

UNIVERSIDADE DO ALGARVE

FACULDADE DE CIÊNCIAS DO MAR E DO AMBIENTE

REMOVAL OF CYANOBACTERIA AND CYANOTOXINS FROM DRINKING WATER BY POWDERED ACTIVATED CARBON ADSORPTION/ULTRAFILTRATION

(Tese para a obtenção do grau de doutor no ramo de Ciências e Tecnologias do Ambiente,
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“Humanity needs practical men, who get the most out of their work, and, without forgetting the general good, safeguard their own interests. But humanity also needs dreamers, for whom the disinterested development of an enterprise is so captivating that it becomes impossible for them to devote their care to their own material profit”.

Marie Curie

Para o Nuno e os meus pais

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Removal of cyanobacteria and cyanotoxins from drinking water by powdered activated carbon adsorption/ultrafiltration

ABSTRACT

PAC/UF was investigated to remove the cyanobacterium *Microcystis aeruginosa* and microcystins, focusing on toxins adsorption onto PAC and the combined effect of the water organic and inorganic matrices, the cells removal and lysis by UF, and PAC contribution to membrane fouling control and microcystins removal by PAC/UF.

The fine-grade mesoporous PAC presented high capacity and fast kinetics for microcystins adsorption from ultrapure-water. In model and natural waters, NOM size governed microcystins-NOM competition, and inorganics contribution was crucial. Main competitor was NOM of closer size, hindering microcystins adsorption through a pore-blocking mechanism. Ionic strength induced the competition of larger compounds and diminished the competition of similar-sized compounds. Kinetic models confirmed the competing mechanisms proposed based on kinetic and isotherm data.

UF ensured absolute removal of *M. aeruginosa* single-cells, although lysis was detected, particularly with cell ageing. However, AOM-driven microcystins rejection attenuated/avoided the permeate degradation. While not affecting the reversible fouling, PAC improved the permeate quality and membrane irreversible-fouling, minimising the chemical cleaning. The worst flux impairment was associated to polysaccharide-like AOM in background inorganics, for which PAC was apparently ineffective.

PAC/UF performed better than PAC+C/F/S. For the usual concentrations of dissolved microcystins in natural waters, 10-15 mgPAC/L achieved the WHO guideline-value.

Key-Words: PAC adsorption, ultrafiltration, cyanobacteria, microcystins, NOM, drinking water.

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TÍTULO DA TESE:

Processo integrado de adsorção em carvão activado em pó e ultrafiltração para remoção de cianobactérias e cianotoxinas em água para consumo humano.

RESUMO

Investigou-se a remoção de *Microcystis aeruginosa* e microcistinas por PAC/UF, principalmente a adsorção das toxinas pelo carvão e o efeito da composição da água, a remoção e lise celular por ultrafiltração, e a contribuição do PAC no controlo da colmatação da membrana e remoção de microcistinas por PAC/UF.

O PAC revelou elevada capacidade e rápida adsorção de microcistinas em água pura. Em águas modelo e naturais, o tamanho da NOM determinou a competição microcistinas-NOM, sendo fundamental o efeito dos iões. Verificou-se maior competição de compostos idênticos, retardando a adsorção por bloqueio de poros. Os iões induziram a competição de compostos maiores e diminuíram a de semelhantes. Os modelos cinéticos confirmaram os mecanismos de competição.

UF removeu totalmente as células de *M. aeruginosa*, mas ocorreu lise especialmente das mais velhas. O material algógeno promoveu a rejeição de microcistinas, atenuando/evitando a degradação do permeado. PAC melhorou a qualidade do permeado e a colmatação irreversível da membrana, minimizando a limpeza química. O fluxo foi especialmente afectado por AOM polissacarídico (com iões), para o qual o PAC foi aparentemente ineficaz.

PAC/UF apresentou melhor desempenho que PAC+C/F/S e com 10-15 mgPAC/L atingiu-se o valor-guia da OMS, partindo de concentrações típicas de microcistinas em águas naturais.

Palavras-Chave: PAC, ultrafiltração, cianobactérias, microcistinas, NOM, água para consumo humano

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AHA	Aldrich humic acid
AOC	Assimilable organic matter
AOM	Algogenic organic matter
CF	Cross-flow
C/F/S	Coagulation/flocculation/sedimentation
CFV	Cross flow velocity
CSTR	Continuous stirred tank reactor
C ₀	Initial concentration
Chl-a	Chlorophyll-a
CP	Concentration polarization
CYN	Cylindrospermopsin
DAF	Dissolved air flotation
DE	Dead-end
DI	Deionised water
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EC	Electric conductivity
EