figure 3.6: Representative contour plot showing the RE profiles of α-pinene in the second-stage BF as a function of methanol and α-pinene concentrations.

Models developed from lab-scale experimental data, where input parameters to the BF such as concentration and gas flow rates are systematically controlled and other physico-chemical and environmental factors are adequately maintained to exhibit high microbial activity, might not accurately predict the efficiency of full-scale BF. Thus, for real-time/full-scale applications, the waste-gas treatment system should be fitted with online measurement devices to periodically monitor process parameters such as inlet concentrations of the pollutant(s), gas-flow rate, pressure drop, relative humidity, temperature, and carbon dioxide generation rate. This information has to be stored in a

large database, and the system has to be equipped with an automatic control system to maintain the desired values of these process variables. The trained neural model can then be integrated with a programmable logic controller (PLC) to ascertain and control the process variables, and also estimate the performance of the system on a regular basis, once every 6h. The neural network model can also be programmed to warn the plant operator of any discrepancies in waste-gas characteristics and concentrations, sudden changes in gas-flow rate, and notify the operator to take suitable actions. The time-series data collected from real-time bioreactor operation can be merged with the already existing database, and the ANN model can be trained in offline/online mode, and the connection weights can be updated before integrating it with the PLC.

3.6 CONCLUSIONS

ANN based models were successfully developed and tested to predict the transient-state performance of a two-stage waste-gas treatment system. The RE_M and RE_{HS} in a first-stage BTF and the RE_P in a second-stage BF were predicted using C_M), C_P and C_{HS} as the inputs to the models. After proper optimization of network parameters, and through vigorous training and testing, the following network topologies were obtained: 3-4-2 and 3-3-1, respectively, for the BTF and the BF. The results from sensitivity analysis showed that the most critical factor that antagonistically affects the RE_M and RE_{HS} in the BTF during transient operations was C_P, while RE_P in the BF was synergistically affected by C_{HS}. The ANN models developed in this work for the two-stage system under transient-state conditions would yield more promising results when tested with adequate online control systems, thus allowing better access to control process variables and improve the performance of bioreactors for waste-gas treatment.

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Chapter 4

One-stage biotrickling filter for the removal of a mixture of volatile pollutants from air: performance and microbial community analysis

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ABSTRACT

The biodegradation of gas-phase mixtures of methanol, α-pinene and H_2S was examined in a biotrickling filter (BTF), inoculated with a microbial consortium composed of an autotrophic H_2S-degrading culture, and pure strains of *Candida boidinii*, *Rhodococcus erythropolis*, and *Ophiostoma stenoceras*. The inlet concentrations of methanol, α-pinene and H_2S varied from 0.05 to 3.3 gm^{-3}, 0.05 to 2.7 gm^{-3}, and 0.01 to 1.4 gm^{-3}, respectively, at empty bed residence times (EBRT) of either 38 or 26s. The maximum elimination capacities (EC_{max}) of the BTF were 302, 175, and 191 $gm^{-3}h^{-1}$, with 100%, 67%, and >99% removal of methanol, α-pinene and H_2S, respectively. The presence of methanol showed an antagonistic removal pattern for α-pinene, but the opposite did not occur. For α-pinene, inlet loading rates (ILRs) >150 $g_{\alpha\text{-pinene}}m^{-3}h^{-1}$ affected its own removal in the BTF. The presence of H_2S did not show any declining effect on the removal of both methanol and α-pinene.

KEYWORDS: Hydrogen sulphide; methanol; α-pinene; paper industry; wood industry

4.1 INTRODUCTION

Wood industries have been constantly striving to reduce their emissions of odorous compounds from various plant operations that usually contain a mixture of volatile organic compounds (VOCs) and volatile inorganic compounds (VICs). Among those, methanol, α-pinene, and hydrogen sulphide (H_2S), are representative hydrophilic, hydrophobic, and inorganic pollutants present in emissions from some pulp and paper- and wood- related industries [1]. The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) and ACGIH threshold limit value (TLV) for industrial workers are set at 200 ppm (260 mg m^{-3}) for methanol, 100 ppm (560 mg m^{-3}) for α-pinene, and 10 ppm (15 mg m^{-3}) for H_2S, respectively, for a 8-h time weighted average concentration and a 40-h work per week [2].

Biodegradation is a well established method for the complete mineralization of volatile organic and inorganic compounds, present in both liquid and gaseous state [3, 4]. It exploits the advantage of the ability of microorganisms to transform hazardous and odorous pollutants into innocuous and inodorous end-products. Among the different bioreactor configurations used to carry out this biodegradation process, biofiltration appears to be a safe, reliable, eco-friendly and economic technique [5, 6, 7]. Biotrickling filters (BTF) exploit the advantages of the conventional biofilter, and uses a trickling nutritive medium that contains nutrients for sustaining microbial activity in the biofilm [8, 9]. The packing in a BTF is generally made of chemically inert materials such as plastic supports, polyurethane foam, lava rock, pall rings, among others, that can be arranged either in a random or a structured manner [8, 10, 6,11]. Nevertheless, BTFs facilitate more consistent operation than traditional biofilters (BFs) due to better control of overall pressure drop, nutrient concentration, and pH, and enable higher pollutant elimination rates to be obtained for a broader range of pollutants [5]. Hence, BTF

are suitable bioreactors for the treatment of complex mixtures of various organic and inorganic pollutants such as mixtures of methanol, α-pinene, and hydrogen sulphide (H_2S).

There are a few publications that investigated the removal of H_2S and VOCs solely. The pH drop due to the accumulation of sulphuric acid from the conversion of H_2S can hinder the activity of microbial populations involved in the biodegradation of VOCs. To avoid bioreactor disfunction, a two-stage bioreactor configuration was recently tested in our laboratory for the combined removal of VOC and VIC. For the purification of waste-gases containing H_2S and VOCs (methanol and α-pinene), H_2S and methanol were degraded in the first-stage reactor by autotrophic bacteria and an acid-tolerant yeast, followed by the effective removal of α-pinene in the second stage by a fungus [1]. In order to improve the biological treatment of such a mixture and the bioreactors design, the development of one-stage bioreactors is suggested here. Previously, studies had been undertaken with a one-stage bioreactor for the removal of gas-phase methanol, α-pinene or H_2S as stand-alone pollutants [12, 13]. When considering VICs and VOCs mixtures, VOCs degrading microorganisms in one-stage BTFs have sometimes shown to tolerate the prevailing acidic conditions over a long period of time, with variable degradation rates, depending on the nature of the pollutants. In a pilot-scale BTF packed with lava rock, the efficient co-treatment of H_2S and VOCs at acidic pH was highlighted, revealing the activity of both chemoautotrophs (H_2S oxidizing bacteria) and heterotrophs (VOC oxidizing bacteria) within the BTF [14]. Cox and Deshusses (2002) [15], reported that the pH (4.5 or 7) of operation did not affect long-term performance of a BTF used for the co-treatment of H_2S and toluene, but the start-up time was longer at the lowest pH of 4.5.

The aim of this work was then to develop a highly efficient one-stage BTF, by utilizing different microorganisms that had proven to be effective for the removal of the mixture of methanol, α-pinene and H_2S. In this context, our objectives were: (i) to evaluate the

performance of a one-stage BTF, inoculated with different microbial species, for the removal of methanol, α-pinene and H_2S, (ii) to study the effect of the empty bed residence time (EBRT of either 38 or 26 s) on BTF performance, (iii) to understand the dynamics of pollutant removal in different sections of the BTF (substrate stratification), (iv) to identify the different types of interaction effects, *i.e.*, antagonistic or synergistic, between pollutants and their removal pattern in the BTF, and (v) to perform microbial community analysis in different sections of the BTF after long-term operation using molecular biology tools.

4.2 Materials and Methods

4.2.1 Nutrient medium composition

The composition of the mineral medium used in the BTF, was (in gL^{-1} of de-ionized water); K_2HPO_4: 0.5, $MgSO_4 \cdot 7H_2O$: 0.1, KH_2PO_4: 4.5, NH_4Cl: 2, and 2 mL trace elements and vitamin solutions [1].

4.2.2 Microbial consortium

The BTF was inoculated with a mixture of (i) an autotrophic H_2S-degrading culture (100 mL leachate from a previously operated BTF), (ii) *Candida boidinii*, a methanol degrading acid-tolerant yeast (~3 gL^{-1}), (iii) a co-culture of *Rhodococcus erythropolis* (~3 gL^{-1}) and (iv) the fungus *Ophiostoma stenoceras* (~3 gL^{-1}) [12, 16]. The latter bacterium and fungus are capable of utilizing α-pinene as their sole carbon and energy source. The different microbial cultures were grown on agar plates (15 gL^{-1}), maintained in desiccators at ambient temperature, and supplied with vapour phase methanol or α-pinene at low concentrations. The BTF was also inoculated with biomass obtained from the leachate (100 mL) of a previously operated two-stage bioreactor, *i.e.*, a biotrickling filter + a biofilter (BTF+BF), as described elsewhere, where methanol, α-pinene and H_2S were collectively treated in gas-phase [1].

4.2.3 Experimental setup

The schematic of the one-stage BTF is shown in Figure 4.1. The BTF was constructed of glass (70 cm high × 9.4 cm inner diameter), and packed with polypropylene pall rings yielding a total working bed volume of 4.55 L. The pall ring bed had an initial porosity of 91% and a specific surface area of 350 m^2m^{-3}. The BTF was provided with gas sampling ports located along the height of the reactor, at 20 cm and at 60 cm (outlet port) from the inlet. The BTF was also provided with filter material sampling ports, to collect biomass samples, uniformly distributed along the column (10 and 50 cm from the inlet). Fittings, connections and tubings were made of either glass or Teflon.

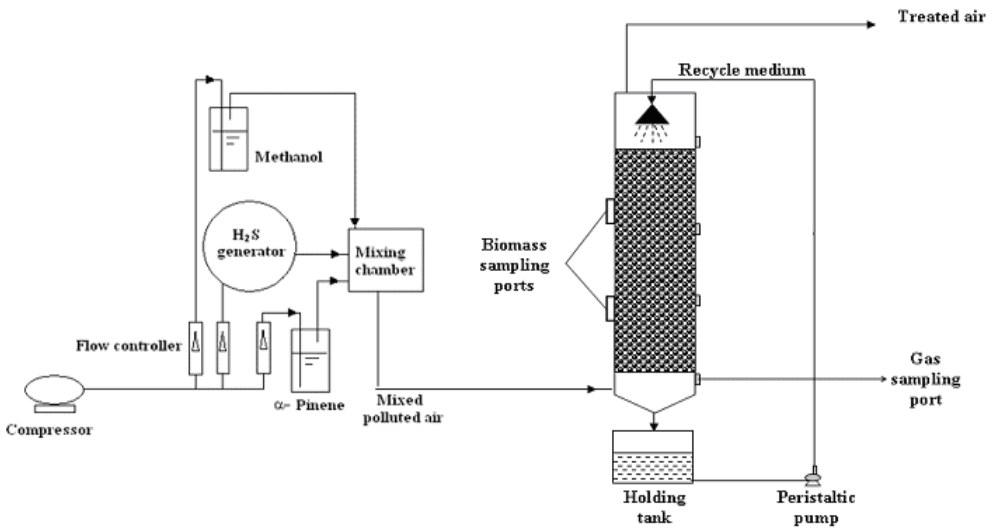


Figure 4.1: Schematic of the one-stage BTF for the combined removal of gas-phase methanol, α-pinene and H_2S.

4.2.4 Inoculation of the BTF

The microbial consortium described above was mixed with 2 L nutrient medium to obtain a uniform suspension of the initial inoculums. This culture was aseptically added to the BTF from the top; the leachate was collected in a collection tank and then continuously re-

circulated at 2.77 Lh^{-1} for the next 4 d, until visible biomass remained attached to the pall rings.

4.2.5 BTF operation

During BTF operation, the target concentrations of the individual pollutants; methanol (0.05 to 3.3 gm^{-3}), α-pinene (0.05 to 2.7 gm^{-3}) and H_2S (0.01 to 1.4 gm^{-3}) were generated at a sea level atmospheric pressure of 101.3 Kpa, at a laboratory temperature of 22±2 ^oC, as described hereafter. A main stream of compressed air was split into two minor and one major flow. The two minor air streams were then bubbled through either liquid methanol or α-pinene, introduced separately in flasks. H_2S was generated by passing the major portion of the air stream over a H_2SO_4 solution into which a solution of Na_2S was dripped. Different gas phase H_2S concentrations were obtained by changing the Na_2S concentration and/or dripping rate [16]. The three streams were combined in a mixing chamber, and fed to the bottom of the BTF column in a counter-current flow mode. The aqueous mineral medium described above was continuously re-circulated over the packed bed using a peristaltic pump (323E/D, Watson-Marlow Limited, Falmouth Cornwall, England) at a constant flow rate of 2.8 Lh^{-1}. The pH of the re-circulated nutrient medium was maintained constant, at 6.0±0.4, by means of a pH electrode (EASYFERM 120, Hamilton) attached to the nutrient collection tank and a controller coupled to an electro-valve (DO 9765T, Dual 3½ Digit pH redox indicator and regulator, Italy), by dosing a 2N NaOH solution to neutralize the acidic metabolites formed during the biodegradation process. Fresh nutrient medium was added once a week to the nutrient tank in order to compensate the loss of medium that occurred due abiotic phenomenon and the prevailing high gas flow rates in the BTF. This ensured adequate supply of nutrients to the attached biomass. Gas samples were collected from the sampling ports and analyzed for residual methanol, α-pinene and H_2S concentrations.

The performance of the BTF was estimated by calculating the elimination capacity (EC, $gm^{-3}h^{-1}$) and removal efficiency (RE, %) of the filter bed for each pollutant at different inlet loading rates (ILR, $gm^{-3}h^{-1}$), according to equations (4.1), (4.2) and (4.3), respectively [6]:

$$\text{Inlet loading rate, } ILR = \frac{Q.S_{in}}{V} \quad (4.1)$$

$$\text{Elimination capacity, } EC = \frac{Q.(S_{in} - S_{out})}{V} \quad (4.2)$$

$$\text{Removal efficiency, } RE = \frac{(S_{in} - S_{out})}{S_{in}} \quad (4.3)$$

Where, Q is the gas-flow rate (m^3h^{-1}), V is the volume of the filter bed (m^3) and S_{in} and S_{out} are, respectively, the inlet and outlet pollutant concentrations (gm^{-3}).

4.2.6 Analytical methods

The H_2S concentration (maximum measurable limit-1000 ppm) was determined using a hand-held sensor (Dräger Sensor XSEC H_2S HC6809180). Inlet and outlet gas-phase concentrations of methanol and α-pinene were measured via gas chromatographic analysis using a Hewlett-Packard 6890 series II GC, and a flame ionization detector (FID). The GC was equipped with a 50 m TRACER column (TR-WAX, ID: 0.32 mm, film thickness: 1.2 μm) and helium was used as the carrier gas (flow rate: 2.0 $mLmin^{-1}$). The temperatures at the GC injection, oven and detection ports were 250, 120 and 250 ºC respectively. The pressure drop (ΔP) across the BTF was measured using a differential U-tube water manometer connected to the top and bottom section of the reactor, with the operational range of 0-40 cm H_2O.

4.2.7 Microbiological analysis

4.2.7.1 Scanning electron microscopic (SEM) observations

The biomass attached to the pall rings was detached (280th day) by sonicating the samples for 15 min, and later prepared for observations under the electron microscope according to the procedure described by [12]. SEM observations were made with a JOEL JSM-6400 SEM working at a voltage of 20 kV and a working distance of 15 mm, and with Oxford Instruments EDX equipment.

4.2.7.2 DNA recovery procedure

DNA was recovered from the biofilm covering the polypropylene pall rings (280th day). Cells were dislodged from the carrier by shaking (Vibro-Shaker MM200, Retsch, Haan, Germany) at rotating frequency of 15 Hz, during 1 min, and DNA was extracted by a commercial extraction kit (FastDNA SPIN Kit for Soil, MP Biomedicals, Irvine, CA). DNA was quantified by absorbance at 260 nm (Biophotometer, Eppendorf, Hamburg, Germany).

4.2.7.3 Polymerase chain reaction (PCR)

The V3 region of the bacterial 16S rRNA gene was PCR amplified using a protocol described by [17]. Negative controls were included to verify the absence of contamination. PCR products were quantified by absorbance at 535 nm after PicoGreen staining (Quant-iT ds DNA HS reagent, Invitrogen, Carlsbad, CA).

4.2.7.4 Denaturing gradient gel electrophoresis (DGGE)

DGGE was performed with Ingeny phor U-2 system (Goes, The Netherlands) according to the protocol of [18], with denaturing gradient ranging from 43 to 63% as previously described [19]. Gel images were analyzed with Gelcompar II software (Applied Maths, Gent, Belgium).

4.2.7.5 Numerical analysis

The diversity was measured by the Shannon index *H'* (Eq. 4) that takes into account both the number of DGGE bands and their relative intensity.

$$H' = -\sum_{i}^{n} p_i \, log(\, p_i \,) \tag{4.4}$$

Where, p_i is the relative abundance of the i^{th} band of the profile.

After exclusion of the rarest bands (*i.e.* less than 3% intensity in all samples) the initial data matrix (relative intensities according to position) was standardized and transformed by square root to down-weight the influence of more abundant species [20]. The pair-wise similarity index ($S_{i,j}$) between community profiles *i* and *j* was calculated by Bray-Curtis coefficient (Eq. 5), that takes the form;

$$S_{i,j} = 100.\left(1 - \sum_{k=1}^{N} \frac{\left| p_{i,k} - p_{j,k} \right|}{p_{i,k} + p_{j,k}} \right) \tag{4.5}$$

Where, $P_{i,k}$ is the relative abundance of the k^{th} band in the profile *i*, and $P_{j,k}$ is the relative abundance of the k^{th} band in the profile *j*, in the transformed matrix. The similarity matrix was used to perform hierarchical clustering with UPGMA linking, using the Gel Compar II software.

4.3 RESULTS AND DISCUSSION

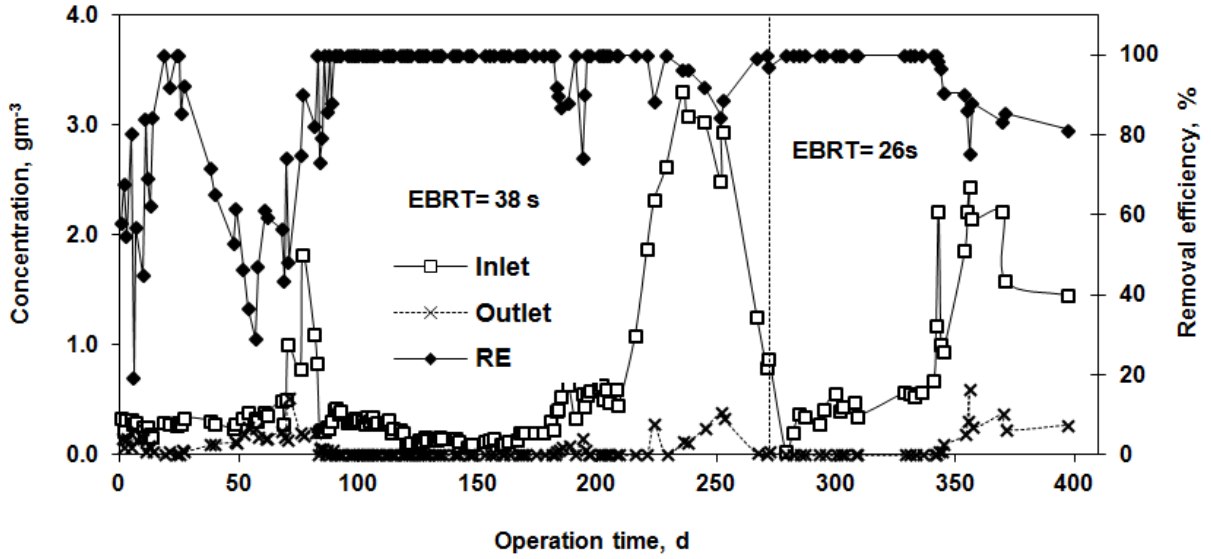
4.3.1 BTF performance at an EBRT of 38s

The BTF was acclimated by passing low concentrations of methanol (<0.5 gm^{-3}), α-pinene (<0.06 gm^{-3}) and H_2S (<0.5 gm^{-3}) through the reactor, at a gas-flow rate of 430 Lh^{-1}, corresponding to an EBRT of 38s (Figure 4.2).

Initially, despite the good removal of methanol and H_2S in the mixture (Figures 4.2 a and c), the removal efficiency (RE) of α-pinene was <50% (Figure 4.2b). This result could be explained more particularly by changes between pure culture growth conditions and pilot-scale environment, competitive exclusion, substrate availability (food to microorganism ratio) and toxic effect of contaminants [21]. These phenomena could induce a lower growth of α-pinene degraders, and more accurately *Rhodococcus sp*. and *Ophiostoma sp*. in the BTF, when compared to the growth of H_2S-degrading bacteria and the methanol-degrading microorganisms. The higher aqueous solubility or/and the rather good biodegradability of methanol and H_2S could explain their high removal in the BTF [22]

The RE profile during start-up was different for each pollutant (Figure 4.2). A high and stable efficiency level was reached after 50 d for hydrogen sulphide (RE-90%) and around 80 d for methanol (RE-100%). In turn, the RE of α-pinene improved only slightly and its value stabilized at about 75-80% after 150 d of BTF operation. Miller and Allen (2005) [23], reported that, in order to observe a significant concentration drop in biofilters, *i.e*., high REs, α-pinene degrading microorganisms would require longer acclimation periods to induce the production of enzymes that facilitate degradation.

In order to evaluate the performance of the system under these operating conditions, the concentration of H_2S was first increased to 1.5 gm^{-3} after the 180^{th} d; then, from days 209 to 254, the concentration of both methanol and α-pinene were increased slowly, from 0.4 to 3.3 gm^{-3} and 0.8 to 2.4 gm^{-3}, respectively, while the H_2S concentration was maintained at 1.5 gm^{-3}. When the concentration of H_2S was increased to 1.5 gm^{-3}, only α-pinene removal was affected and its removal efficiency decreased to 60%.When the concentration of VOCs was increased, the elimination of methanol and H_2S (100% RE) remained stable, while the removal of α-pinene decreased dramatically from 60% to 20%.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Removal efficiency, %
Operation time, d
EBRT= 38 s
EBRT= 26s
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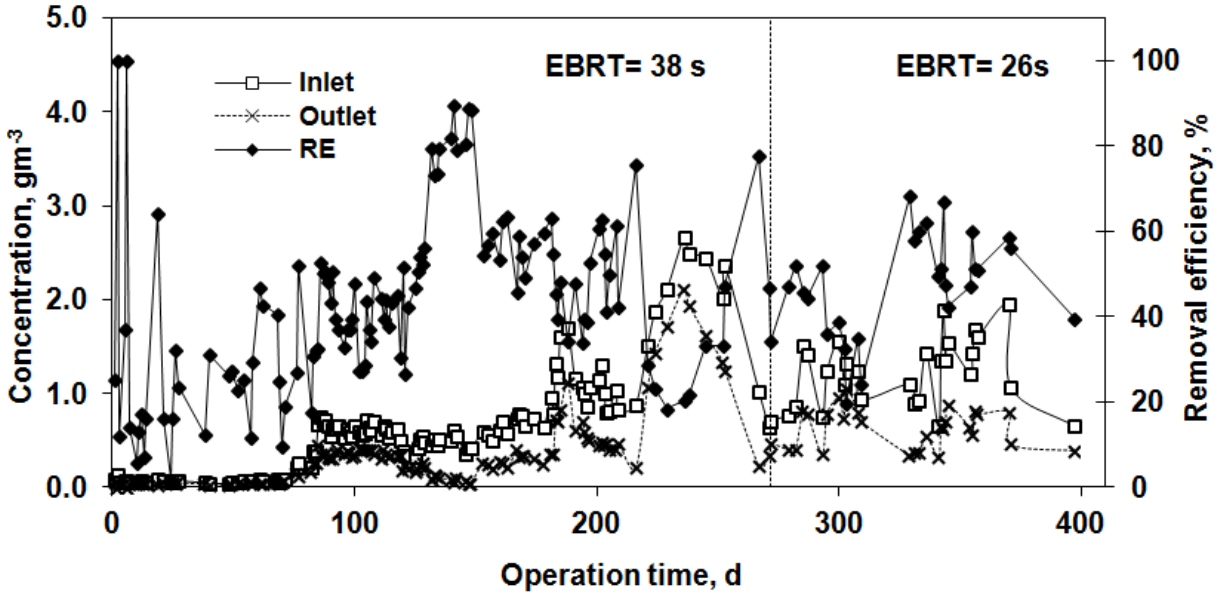
(a)


Concentration, gm-3
Removal efficiency, %
Operation time, d
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EBRT= 26s
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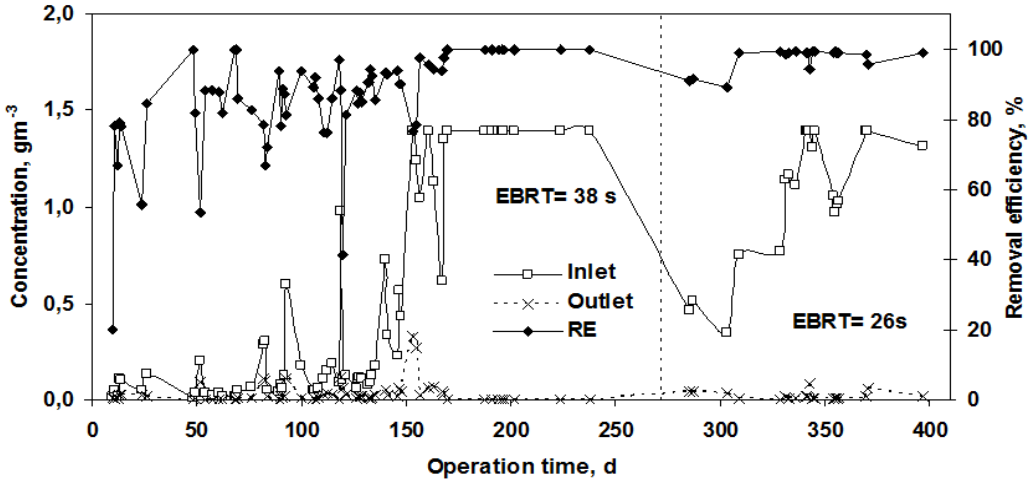
(b)



(c)

Figure 4.2: RE profile of; (a) methanol, (b) α-pinene, and (c) hydrogen sulphide at different initial concentrations and EBRTs.

4.3.2 BTF performance at an EBRT of 26s

In a second phase, experiments were carried out at a flow rate of 630 Lh^{-1}, for 118 d. From days 270 to 340, the inlet concentrations of methanol, α-pinene and H_2S were varied between 0.05 and 0.8 gm^{-3}, 0.7 and 1.3 gm^{-3}, and 0.3 and 0.7 gm^{-3}, respectively. In this concentration range, methanol and H_2S REs were 100% and >85%, respectively. However, the removal of α-pinene remained low (~20%) even when the concentration of methanol was lower than that of α-pinene. After the 340th d of operation, when the concentrations of both methanol (0.8 to 2.5 gm^{-3}) and α-pinene (1.3 to 1.9 gm^{-3}) were increased, the removal of α-pinene improved, stabilizing between 50 and 70% towards the end of this whole experimental period (Figure 4.2). The removal levels of both methanol and H_2S were consistently high in this phase, with 100% and >90% RE, respectively. The RE of α-pinene increased and achieved 60%. The observed biodegradation order, methanol > H_2S > α-pinene, may be due to limitations in biodegradability and preferential biodegradation of hydrophilic substrates compared to hydrophobic ones [24, 25].

The pressure drop in the BTF was <0.5 cm H_2O, during the first 100 d of operation, before stabilizing at around 0.8 cm H_2O for an EBRT of 38s. However, at an EBRT of 26s, due to relatively high gas-flow rates (630 Lh^{-1}), and due to the fact that α-pinene degraders grew well, leading to a somewhat better removal of α-pinene at 26s than 38s, the pressure drop increased to about 2 cm H_2O. This pressure drop value is comparable to the pressure drop observed in a previously operated acidic BTF for methanol and H_2S removal (<2 cm H_2O), and comparable with some of the literature observations from BTFs, where the pressure drop was found to vary between 0.3 to 2 cm H_2O [26]. Despite the long-term BTF operation, detachment of biomass did not occur at these two EBRTs (38 and 26s) as the aqueous mineral medium was continuously re-circulated over the packed bed at a constant flow rate of 2.8 Lh^{-1}.

4.3.3 Pollutant removal profile along the bed height

Substrate stratification profiles for methanol, α-pinene and H_2S removal was studied by measuring their concentration profiles along the bed height. The normalized methanol, α-pinene and H_2S concentrations *vs* bed height are shown in Figure 4.3, measured at a constant EBRT of 26s (300^{th} d). The concentrations of the individual pollutants were as follows: MeOH - 1.2 gm^{-3}, α-pinene - 0.35 gm^{-3}, and H_2S - 0.3 gm^{-3}, respectively. For all three pollutants, the biodegradation occurred mainly in the inlet section of the BTF. At these concentration levels, the first section (20 cm from the inlet) removed almost all the incoming methanol and nearly 88% of H_2S, while α-pinene removal was only 30%. α-Pinene removal in the later section of the filter bed improved only slightly (9%), reaching an overall α-pinene removal efficiency of 39%. This observed removal efficiency distribution may be due to a higher concentration of active H_2S degraders, methanol degraders and α-pinene degraders in the section close to the gas inlet than in the top of the BTF.

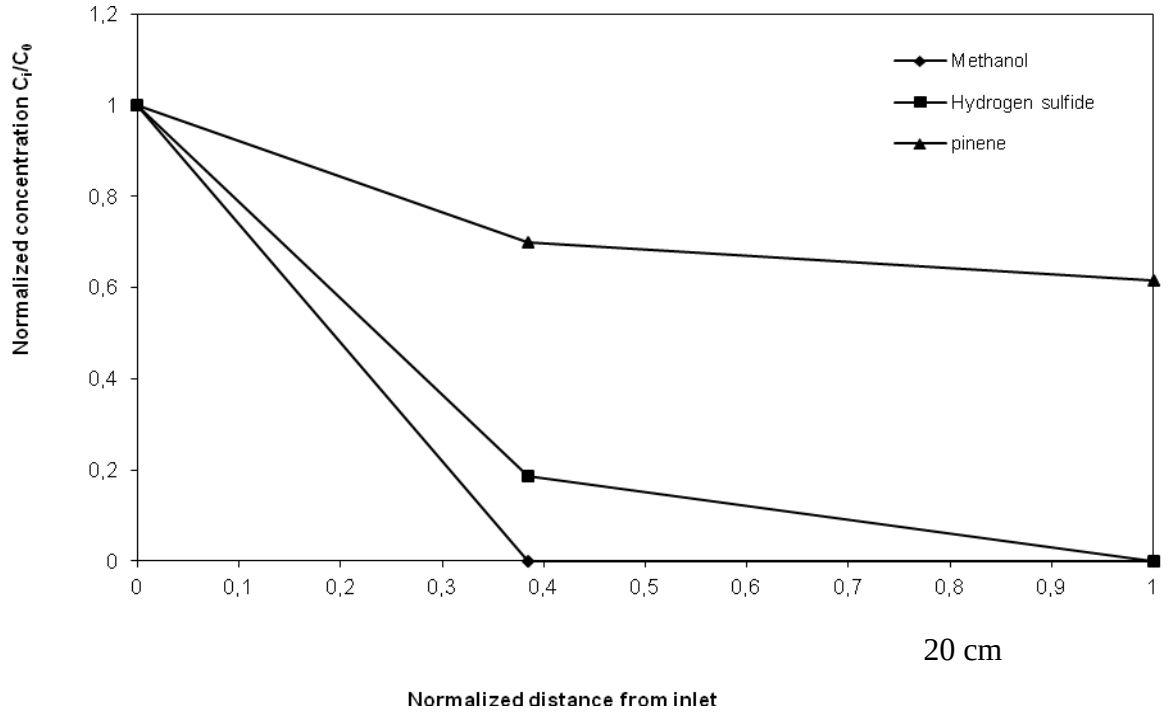


Figure 4.3: Normalized concentration profile along the bed height at an EBRT of 26 s (300th day); MeOH - 1.2 gm^{-3}, α-pinene - 0.35 gm^{-3}, and H_2S - 0.3 gm^{-3}. Gas sampling ports were located along the height of the reactor, at 20 cm (Port 1) and at 60 cm (Port 2) from the inlet.

4.3.4 Elimination capacity (EC) profiles

In order to estimate the limits within which the BTF functions, the EC is plotted against the ILR of methanol, α-pinene and H_2S, at both EBRTs, in Figures 4.4 a, b and c, respectively. For methanol and H_2S, a near linear relationship (slope = 1) between both variables was observed up to an inlet load of 337 $g_{methanol}m^{-3}h^{-1}$, and 192 g_{H_2S} $m^{-3}h^{-1}$, at both EBRTs. The EC does not reach the maximum value allowed to estimate the limits within which the biofilter functions. Higher EC could thus have been reached. Conversely, the EC *vs* ILR profile for α-pinene was somewhat different. At an EBRT of 38s, the EC increased linearly up to an ILR of 100 $g_{\alpha\text{-pinene}}m^{-3}$ h^{-1}, then the EC stabilized around 50-60 $gm^{-3}h^{-1}$ for ILRs >100 $g_{\alpha\text{-pinene}}m^{-3}$ h^{-1}. Two distinct operating regions can thus be interpreted from Figure 4.4b (EBRT = 38s), and discussed. It could be suggested that the region before an ILR of 100 $gm^{-3}h^{-1}$ corresponds to

the diffusion limiting region (DLR), while the region >100 $gm^{-3}h^{-1}$ corresponds to the reaction limited region (RLR). Presumably, the RLR occurs when the amount active α-pinene degrading microorganisms is insufficient to degrade all the gas-phase pollutant that could possibly be transferred to the biofilm. Under this condition, the quantity of pollutant that is transferred to the biofilm is always limited by the biodegradation capacity of the microbial community present in that biofilm. In BTFs, the trickling liquid, usually a well-defined nutrient medium, acts as a major medium for oxygen and substrate transport from the gas-phase to the biofilm [27]. As a result of the continuously tricking water phase in BTFs, the removal efficiencies of hydrophobic pollutants such as α-pinene do sometimes not reach 100%, even at low inlet loads, thereby affecting the maximum EC that can be reached [28]. On the other hand, at an EBRT of 26s, these two regions were not observed as the EC increased with the ILR during the whole experiment. The increase of the α-pinene degradation activity at an EBRT of 26s (EC_{max}-175 $gm^{-3}h^{-1}$, Figure 4.4c) could be due to the selective pressure imposed onto the α-pinene degraders, after long term operation under non-sterile conditions, and the possible emergence of strains that were better adapted to high gas-flow rates and high α-pinene concentrations [29].

Figure 4.4d shows the total EC (EC_{Total}) of VOCs as a function of the total ILR of VOCs, which was based on the total (methanol + α-pinene) concentration fed to the system. As shown in the figure, a high EC_{Total} (477 g_{VOC} $m^{-3}h^{-1}$) was achieved at an EBRT of 26s with almost 90% RE, and the corresponding EC_{max} for methanol and α-pinene, were 302 and 175 $gm^{-3}h^{-1}$, respectively. Also, as seen from the data points scattering, the performance of the BTF to remove VOCs was close to 90% at an EBRT of 38s, while the total VOC removal did hardly drop at a shorter EBRT of 26s.

4.3.5 Microbial component investigation

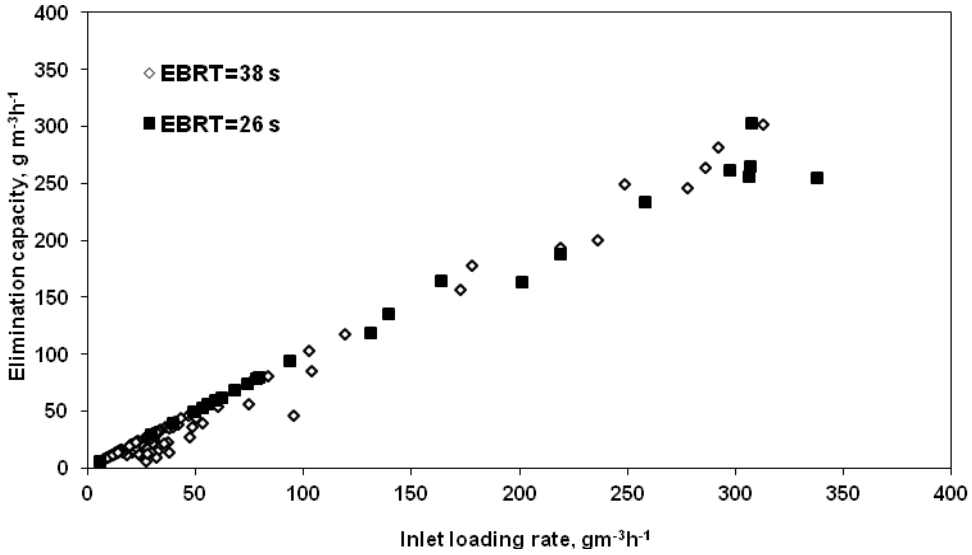
SEM observations (day 280; EBRT of 26s) highlighted the colonization of pall rings by bacterial and fungal biomass. The observed hyphal growth and morphology of fungi looked similar to the hyphae of *Ophiostoma sp*. as reported previously for a biofilter treating α-pinene [30, 1]. In both bacteria- and fungi-inoculated biofilters, some authors have reported that the inoculated microorganisms may sometimes remain dominant even after continuous operation of several months, above all under rather selective or extreme conditions [31, 12, 32]. To provide a better understanding of microbial implications in biotechniques for waste gas treatment [33, 18], molecular tools such as nucleic acid fingerprinting, have been applied to gain insight into the diversity and structure of microbial communities. The total bacterial community structure was explored along the height of the column, after long-term operation of the BTF, in order to evaluate the persistence of the inoculated microorganisms (autotrophic H_2S-degrading culture and *Rhodococcus* sp.), under the influence of different operating conditions. Species richness and Shannon diversity index (*H'*) were determined through the univariate DGGE pattern analysis (Figure 4.5). The species richness (6 bands for the autotrophic H_2S-degrading culture and 21 and 18 bands for BTF samples collected at 10 cm and 50 cm distance from the inlet, respectively) and diversity (*H'* = 1.2 for the autotrophic H_2S-degrading culture and H' = 2.8 and 2.1 for BTF samples collected at 10 cm and 50 cm distance from the inlet, respectively) is higher in BTF samples, when compared to the inoculated community (autotrophic H_2S-degrading culture). The low diversity of the inoculum can be explained by the emergence of a specific community able to degrade H_2S. As illustrated by clustering (Figure 4.5), two distinct groups could clearly be separated on the basis of species composition and relative abundances: autotrophic H_2S-degrading culture, and BTF samples. Moreover, the DGGE profile analysis highlights that two populations only coming from the autotrophic H_2S-degrading culture were maintained in the BTF. It has been reported that the structure of the microbial community developing in bioreactors after

acclimatization is usually dramatically divergent from the original inoculum even if the system has been seeded with an inoculum that was previously adapted to the contaminants [34, 19]. In this study, as the inoculum had previously been adapted to H_2S, this divergence seems to highlight the impact of the contaminants (the BTF was fed a mixture of H_2S, methanol and α-pinene) on both species composition and relative abundances with the development of specific methanol and α-pinene-degrading communities.

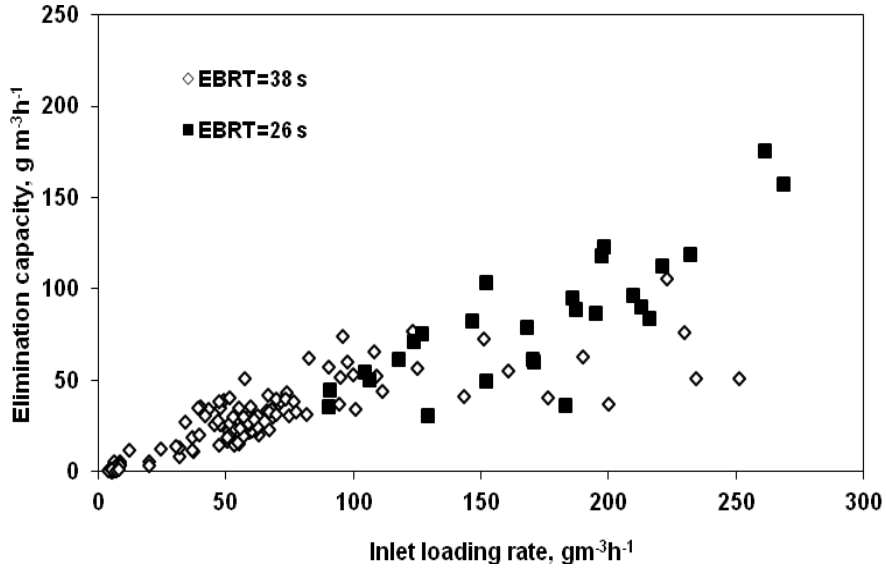
The results from the DGGE profile analysis appeared to reveal the presence of the inoculated *Rhodococus* strain within the BTF after long-term operation. This is not surprising as this microorganism had been selected for its potentiality to degrade α-pinene. Besides, this work also reveals the emergence of species which were not detected in the inoculum. They may proceed from the inoculum wherein their abundance was below the detection limit of the analytical method and the polluted gaseous effluent or aerosols through immigration mechanisms [35, 21]. Difference in diversity (2.8 for level 1 and 2.1 for level 2) and stratification of the microbial structures along the filter bed (percentage of similarity of 50-55% between level 1 and 2) were also evidenced. This longitudinal distribution of microbial communities seems to be correlated with the stratification pattern of the RE profiles of different pollutants. Methanol and H_2S were almost removed in the first 20 cm of the filter bed, while α-pinene removal (RE-39%) required the total height of the BTF. This result can be explained by differences in mass transfer and biodegradation capacities. Moreover, higher microbial population diversity was observed near the gas inlet port, suggesting that the constant availability of various resources provided adequate conditions for the development of a more diverse microflora [17].

Several published works in biological waste-gas treatment systems not only emphasized the higher microbial diversity near the inlet sections, but also markedly different community

structures down the biofilters in relation with macroscopic parameters [21](Cabrol and Malhautier, 2011).



(a)



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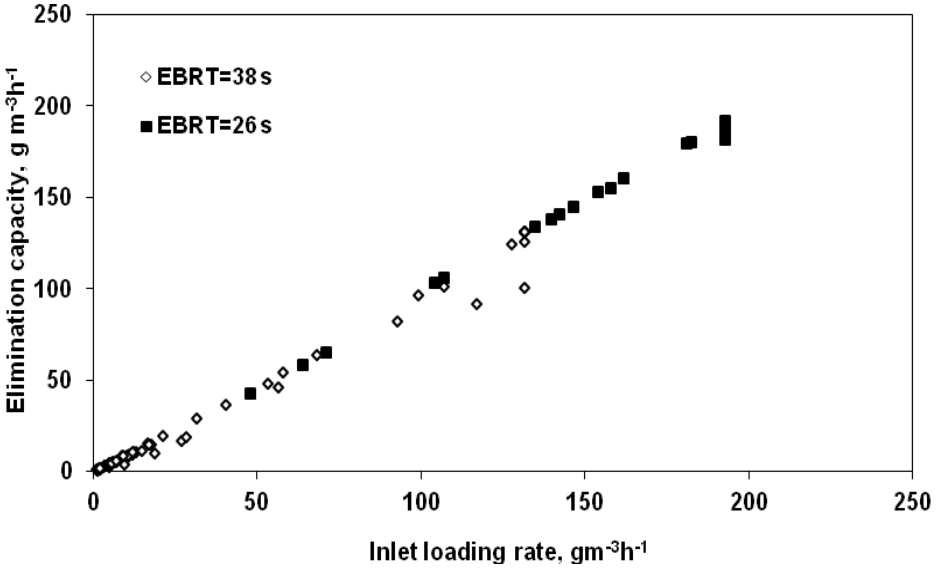

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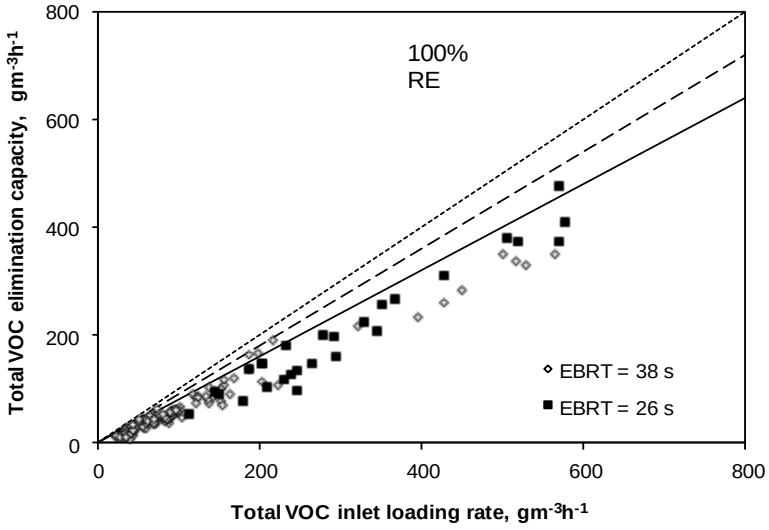

(d)

Figure 4.4: Influence of ILR on the EC of BTF for; (a) methanol, (b) α-pinene, (c) hydrogen sulphide removal, and (d) total VOC load *vs* total VOC EC of the BTF.

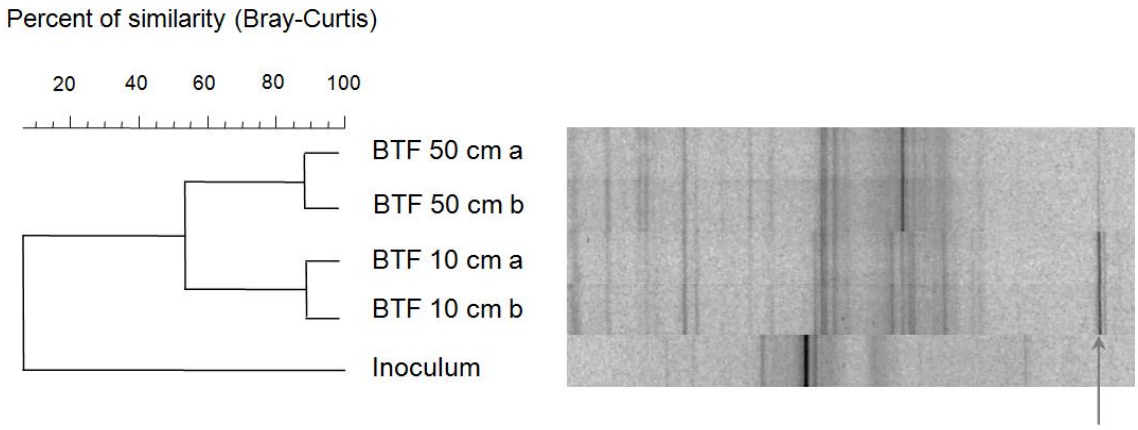

Figure 4.5: Characterization of microbes present in the BTF: UPGMA clustering of DGGE patterns based on Bray-Curtis similarities. BTF represents samples from the BTF, while the number next to the pilot name indicates the sampling depth from the gas inlet. Duplicate samples (a and b) have been realized. Inoculum corresponds to a sample from the H_2S autotrophic-degrading culture. *Rhodococcus* population (grey arrow) is indicated.

4.3.6 Practical implications and future work

The very high EC_{Total} (477 g_{VOC} $m^{-3}h^{-1}$) obtained in this single-stage BTF for a mixture of hydrophobic and hydrophilic VOCs together with an EC_{max} of 191 $gm^{-3}h^{-1}$ for H_2S prove the potential application of this technique for industrial purposes, for example in the pulp and paper and wood-related industries. The type of inoculum, whether mixed or pure cultures, and its propensity to get acclimated to the target gas-phase pollutant plays a crucial role in the removal of pollutants in the BTF. For full-scale waste-gas treatment systems, considering the practical difficulty to maintain the original inoculum within the system under non-sterile conditions, it is worth being aware that the inoculated biocatalyst does not necessarily need to remain dominant as long as performance remains high. In this study, among the different pure cultures inoculated in the BTF, only the *Rhodococus* strain remained dominant even after long-term operation. For successful long-term operation, the BTF should also be able to handle fluctuations in nutrient concentrations and pollutant loads, as this would alter the

composition of the microbial community within the BTF. Research is presently being carried out in order to evaluate the reactor´s performance under more vigorous transient conditions, and by subjecting the BTF to pollutant starvations.

4.4 CONCLUSIONS

A single-stage BTF, set-up for the removal of mixed VOC/VIC, can effectively overcome space constraints at industrial facilities by inoculating different microbial populations. The EC improved with operation time (EBRT-26s), reaching 302, 175 and 191 $gm^{-3}h^{-1}$, for methanol, α-pinene and H_2S, respectively. Methanol and H_2S degraders were active soon after start-up, while the performance of α-pinene degraders improved slowly due to the slow microbial adaptation. Some of the inoculated bacteria were still detected in the BTF after long-term operation. The distribution of microbial populations in the BTF correlated well with the stratification pattern of the RE profiles of different pollutants.

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Chapter 5

One-stage bioreactor: neural modeling and performance under transient conditions

The modified version of this chapter was published as:

López, M.E., Boger, Z., Rene, E.R., Veiga, M.C., Kennes, C. (2014) Transient-state studies and neural modeling of the removal of a gas-phase pollutant mixture in a biotrickling filter. Journal of Hazardous Materials, 269, 45-55.

ABSTRACT

The removal efficiency (RE) of gas-phase hydrogen sulfide (H), methanol (M) and α-pinene (P) in a biotrickling filter (BTF) was modeled using artificial neural networks (ANNs). The inlet concentrations of H, M, P, unit flow and operation time were used as the model inputs, while the outputs were the RE of H, M and P, respectively. After testing and validating the results, an optimal network topology of 5-8-3 was obtained. The model predictions were analyzed using Casual Index (CI) values. M removal in the BTF was influenced positively by the inlet concentration of M in mixture (CI=3.79), while the removal of P and H were influenced more by the time of BTF operation (CI=25.36, 15.62). The BTF was subjected to different types of short-term shock-loads: 5-h shock-load of HMP mixture simultaneously, and 2.5-h shock-load of either H, M, or P, individually. It was observed that, short-term shock-loads of individual pollutants (M or H) did not significantly affect their own removal, but the removal of P was affected by 50%. The results from this study also show the sensitiveness of the well-acclimated BTF to handle sudden load variations and also revival capability of the BTF when pre-shock conditions were restored.

KEYWORDS: Biotrickling filter, neural modeling, casual index, interaction effects, shock-loads

5.1 INTRODUCTION

The gradual strengthening of domestic paper demand alongside price levels in the global raw material markets and economic growth has promoted an increase in the production output from the pulp and paper industry. The pulp and paper industry has constantly been striving to reduce its emissions of odorous compounds from various plant operations that usually contain a mixture of volatile organic compounds (VOCs) and volatile inorganic compounds (VICs). Hydrogen sulfide (H), methanol (M) and α-pinene (P) are, respectively, representative inorganic, hydrophilic and hydrophobic pollutants present in emissions from pulp and paper industries [1]. Among the different treatment techniques used to eliminate these compounds from waste-gas emissions, biodegradation is the most versatile and promising option, considering the degree of treatment achieved and their low cost [2-5]. Biodegradation exploits the inherent advantages of microorganisms by transforming hazardous pollutants to innocuous end-products.

There are however only few publications that have focussed on the simultaneous removal of H (a VIC) and VOCs. In those studies, the pH of the biofilm was shown to drop when H was converted to sulphuric acid, which in turn hindered the activity of the microbes that were degrading the VOC [6-10]. Among the different bioreactors tested for handling a mixture of VIC and VOC in waste-gas emissions, biotrickling filters (BTF) have proven to be more advantageous and effective than other bioreactor configurations [3,4,11-13]. BTF use a trickling nutrient medium for sustaining microbial activity of the attached biofilm [14]. The medium also acts as a buffer, especially for compounds that are difficult to degrade and for compounds that generate acidic metabolites [15].

In an effort to understand the mechanism of pollutant removal from a waste-gas mixture containing VICs and VOCs, and to achieve high biotreatment efficiencies, two bioreactor configurations were proposed recently in our laboratory. The first configuration was a two-

stage system comprising a BTF and a biofilter (BF), wherein H and M were degraded in the first-stage BTF by autotrophic bacteria and an acid tolerant yeast (*Candida boidinii*) followed by the removal of the hydrophobic VOC, α-pinene, in the second-stage BF by a fungus, *Ophiostoma stenoceras* [9]. The second configuration was a single-stage BTF that was inoculated with a mixture of an autotrophic H_2S-degrading culture, *Candida boidinii, Rhodococcus erythropolis* (terpenes degrading microorganism) and *Ophiostoma stenoceras*. In the latter, high maximum elimination capacities (EC) of 191, 302 and 175 $gm^{-3}h^{-1}$ were reached, with >99%, 100% and 67% removal of H, M and P, respectively [16].

Traditionally, the performance of conventional waste-gas treatment systems have been modeled using process-based models that considers mass balance principles, simple reaction kinetics and a plug flow behavior of the air stream [3,4,13]. Phenomenological models are anchored on the underlying physico-chemical and biological processes and the results obtained generally provide a good understanding and interpretation of the system dynamics. An alternate modeling procedure consists of a data-driven approach wherein the principles of artificial intelligence (AI) are applied with the help of artificial neural networks (ANNs). The concept of neural network modeling has widespread applications in the field of applied science and environmental engineering [17-21]. ANN was used for modeling the behaviour of a large wastewater treatment plant in Israel [20]. However, ANNs were only very recently used for modeling waste-gas treatment systems such as BFs and BTFs [22-26]. Rene et al. [23] modeled the performance of a BF (RE, %) using a backpropagation neural network (BPNN) wherein inlet styrene concentration and unit flow (UF= gas-flow rate/volume, h^{-1}) were used as the inputs. The best network topology obtained through trial and error was found to be 2-4-1. The ANN model is considered (wrongly) as a "black box", but system knowledge can be elicited from the trained ANN model by the Causal Index (CI) calculations [27]. ANNs can be considered as a mathematical structure that is contrived to mimic the biological neural

system in terms of the information processing functions of neurons [21]. These data-driven models can also be used to identify complex patterns in datasets, which often are not represented by mathematical formulae.

One of the specific objectives of this research was to model the long-term performance data of a BTF [16] using a multilayer perceptron (MLP), as shown in Fig. 5.1, in terms of H, M and P removal efficiencies (REs), and envisage the most important parameter affecting the RE of individual pollutants using CI values. As a continuation of our sustained research efforts to better understand the performance of such BTF under different operating conditions, this study was planned with the following objectives: (i) identify the interaction effects between different pollutants from the ANN model, (ii) understand the interaction pattern among the VOCs, *viz.*, M and P, and (iii) study the effect of transient-state operating conditions on the BTFs performance.

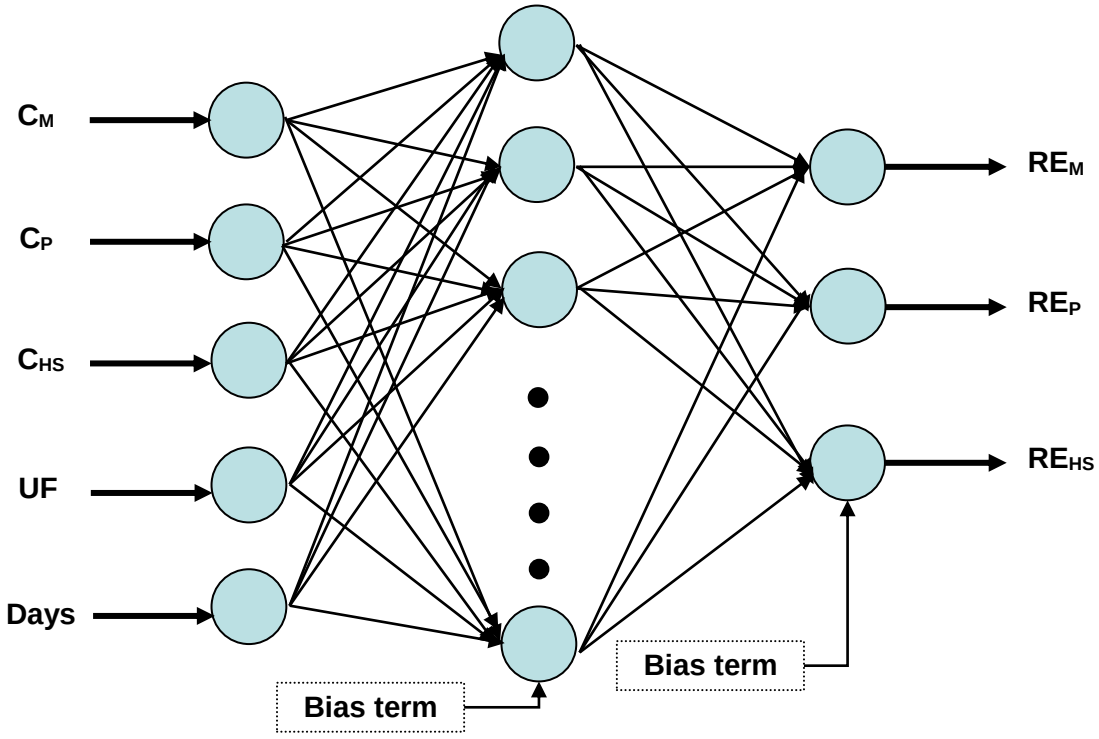

Figure 5.1: Schematic of a MLP used to model the performance of the BTF

(architecture: 5-8-3)

5.2 MATERIALS AND METHODS

5.2.1 Microorganisms and medium composition

The BTF was originally inoculated with a mixture of an autotrophic H-degrading culture, as well as *Candida boidinii*, a M degrading acid-tolerant yeast, *Rhodococcus erythropolis* and *Ophiostoma stenoceras* [16]. The composition of the mineral salt medium used in the BTF, was (in gL^{-1} of de-ionized water); K_2HPO_4: 0.5, $MgSO_4 \cdot 7H_2O$: 0.1, KH_2PO_4: 4.5, NH_4Cl: 2, and 2 mL trace elements and vitamin solutions.

5.2.2 BTF setup and operation

The BTF (Fig. 5.2) was constructed of glass, with 94 mm inner diameter (ID)×700 mm height (total operating volume of 4.55 L), and packed with polypropylene pall rings [16]. The gas-phase concentrations of the individual pollutants, H, M and P, were generated as described elsewhere [9, 16]. The three pollutant streams were combined in a mixing chamber, and fed through the bottom of the BTF, while the nutrient medium was continuously recirculated over the Pall ring bed using a peristaltic pump (323E/D, Watson-Marlow Limited, England), at a constant volumetric flow rate of 2.77 Lh^{-1}. The pH of the recirculated nutrient medium was maintained constant, at 6.0±0.4, by dosing a 2N NaOH solution. After estimating and reporting the maximum performance of the BTF [16], the interactions between the VOCs (M and P) were tested by holding the concentration of one pollutant constant, in the absence of H, and increasing the concentration of the other VOC from low to high levels. The transient-state performance of the BTF, in the form of short-term shock-loads, was tested by: a) increasing the concentration of all three pollutants simultaneously for 5-h, or b) increasing the concentration of only one pollutant, either H, M or P, for 2.5-h, while maintaining the concentration of the other two pollutants nearly constant. Two empty bed residence times (EBRTs) were tested during long-term steady-state experiments (38 and 26s), while the EBRT was maintained constant at 26s during studies on interaction effects and shock-loads.

The performance of the BTF was assessed by estimating the RE (%) of individual pollutants, and the elimination capacity (EC, $gm^{-3}h^{-1}$) under different inlet loading rates (ILRs) [5].

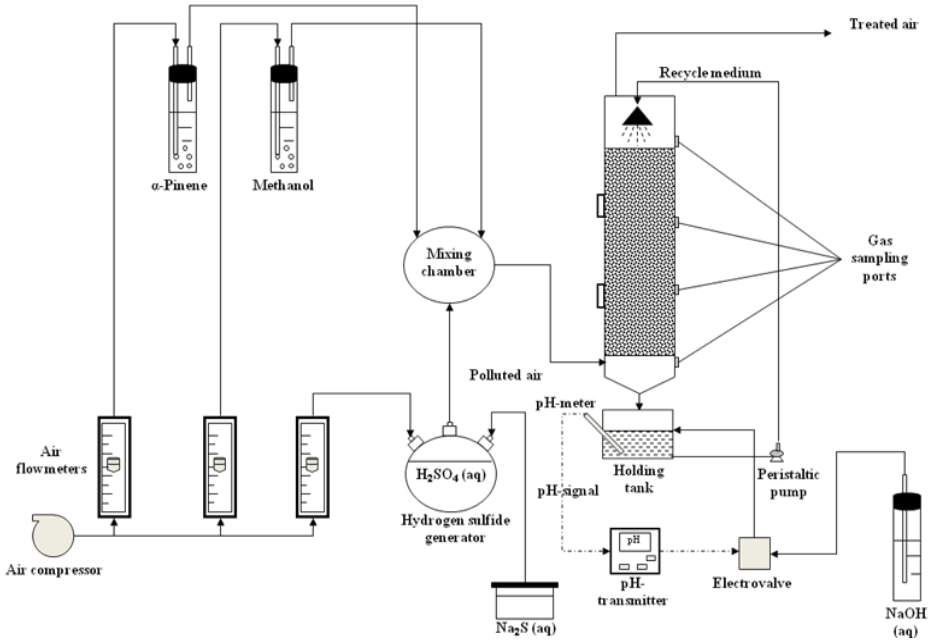

Figure 5.2: Schematic of the one-stage BTF for the removal gas-phase methanol, α-pinene, and hydrogen sulfide from polluted air

5.2.3 Analytical methods

The inlet and outlet H concentrations (maximum measurable limit of 1000 ppmv) were measured using a hand-held sensor (Dräger Sensor XSEC H_2S HC6809180). Some of the final results were also obtained with a GC Tracer. Gas-phase concentrations of M and P, as well as M in the liquid-phase (collected from the nutrient tank and centrifuged to remove the suspended biomass) were measured *via* gas chromatographic analysis using a Hewlett-Packard 6890 series II GC, equipped with a flame ionization detector (FID) [9].

5.2.4 ANN model development

5.2.4.1 Model input-outputs and data division

A three layered ANN (input-hidden-output layer) was developed for the BTF using inlet concentrations of H (C_{HS}), M (C_M), P (C_P), *UF* and BTF operational time (days) as the model inputs, while the RE of H (RE_{HS}), M (RE_M) and P (RE_P) were used as the outputs (Fig. 5.1).

The reason for including BTF operation time as one of the model inputs can be justified as follows: the operation time appeared to influence the degree of acclimation and the prevalence of active P-degrading microbial community within the BTF, and the performance of the BTF to remove P improved only after ~150 d, although, at that time during experiments, the RE of P was suspected to be largely influenced by the antagonistic interaction effects resulting from the presence of M, an easily biodegradable VOC in the gas-phase mixture [16].

The experimental data (112 data points) were non-randomly divided into training (N_{Tr}:64%), test (N_{Te}:25%), and validation sets (N_v:11%) [18,21]. The test data was kept aside during network training and was used only for evaluating the predictive potentiality of the trained network, while the validation set was used to periodically check the error convergence during training. The closeness of prediction between the experimental and model predicted outputs were evaluated by computing the coefficient of determination (R^2) and mean average percentage error (*MAPE*) values [18,25]. The data were also normalized and scaled to the range of 0 to 1 using Eq. 5.1, so as to suit the transfer function in the hidden (sigmoid) and output layer (pure linear).

$$\hat{X} = \frac{X - X_{min}}{X_{max} - X_{min}} \qquad (5.1)$$

where, $\hat{X}$ is the normalized value, X_{min} and X_{max} are the minimum and maximum values of X respectively.

5.2.4.2 Network parameters

The internal parameters of the back propagation network namely epoch size, error function, number of neurons in the hidden layer (N_H), learning rate (η), momentum term (α), training cycle (T_c) and transfer function are to be appropriately selected (using trial and error) to obtain the best network architecture that gives high predictions for the performance variables (Table 5.1). In this study, the number of neurons in the input layer (N_I = 5) and output layer

(N_O = 3) were chosen based on the number of input and output variables to the network. The connection weights were initialized using the inbuilt function of the software, with random values, and adjusted in order to minimize the network error. Several network architectures were trained until high R^2 values were achieved between the model fitted and experimentally determined RE profiles. The best network topology was selected based on the high R^2 values. A detailed study on the effect of internal network parameters on the performance of back propagation networks [28] and the procedure involved in selecting the best network topology have been described elsewhere [21,23,25,26,]. The MLP was developed using the NNMODEL shareware version software (Version 1.4, Neural Fusion, NY).

Table 5.1: Network training parameters for choosing the best network architecture

Training parameters	Range of values	Best value
Training cycle	1000 – 20,000	10,000
Number of neurons in input layer	5	5
Number of neurons in hidden layer	5-12	8
Number of neurons in output layer	3	3
Learning rate	0.1-0.9	0.8
Momentum term	0.1-0.9	0.8
Fixed parameters during training		
Error tolerance	0.0001	
Epoch size	70	
Training algorithm	Back propagation	
Number of data points used	112	
Number of training data set	71	
Number of test data set	29	
Number of validation data set	12	

5.2.4.3 Discovering relationships in the trained ANN

Once an ANN is trained, there are several techniques available to gain knowledge of the modeled system by simple analysis of the trained ANN [29]. One of them is the Causal Index (CI) proposed by Baba et al. [27]. The CI is calculated as the sum of the products of all "pathways" between each input to each output (Eq. 5.2),

$$CI = \sum_{j=1}^{h} W_{ji} \times W_{kj} \qquad (5.2)$$

where there are '*h'* hidden neurons, W_{ji} are the connection weights between input *i* to hidden neuron *j*, and W_{kj} are the connection weights from hidden neuron *j* to output *k*, respectively.

Examining the CI for each output as a function of the inputs number reveals the direction (positive or negative) and the relative magnitude of the relationship of the inputs on the particular output. Although somewhat heuristic, it is more reliable than local sensitivity checks, and it was found that engineers recognize from their own experience some of the CI relationships and thus are more likely to accept the new knowledge revealed by the CI analysis of the ANN model (Zvi Boger, unpublished). The CI coefficients advantage is that they do not depend on a particular input vector, but on the connection weight set that represents all the training input vectors. This is also one of their limitations, as a local situation may be lost in the global representation.

5.3 Results and discussions

5.3.1 Maximum performance of the BTF

The long-term performance of the BTF was evaluated for ~400 d by varying the concentrations of individual H, M and P, at two different EBRTs of 38s and 26s. Regarding to EC *vs* ILR profiles, for M and H removal, a near linear relation (slope = 1) between the two variables was observed up to an inlet load of 337 and 192 $gm^{-3}h^{-1}$, respectively. However, for P, the EC increased with an increase in ILR, up to a maximum, yet at a slower rate, but then it almost stabilized within a rather wide range. A high EC_{Total} (477 $gVOCm^{-3}h^{-1}$) was achieved

at an EBRT of 26s with ~90% RE, and the corresponding EC_{max} for M, P, and H were 302, 175, and 191 $gm^{-3}h^{-1}$, respectively. Microscopic observations of biomass attached to the pall-rings, at different bed heights, as well as results from molecular biology analysis suggested that some microorganisms of the original inoculum were still present in the BTF after long-term operation, and some new microbial species appeared in the long run as well [16].

5.3.2 Development of the neural network model

The performance data of the BTF reported by López et al. [16] were modeled using a three-layered ANN, with different combinations of network parameters (Table 5.1) so as to achieve high R^2 values (target value = 1, *i.e.*, 100% correlation between measured and predicted variables) and low *MAPE* values. This was achieved by a vigorous trial and error approach, by keeping some training parameters constant and by slowly moving the other parameters over a wide range of values, as suggested in some previous works [19,25]. The following observations were made during network training: (i) increasing the N_H from 5 to 8 increased the R^2 values from ~0.6 to 0.82, but this value did not improve during training when the N_H were increased beyond 8, and hence 8 was considered as the optimum N_H, (ii) T_c appears to have a larger influence on increasing the R^2 values and it was observed that the model predictions were high (>0.82) and significant when the T_c was set to 10,000, (iii) similarly, increasing the η from 0.1 to 0.8 increased the mapping efficiency of the network, and (iv) high values of α (0.8) showed R^2 values >0.8 in the training and test data during the predictions of RE profiles of different pollutants. Thus, it can be concluded that high η (0.8), high α (0.8), and a T_C of 10,000 with 8 neurons in the hidden layer are favourable values of the internal network parameters. The experimental and model fitted removal profiles of M, P and H are shown in Fig. 5.3, for the training and test datasets. The R^2 values during training were 0.8272, 0.8762, and 0.8852 (*MAPE* values: 0.92, 13.8 and 2%) for REs of M, P and H, respectively. Thus, only about 12-18% of the total deviations in the training data could not be

explained by the model for predicting the RE profile of these compounds in the BTF. Among the test data predictions (Figs. 5.3D-F), although the model mapped both H and M removal adequately, it was not able to map P removal well mainly due to the scatteredness of the RE profiles from ~20 to 80% (Fig. 5.3E). This could be explained by the slow growth of P degraders compared to the growth of H and M degrading microorganisms, resulting in low P removals, and the relatively longer acclimation times (~150 d) required by P degraders at an EBRT of 38s to start utilizing P as the carbon source [16]. The best network architecture for the BTF was found to be 5-8-3.

5.3.3 Interaction effects between input parameters

The CI values were examined for each output as a function of the inputs and their connection weights between neurons in different layers (Tables 5.2 and 5.3), and the gathered information is particularly useful in identifying the effect of key parameters on the output(s) of the developed ANN Model [30]. This approach has been reported to be semi-quantitative, although it would serve as a guide to reduce the amount of experimentation required [31]. From the CI values shown in Table 5.3, it is clearly evident that the RE of M is influenced by its own concentration, in the *+ve* direction (3.796), while the concentration of P negatively influences M removal (-9.612). This can partly be explained by the reported biodegradation order of the pollutants in the BTF, M>H>P [16], and due to slower (bio)degradation rates of these pollutants in the mixtures caused by substrate inhibition from toxicity, non-competitive inhibition, competitive inhibition, and the preferential utilization of hydrophilic substrates compared to the hydrophilic ones [32,33].

Concerning H and P removal, the operating time of the BTF appears to strongly influence the removal of these pollutants, as evident from the high *+ve* CI values of 15.625 and 25.368, respectively. For all the pollutants, an increase in the gas-flow rate, *i.e.*, UF, showed an antagonistic effect on the RE. In BFs and BTFs, it is not unusual to observe a decrease in the

RE profiles of the gas-phase pollutant due to an increase in the gas-flow rate, *i.e.*, a decrease in the EBRT. The REs of the pollutant in BFs and BTFs are mainly controlled by the mass transfer rate of the pollutant from the gas-phase to the biofilm-phase, and by the thickness of the gas-liquid interface layer, which is in fact controlled by the EBRT and the trickling rate of the aqueous phase. At high EBRTs (*i.e.*, low gas-flow rates), there is more contact time between the biofilm-layer and the pollutant, and thus better removal of the pollutant [34,35]. The better removal of P at an EBRT of 26s (EC_{max}:175 $gm^{-3}h^{-1}$), compared to an EBRT of 38s, could have resulted from the selective pressure imposed onto the P degraders, after long-term operation under non-sterile conditions.

Table 5.2: Connection weights of the developed ANN model (5-8-3)

Input layer to hidden layer								
	HID1	HID2	HID3	HID4	HID5	HID6	HID7	HID8
C_M	-2.741	4.271	-3.563	16.230	-13.631	1.638	-2.551	33.009
C_P	-0.972	-4.068	1.406	-2.546	-9.217	-1.848	11.273	0.313
C_{HS}	-1.745	-1.459	0.163	-1.088	-0.503	-2.734	-6.334	-8.522
UF	-1.653	-11.234	0.929	-3.006	-6.480	-7.491	-3.528	1.449
Days	-3.188	2.372	-0.635	-9.578	7.634	0.367	-10.413	-31.471
Bias	2.243	4.128	-1.209	1.720	4.011	1.759	2.136	5.442

Hidden layer to output layer				
	RE_M	RE_P	RE_{HS}	HID1-HID8-Hidden layer neurons
HID1	-2.342	2.743	-3.492	Bias-Bias term
HID2	5.909	2.333	5.313	***Input to the model***
HID3	4.707	0.640	-0.157	C_M – Inlet concentration of methanol, gm^{-3}
HID4	0.069	2.568	-0.094	C_P – Inlet concentration of α-pinene, gm^{-3}
HID5	0.692	8.151	-0.338	C_{HS} – Inlet concentration of hydrogen sulfide, gm^{-3}
HID6	0.348	5.590	1.184	*UF* – Unit flow, h^{-1}
HID7	-0.246	8.149	1.864	*Days* – BTF operation time, days
HID8	0.178	-3.018	-0.270	***Output of the model***
Bias	0.219	-0.513	1.332	RE_M – Removal efficiency of methanol, %
				RE_P – Removal efficiency of α-pinene, %
				RE_{HS} – Removal efficiency of hydrogen sulfide, %

Table 5.3: Casual index (CI) values for the trained ANN Model

Parameter	RE_M, %	RE_P, %	RE_{HS}, %
C_M, gm^{-3}	3.796	-5.588	5.310
C_P, gm^{-3}	-9.612	-10.941	-0.922
C_{HS}, gm^{-3}	1.670	-6.749	-1.332
UF, h^{-1}	-2.562	-20.393	-8.561
Days	1.381	25.368	15.625

Note: C_M, C_P and C_{HS} are the inlet concentrations of methanol, α-pinene and hydrogen sulfide, respectively; *UF*-unit flow; *Days*-BTF operation time; RE_M, RE_P and RE_{HS} are the removal efficiencies of methanol, α-pinene and hydrogen sulfide, respectively.

Figs. 5.4 (A-C) depicts important contours for the removal of P in the BTF, as a function of different combinations of input parameters. These complex contours reveal adequate information about the range of conditions required to achieve the desired RE of P, which can be interpreted as follows: P concentrations >1.8 gm^{-3}, irrespective of the M concentrations leads to RE >65% (Fig. 5.4A). However, for M concentrations >1.5 gm^{-3}, and P concentrations <1.5 gm^{-3}, the RE of P decreased, (ii) an increase in the UF from low to high values, irrespective of the varying H concentrations (CI=-20.393), decreased the RE of P (Fig. 5.4B), and (iii) an increase in the BTF operating time improved the RE of P (97.7%), for concentrations <0.9 gm^{-3}**;** this increase however depended on the concentration levels of the other two pollutants in the mixture (Fig. 5.4C). Briefly stating, the predictive ability of the developed ANN model was reflective of the actual experimental behaviour, and with the help of CI estimation, the best operating conditions of the BTF, and the synergistic and antagonistic interactions between the five input parameters were envisaged.

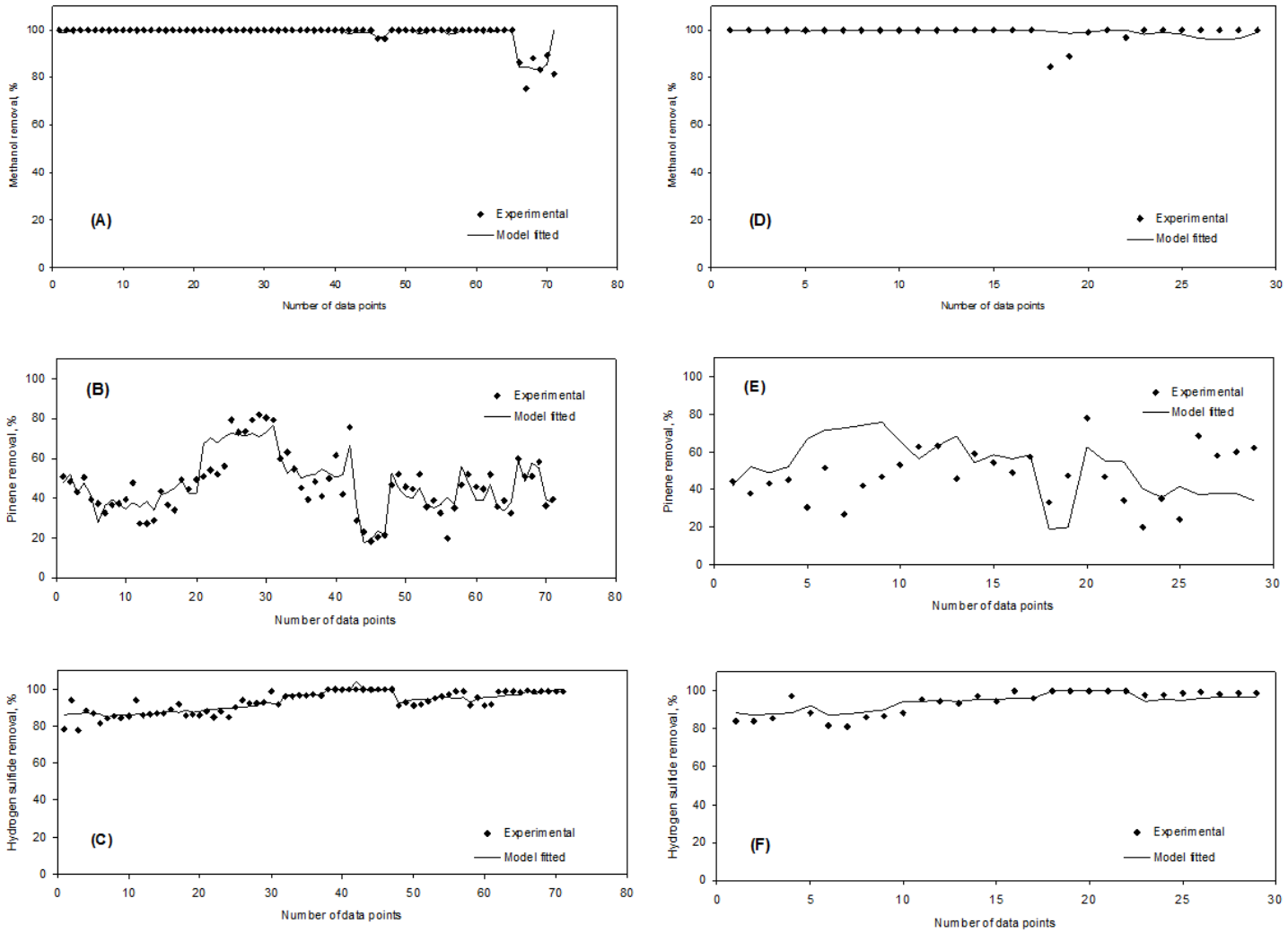

Figure 5.3: Experimental and ANN model fitted profiles: Training data for the removal of (A) methanol, (B) α-pinene, and (C) hydrogen sulfide, and test data for the removal of (D) methanol, (E) α-pinene, and (F) hydrogen sulfide

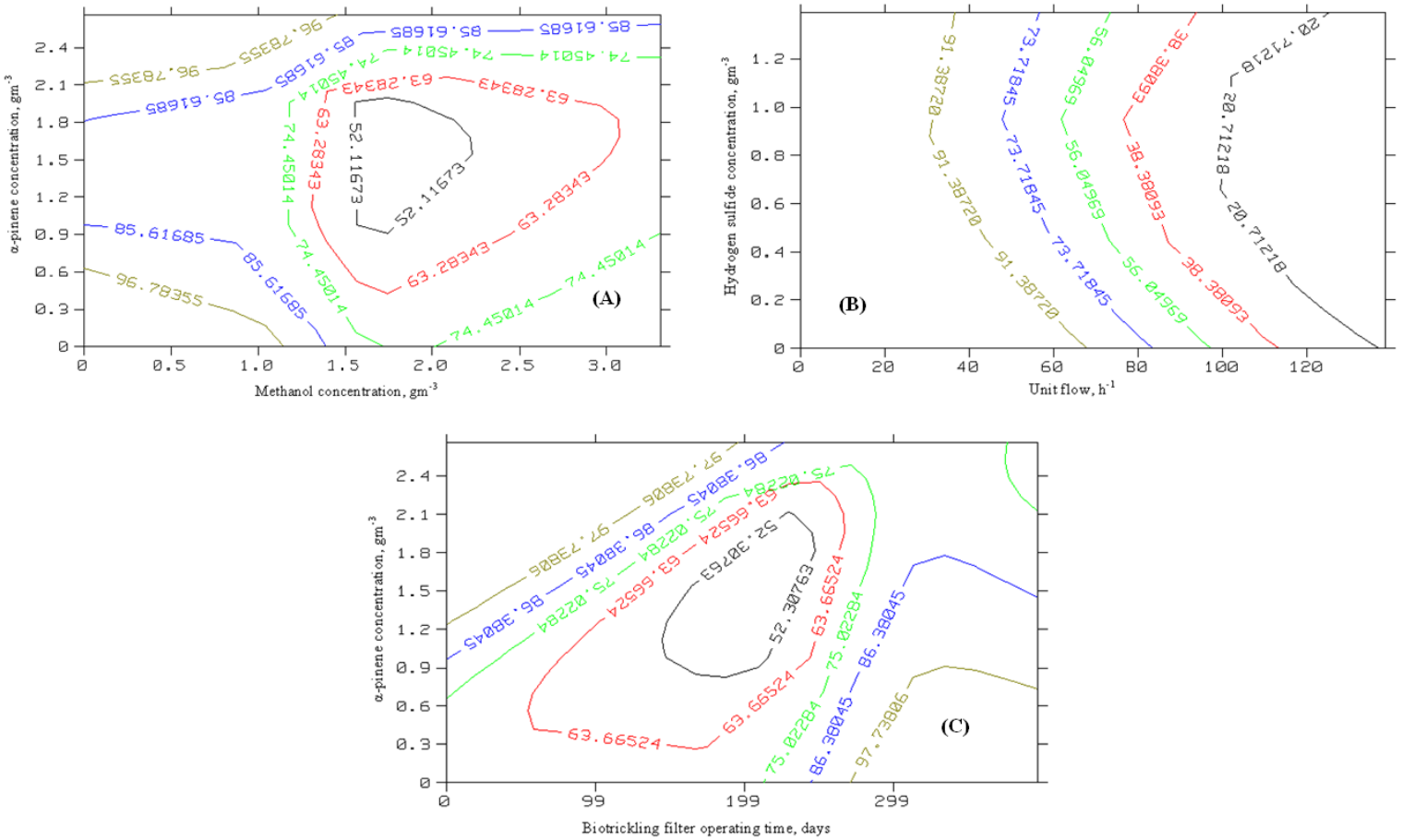

Figure 5.4: Removal of α-pinene as a function of: (A) inlet methanol and α-pinene concentrations, B) unit flow and hydrogen sulfide concentrations, and C) BTF operational time and α-pinene concentrations

5.3.4 Interaction between VOCs

An understanding of the interaction effects between the different VOC species and a prior estimation of their optimal range of concentrations that will not cause self and mutual inhibition to the removal of other pollutants can be beneficial to maintain long-term BTF performance and prevent the biofilm from losing its activity. Thus, for VOCs like M and P having different physico-chemical properties and biodegradation rates, it is expected to observe interactive effects that could affect the overall VOC removal in the bioreactor. Experiments were performed at a constant EBRT of 26s, by increasing the concentrations of either M or P, and by maintaining the concentration of the other pollutant at low values, resulting in varying ILRs of M or P to the BTF. During these experiments (~512h), H was not supplied to the bioreactor. Fig. 5.5 shows the effect of increasing M and P loading rates on the removal of M and P from the BTF. From Figs. 5.5 A and B, it can be seen that, an increase in the ILR of M (ILR_M) from 60 to 200 $gm^{-3}h^{-1}$, (ILR_P: ~50 $gm^{-3}h^{-1}$), decreased its removal from 100 to 75%. At this stage (100h), the removal of P decreased by ~15% due to an increase in M concentration. However, M concentration in the nutrient collection tank also started to build up, increasing from an initial value of 0 (time t=0h), to ~9 gL^{-1} (t=128h). The gas-phase M concentrations were reduced to low values (ILR_M~50 $gm^{-3}h^{-1}$) for the next 72h, in order to remove the accumulated M from the liquid-phase. The gas-phase concentrations of M were then increased when M in the liquid-phase was completely removed through biodegradation, to nearly similar values, reaching an ILR_M of ~190 $gm^{-3}h^{-1}$ at the 320^{th} h. This increase once again led to the build up of M in the liquid-phase. A similar strategy was followed in order to eliminate the sorbed fraction of M from the liquid-phase. In order to envisage the maximum performance of the system to varying concentrations of M, the ILR_M was increased to a maximum of ~508 $gm^{-3}h^{-1}$.

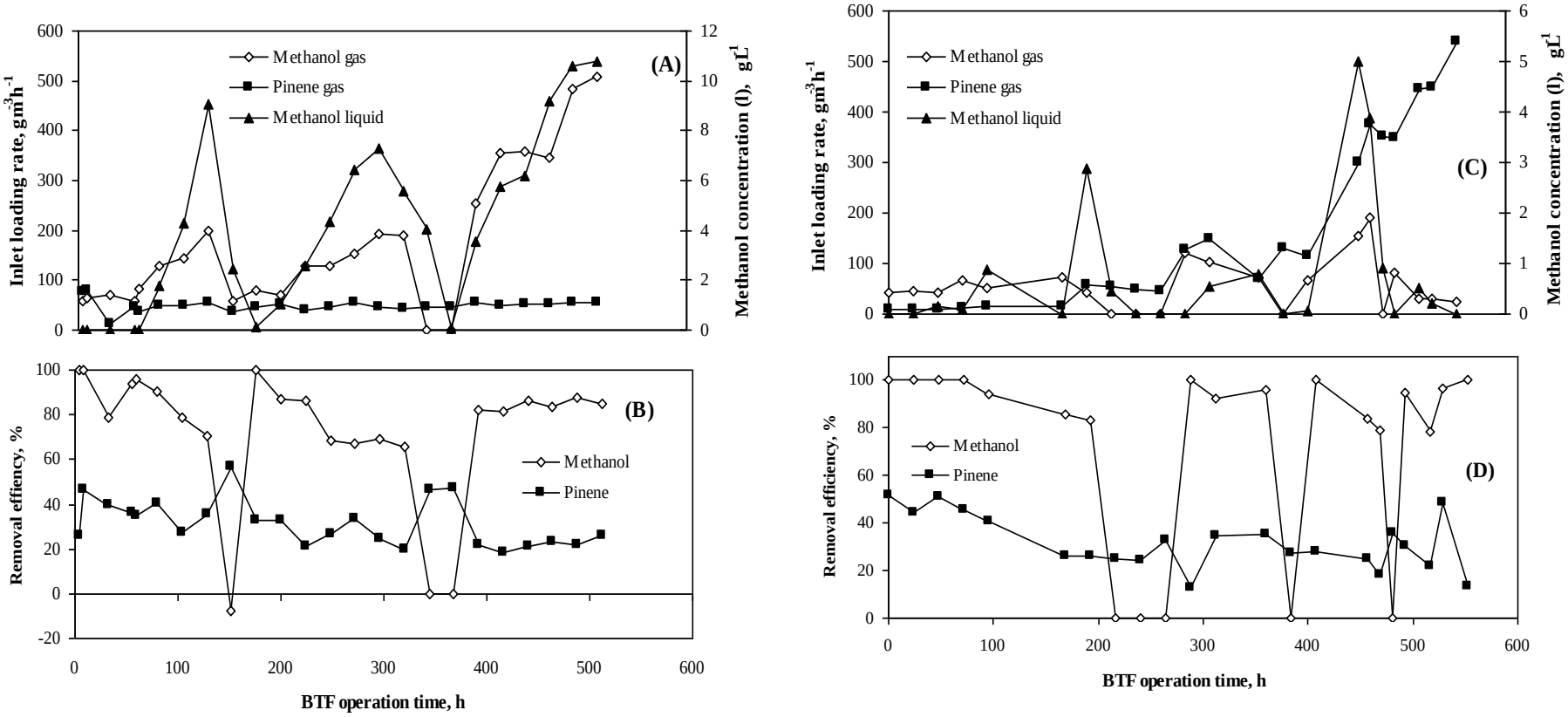

Figure 5.5: Effect of increasing methanol (A, B) or α-pinene (C, D) load on the evolution of liquid-phase methanol profiles (A, C) and RE of gas-phase M and P (B, D) in the BTF. Gas-phase methanol was stopped for few hours in order to completely remove the liquid-phase methanol from the trickling liquid-phase

Despite this increase, the RE of M was maintained at ~82% reaching an EC_{max} of 430 $gm^{-3}h^{-1}$, while the RE of P decreased to 20%. Similar studies were also conducted by varying the P loads from low to high values (10 to 538 $gm^{-3}h^{-1}$) and by maintaining low M loads (<200 $gm^{-3}h^{-1}$), over a period of 552h. The following interactions were observed in this study: (i) an increase in the ILR_P from low to high values decreased its removal significantly from ~50 to 14%, while the removal of M was only slightly affected (~20 to 25%) depending on both the ILR of M and P supplied to the BTF (EC_{max} of P: 218 $gm^{-3}h^{-1}$), and (ii) despite low ILRs of M, the build up of M occurred, peaking to 2.9 and 5 gL^{-1} on the 192th and 456th h of BTF operation. As done previously, by lowering and/or by completely stopping the ILR of gas-phase M (Fig. 5.5 C) to the BTF for few hours, and by maintaining the same trickling rate, the liquid-phase M could be easily removed from the system, through biodegradation.

5.3.5 Effect of individual and combined shock-loads on the BTF performance

Several lab-scale experimental results have shown that sudden fluctuations in pollutant ILRs (due to variations in both inlet concentration and EBRT) either increased or decreased the RE profiles, but did not pose a threat or deteriorate (zero removal of the target pollutant) the performance of biological waste-gas treatment systems [36-40]. In this study, the BTF was subjected to short-term shock-load perturbations (5-h), by imparting a sudden high load of all three pollutants (Fig. 5.6). Furthermore, in order to analyze and identify how the load fluctuation of only one pollutant would affect the removal of the remaining compounds, short-term shock-loads of 2.5-h were applied to individual pollutants, while holding the concentrations of others constant (Figs. 5.7, 5.8 and 5.9). The experiments were conducted at the same EBRT of 26s. In case of a simultaneous shock-load of all three pollutants (Fig. 5.6), the RE of H reduced from an initial value of 100 to 94% during the perturbation step, while P removal decreased to about half its initial value, from 28 to 14%.

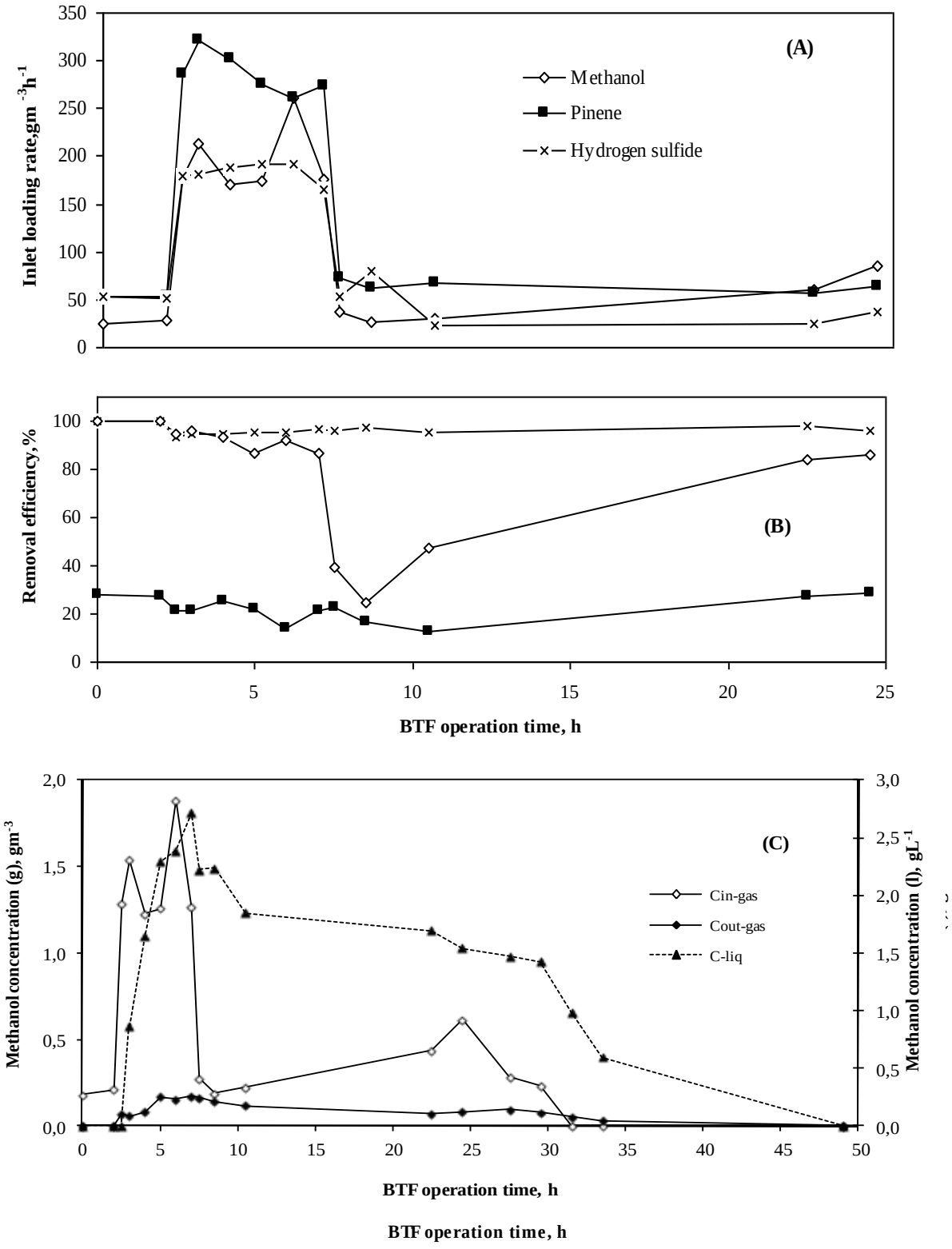

Figure 5.6: Effect of simultaneous H, M and P shock-load on the performance of the BTF: (A) ILR profiles of H, M and P, (B) RE profiles of H, M and P, and (C) liquid-phase methanol concentration profiles during the shock-load

In the case of M, REs dropped only from 100 to 84 % during the shock-load. However, when the inlet concentrations were restored again to values <0.6 gm^{-3}, M removal from the gas-phase, decreased by up to 25%, due to the accumulation of high M concentrations in the liquid-phase (~2.7 gL^{-1}), and partly due to the stripping of liquid-phase M by the exiting non-treated air from the BTF. As observed previously, the liquid-phase M gradually biodegraded within the BTF in ~40h, when the M concentrations were reduced. The EC_{max} of H, M and P from this study were 183, 239 and 76 $gm^{-3}h^{-1}$ at ILRs of 192, 260 and 302 $gm^{-3}h^{-1}$, respectively.

When shock-loads were applied individually as H, M or P (Figs. 5.7, 5.8 and 5.9), more interaction effects were observed. For example, in the case of H shock-loads (Fig. 5.7), it can be seen that, when the ILR of H was increased from ~40 to 192 $gm^{-3}h^{-1}$, the RE of M dropped from 100 to 85%, while the RE of P was maintained constant at 20% during the perturbation. However, the RE of P showed *–ve* RE profiles, presumably due to the accumulation of P in the bioreactor, leading to unusually high concentrations of P in the outlet compared to the inlet of the BTF. Similar *–ve* RE profiles for P were also noticed when the BTF was subjected to perturbations of P alone (Fig. 5.9), when the ILR_P was increased from 25 to ~415 $gm^{-3}h^{-1}$ for 2.5-h. Although high P shock-loads did not alter the RE profiles of P, when pre-shock conditions were re-stored *–ve* RE of P was noticed. Increasing the ILR of M from 50 to 600 $gm^{-3}h^{-1}$ (Fig 5.8) did not largely affect the removal of M and H (RE>90%), while the RE of P dropped by almost 35%. On the other hand, the results from P shock-load tests show that, the RE of both M and H remained largely unaffected, while the RE of P dropped from 25 to 15%. This phenomenon was also reported in earlier studies, which was attributed to the low solubility of P in the liquid-phase and improper residence times of that pollutant in the BTF, that eventually led to high mass transfer resistance in the trickling liquid (Rene et al., 2010).

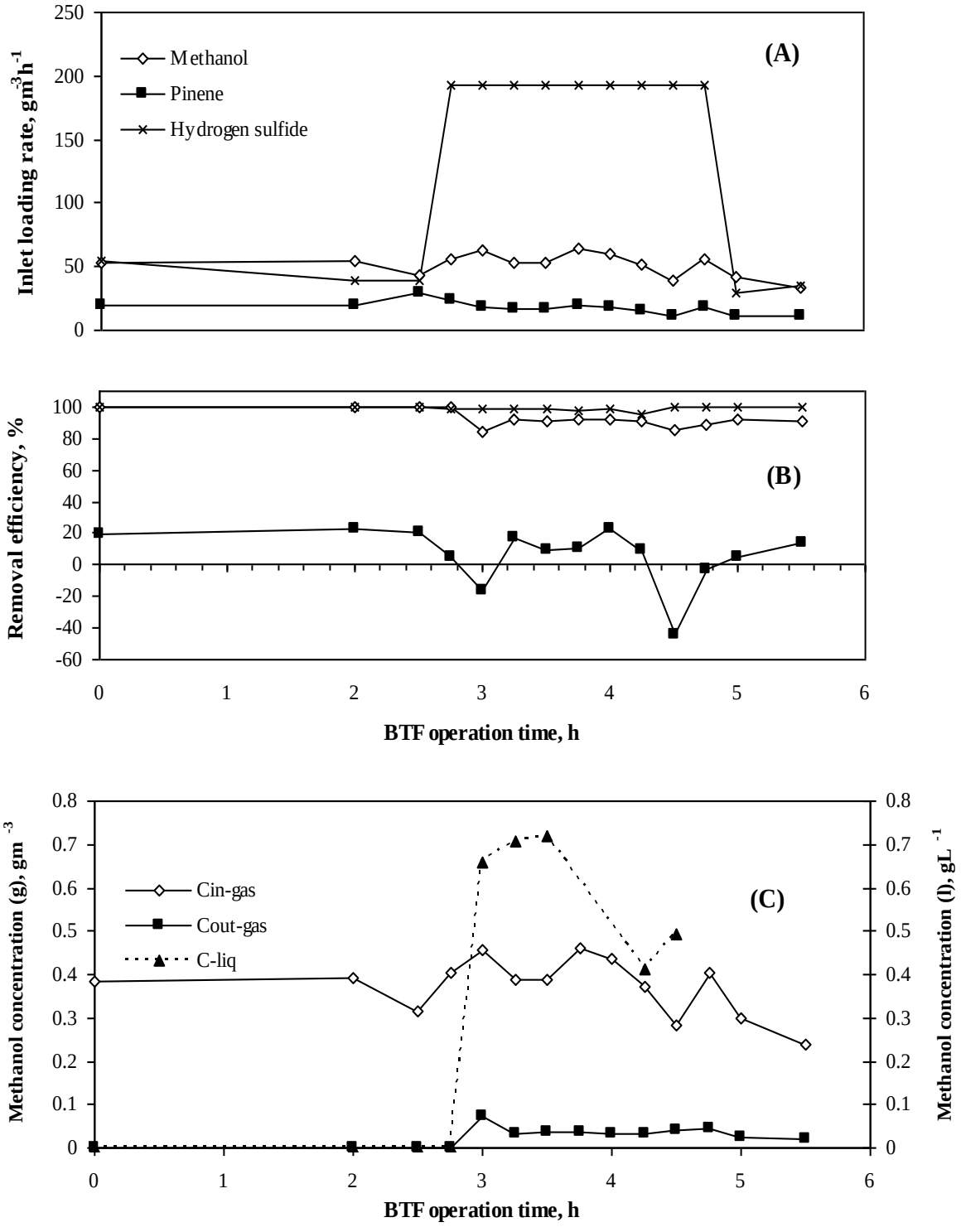

Figure 5.7: Effect of hydrogen sulfide shock-load on the performance of the BTF: (A) ILR profiles of H, M and P, (B) RE profiles of H, M and P, and (C) liquid-phase methanol concentration profiles during the hydrogen sulfide shock-load

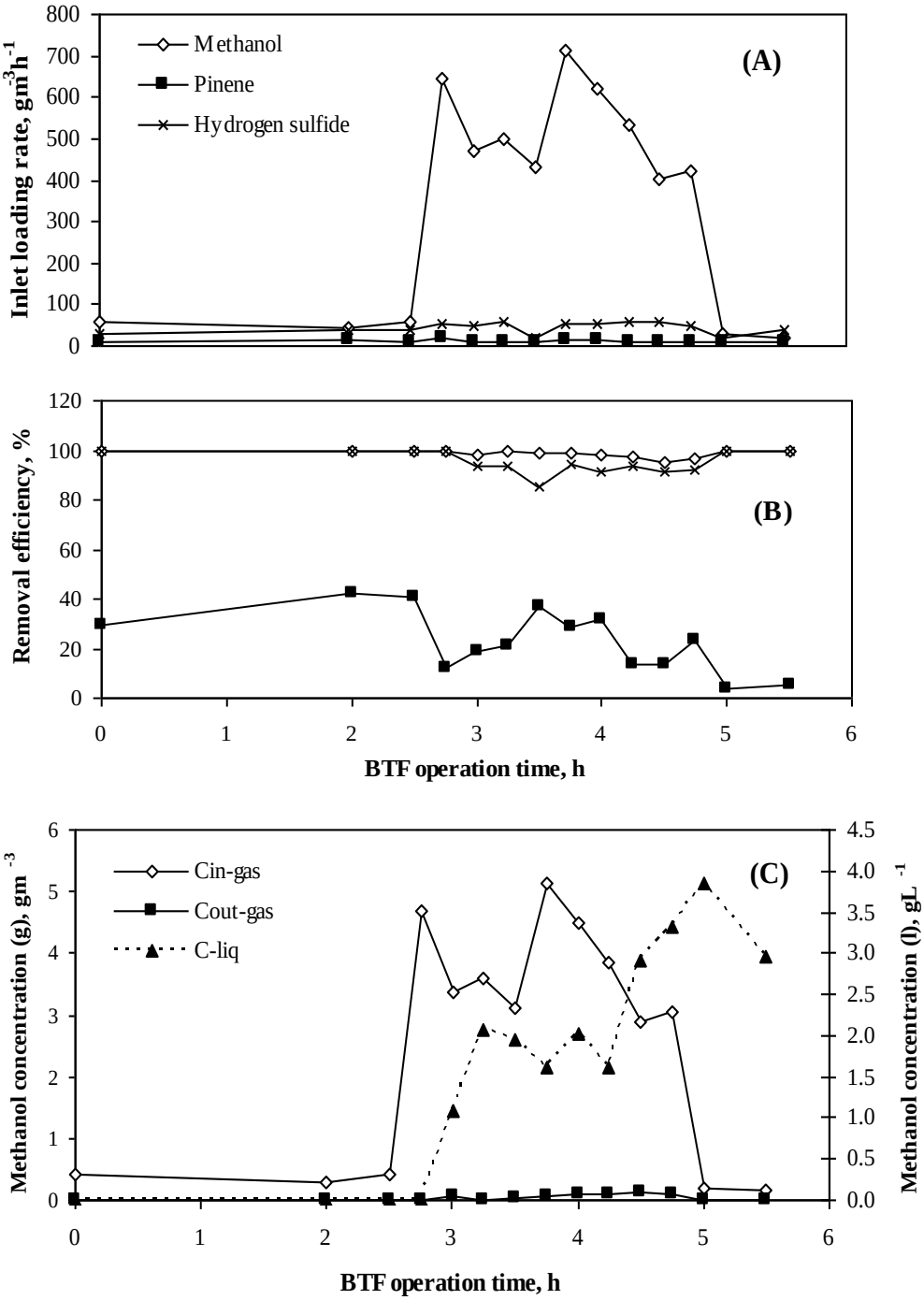

Figure 5.8: Effect of methanol shock-load on the performance of the BTF: (A) ILR profiles of H, M and P, (B) RE profiles of H, M and P, and (C) liquid-phase methanol concentration profiles during the methanol shock-load

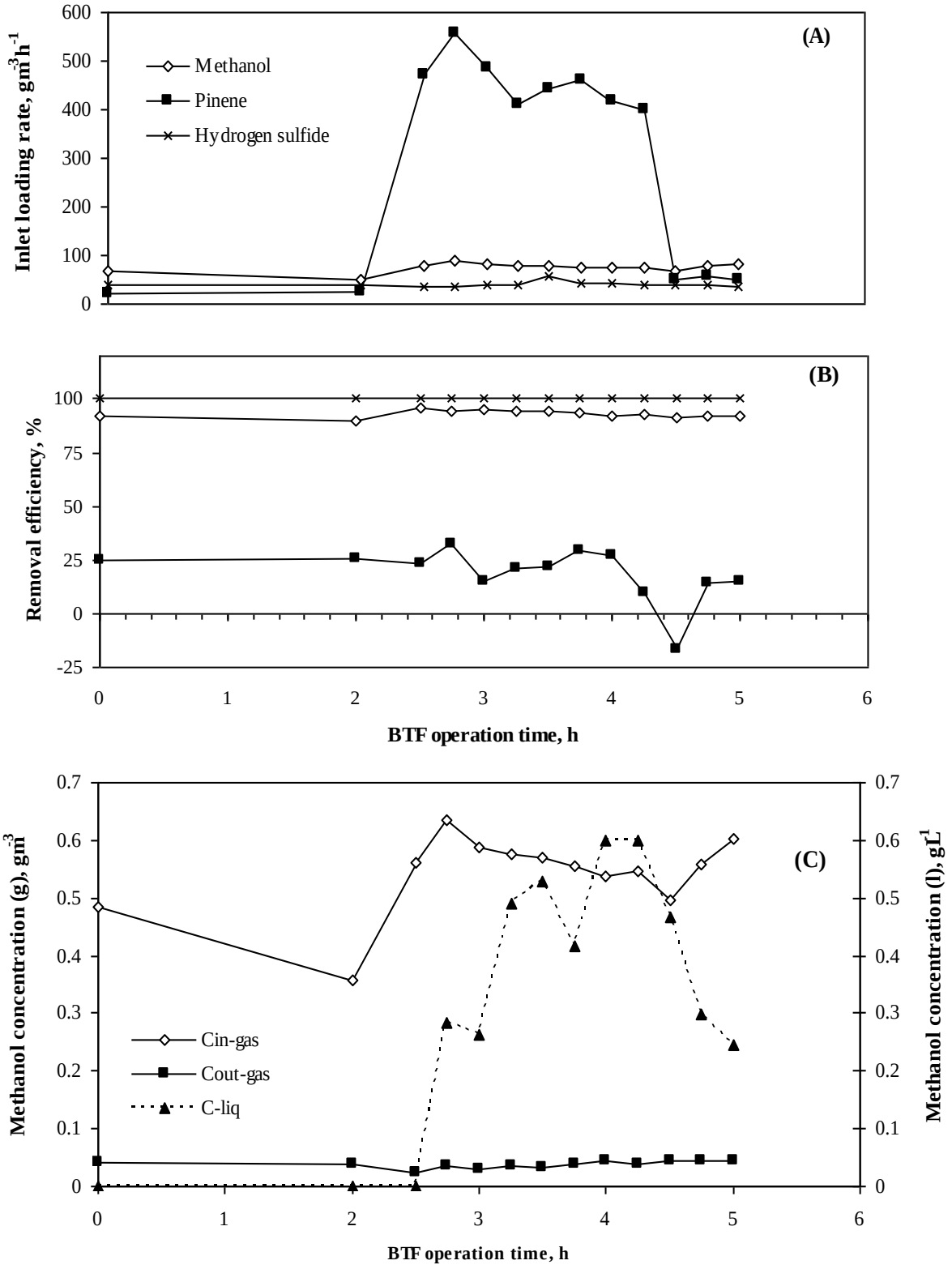

Figure 5.9: Effect of α-pinene shock-load on the performance of the BTF: (A) ILR profiles of H, M and P, (B) RE profiles of H, M and P, and (C) liquid-phase methanol concentration profiles during the α-pinene shock-load

This occurrence of relatively short, transient negative removal profiles for the hydrophobic pollutant P could also be attributed to the partial adsorption of P to the surface of the biofilm, packing material and biomass related compounds, and also absorption into the liquid-film flowing over the packing material. As reported by Mendoza et al. [41], in such cases, the pollutant would be retained for a somewhat longer period in the BTF than the actual or computed mean residence time of the pollutant. The build up of M in the liquid-phase was also evident during all these shock-load tests (Figs 5.7C, 5.8C and 5.9C). The concentrations of M, however, depended on the ILR of M to the BTF. During M perturbations (Fig 5.7), the liquid-phase concentrations of M increased gradually from 0 to 4 gL^{-1} within 2.5-h. This distinctly exemplifies the fact that absorption is one of the main contributing factors governing the removal of hydrophilic pollutants like M in biofilm reactors. The EC_{max} values of H, M and P during individual short-term shock-load tests were found to be 192, 703 and 180 $gm^{-3}h^{-1}$ at ILRs of 192, 710 and 560 $gm^{-3}h^{-1}$, respectively.

5.4 CONCLUSIONS

A three-layered ANN model (5-8-3) was developed to predict the performance of a BTF using inlet concentrations of H, M, and P, UF and operational time as the input parameters. The CI coefficients revealed the relationships between the operating parameters and the pollutants REs that may help optimal design of future bioreactors. The RE of all three pollutants was affected by UF (*-ve* CI), while BTF operating time synergistically improved their REs (*+ve* CI). The results from perturbation tests showed EC_{max} values of 183, 239 and 76 $gm^{-3}h^{-1}$ at ILRs of 192, 260 and 302 $gm^{-3}h^{-1}$, respectively, for H, M and P.

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Chapter 6

Concluding remarks and future perspectives

Some aspects described in this chapter were published in:

López, M.E., Rene, E.R., Veiga, M.C., Kennes, C. (2010) One-stage biotrickling filter for the simultaneous removal of hydrogen sulphide, methanol and α-pinene. Chemical Engineering Transactions, 23, 327-332.

López, M.E., Rene, E.R., Veiga, M.C., Kennes, C. (2010) Waste gas treatment in the pulp and paper industry: A comparison of reactor performance. Journal of Biotechnology, 150(Supplement):40-41.

6.1 Background information

There are only a few publications that focussed on the removal of air emissions containing H_2S and volatile organic compounds (VOCs) (Example: gaseous emissions from wastewater treatment facilities, and pulp and paper industry), using biological waste-gas treatment systems. In those studies, the pH of the biofilm was shown to drop when H_2S was converted to sulphuric acid, which in turn hindered the activity of the microbes that were degrading the VOC. Recently, our research group has been involved in the process of developing one-stage and two-stage bioreactors for the removal of gas-phase methanol, α-pinene and H_2S, either as stand-alone pollutants or as mixtures. This PhD study is a continuation of that initiative to develop high performance bioreactors, by utilizing different microorganisms that had earlier proved to be effective for the removal of these pollutants, *i.e.* methanol, α-pinene and H_2S.

6.2 Comparison of one- and two-stage bioreactors performance

Pulp, paper and wood-related industries produce toxic air-pollutants like H_2S, α-pinene and methanol, which appear at different stages of unit operations. In order to efficiently handle this pollutant mixture, both a two-stage bioreactor (BTF→BF) and a single-stage BTF were operated separately and their performance was compared. In the two-stage bioreactor, the first stage BTF was inoculated with a mixture of an autotrophic H_2S degrading culture and an acid-tolerant methanol degrading yeast (*Candida boidinii*), while an *Ophiostoma stenoceras* sp., was used to inoculate the second-stage BF. In the second experiment, with the one-stage BTF, a mixture of the above mentioned consortium was used and a *Rhodococcus* strain was added. The BTFs were packed with pall rings, while the BF was packed with a mixture of perlite and pall rings. The empty bed residence times (EBRTs) used in the two-stage bioreactor were: 83.4, 41.7 and 27.8 s (BTF) and 146.4, 73.2 and 48.8 s (BF). In the one-stage BTF, EBRTs of 38 and 26 s were used.

Concerning the key results achieved in these two bioreactor configurations, the performance of the two different bioreactors is compared in Figure 6.1. In the two-stage bioreactor, H_2S and methanol were better removed in the first-stage BTF with elimination capacities (ECs) of 45 and 894 $gm^{-3}h^{-1}$, respectively, when compared to α-pinene (35 $gm^{-3}h^{-1}$). In the second-stage BF, the EC was 138 $gm^{-3}h^{-1}$ for α-pinene, yet still a high EC was observed for methanol (~ 315 $gm^{-3}h^{-1}$). In the one-stage BTF, the highest ECs were observed for methanol (302 $gm^{-3}h^{-1}$) followed by H_2S (191 $gm^{-3}h^{-1}$) and α-pinene (175 $gm^{-3}h^{-1}$). The behavior of the one-stage BTF was explored when maintaining the pH at a constant value (6.0 ± 0.3), leading to better removal of the hydrophobic pollutant (α-pinene) by the fungus, when compared to the other reactor configuration. It also helped to maintain a high activity for the surviving bacterial and yeast populations that removed methanol and H_2S. After long-term operation, the results from microbial community analysis (samples collected along the filter bed height), showed that the inoculated autotrophic H_2S-degrading culture was less diverse than the BTF samples. The low diversity of the inoculum can be explained by the emergence of a specific community able to degrade H_2S. A DGGE profile analysis of BTF samples after long-term operation suggests that two populations coming from the original autotrophic H_2S-degrading culture, as well as the inoculated *Rhodococcus* strain are dominantly present within the BTF.

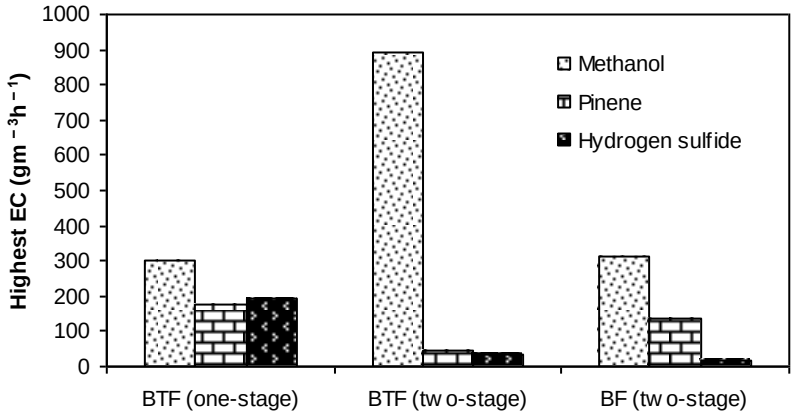

Figure 6.1: Highest elimination capacities reached for the three compounds in the one - stage and two - stage systems

6.3 Interaction effects

6.3.1 Two-stage reactor

The methanol degrader (a yeast) appeared to tolerate very low pHs below 3.0, but the α-pinene degrader (a fungus) did only tolerate mild acidification (around pH 4.0), while the pH dropped below 3.0 in the first-stage reactor removing H_2S and methanol. In the BTF, the presence of methanol had a significant effect on H_2S removal, at high inlet loading rates of methanol. For methanol loading rates less than 66 $gm^{-3}h^{-1}$, though 100% methanol was removed, more than 90% H_2S was removed for H_2S loads lesser than 18 $gm^{-3}h^{-1}$. The presence of α-pinene in the waste gas stream did not appear to show any antagonistic nor synergistic effect on H_2S and methanol removal in the BTF. In the BF, α-pinene removal was not affected by the presence of non-degraded methanol from the first stage. Thus, it can be concluded that the high EC achieved in the BF can be attributed to the dominant presence of the filamentous fungus *Ophiostoma stenoceras* which acts as a biological catalyst for rapid mass transfer of the hydrophobic pollutant, α-pinene, from gas phase to the aqueous biofilm.

6.3.2 One-stage reactor

In the one-stage BTF, the concentration of methanol (a hydrophilic pollutant) in the nutrient collection tank started to build up, increasing from an initial value of 0 to a final value of 9 gL^{-1}. However, when the gas-phase methanol concentrations were reduced to low values, the accumulated liquid phase methanol concentrations were removed by biodegradation. An increase in the inlet loading rate of α-pinene (ILR_P) from low to high values decreased its removal significantly from ~50 to 14%, while the removal of methanol was only slightly affected (~20 to 25%) depending on both the ILR of methanol and α-pinene supplied to the BTF (EC_{max} of α-pinene: 218 $gm^{-3}h^{-1}$). Regarding synergistic and antagonistic effects, the presence of H_2S did not have any effect on the removal of methanol and α-pinene, and the presence of these two volatile organic compounds (VOCs) did not hinder the activity of the

autotrophic H_2S degraders. The presence of methanol, an easily biodegradable hydrophilic VOC, affected the removal of α-pinene in the BTF, while the reverse did not occur.

6.4 Neural network modeling

The removal efficiency of methanol (RE_M) and the removal efficiency of hydrogen sulfide (RE_{HS}) in the first-stage BTF and the removal efficiency of α-pinene (RE_P) in the second-stage BF were predicted using the inlet concentrations of methanol, α-pinene and H_2S as the inputs to the models. After proper optimization of network parameters, and through vigorous training and testing, the following network topologies were obtained: 3-4-2 and 3-3-1, respectively, for the BTF and the BF. The results from sensitivity analysis showed that the most critical factor that antagonistically affects the RE_M and RE_{HS} in the BTF during transient operations was the inlet concentration of α-pinene, while RE_P in the BF was synergistically affected by the concentration of H_2S.

Concerning ANN modeling of the one-stage BTF performance, a three-layered ANN model (5-8-3) was developed to predict the performance of the BTF using inlet concentrations of H_2S, methanol, α-pinene, unit flow (UF) and operational time (in days) as the input parameters. Casual Index (CI) estimations were used to identify the most influential model parameter affecting the removal of individual pollutants. The CI coefficients revealed the relationships between the operating parameters and the pollutants REs that may help optimal design of future bioreactors. The removal efficiencies of all three pollutants was affected by unit flow (*i.e.*, EBRT), while BTF operating time synergistically improved their removal efficiencies.

6.5 Neural network modeling coupled to real-time bioreactor operation

For real-time/full-scale applications, the BTF should be fitted with online measurement devices to periodically monitor process parameters such as inlet concentrations of the

pollutant(s), gas-flow rate, pressure drop, relative humidity, temperature, and carbon dioxide generation rate (Figure 6.2).

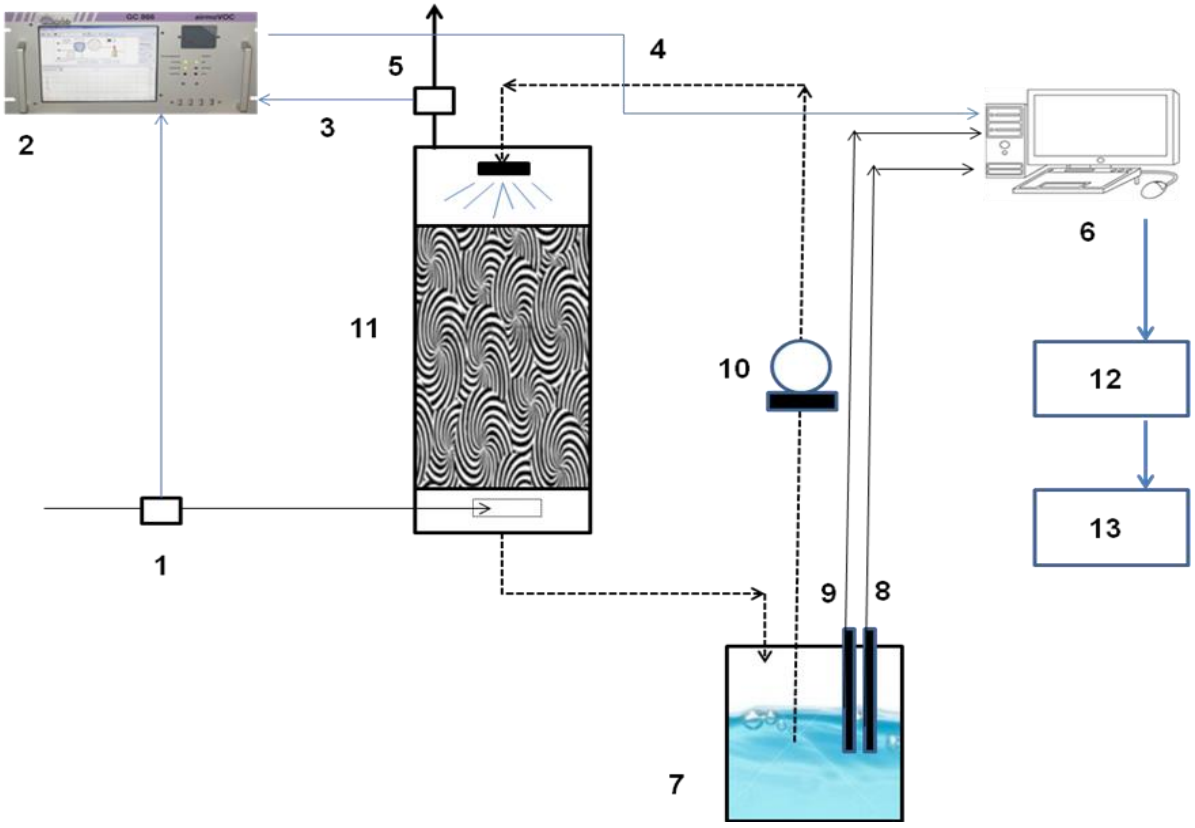

Figure 6.2: Schematic of a BTF fitted with online monitoring and control devices. (1) monitoring inlet concentrations, (2) analysis of pollutants using gas chromatography, (3) monitoring outlet concentrations, (4) monitored data to the computer, (5) treated gas, (6) data storage and modeling device, (7) nutrient tank, (8) pH sensor, (9) pS sensor, (10) pump for nutrient recycling, (11) BTF, (12) programmable logic controller, and (13) actuators

This information has to be stored in a large database, and the system has to be equipped with an automatic control system to maintain the desired values of these process variables. The trained neural model can then be integrated with a programmable logic controller (PLC) coupled to actuators to ascertain and control the process variables, and also predict the performance of the system on a regular basis (for instance, once every 6h). The neural

network model can also be programmed to warn the plant operator of any discrepancies in waste-gas characteristics and concentrations, sudden changes in gas-flow rate, and notify the operator to take suitable actions. The time-series data collected from real-time bioreactor operation can be merged with the already existing database, and the ANN model can be trained in offline/online mode, and the connection weights can be updated before integrating it with the PLC (Figure 6.3).

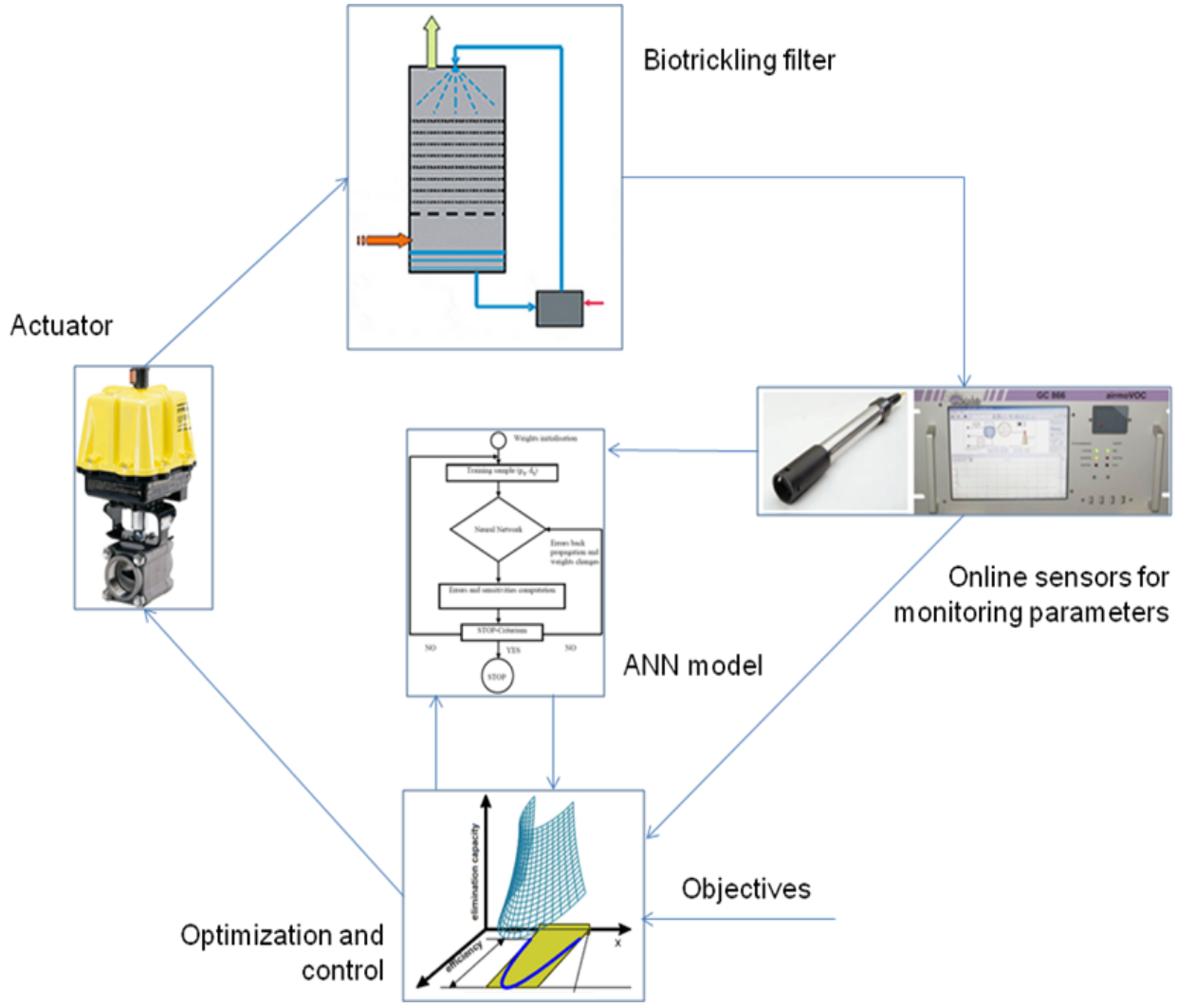

Figure 6.3: Integrated online monitoring, optimization and control of BTF operation using neural networks

6.6 Future perspectives

The following research directions are suggested in order to completely envisage aspects pertaining to bioreactor performance and neural network modeling, keeping in mind the practical implication of applying bioreactor technology (BT) for treating pulp and paper emissions:

(i) Estimate the bio-kinetics and characterize the biomass present in the BTF using actual pulp and paper wastewater effluents,

(ii) Transient state experiments should be performed under nitrogen and phosphorus limiting conditions in order to clearly understand the metabolic assimilation pathway of the microbial consortia,

(iii) Technologies for the treatment of greenhouse gas emissions from the pulp and paper industry should be developed and integrated (for example: algae photobioreactor coupled to a BTF),

(iv) Development of more versatile mathematical models coupled to neural network based models to describe steady and transient-state behavior of BTF and BF operation,

(v) Understanding the interactions between mixtures of gas phase pollutants (emissions from pulp and paper industry) in bioreactors, including methyl mercaptan, dimethyl sulfide, dimethyl disulphide, oxides of sulfur nitrogen and chlorinated VOCs,

(vi) Perform cost-benefit analysis of bioreactor operation during steady and transient-state operations,

(vii) Exploring the application of fuzzy-logic based models for biological waste gas treatment systems, and

(ix) Development of new algorithms that would avoid the conventional trial-and error approach for determining the optimal network topology during neural network modeling.

LIST OF PUBLICATIONS

IN REFEREED INTERNATIONAL JOURNAL

1. López, M.E., Rene, E.R., Veiga, M.C., Kennes, C. (2015) Modeling the removal of volatile pollutants under transient conditions in a two-stage bioreactor using artificial neural networks. Journal of Hazardous Materials (*Submitted*).

2. Rene, E.R., Kara, S., Krishnan, J., Pakshirajan K., López, M.E., Murthye, D.V.S., Swaminathan, T. (2015) Start-up, performance and optimization of a compost biofilter treating gas-phase mixture of benzene and toluene. Bioresource Technology 190, 529–535.

3. López, M.E., Boger, Z., Rene, E.R., Veiga, M.C., Kennes, C. (2014) Transient-state studies and neural modeling of the removal of a gas-phase pollutant mixture in a biotrickling filter. Journal of Hazardous Materials, 269, 45-55.

4. López, M.E., Rene, E.R., Malhautier, L., Rocher, J., Bayle, S., Veiga, M.C., Kennes, C. (2013) One-stage biotrickling filter for the removal of a mixture of volatile pollutants from air: performance and microbial community analysis. Bioresource Technology, 138, 245-252.

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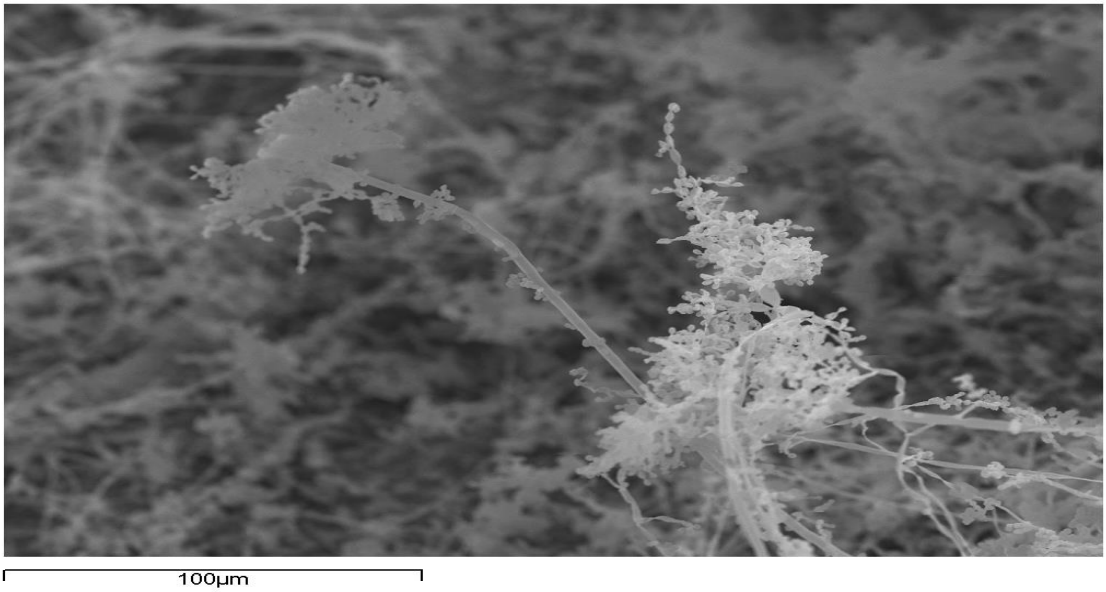

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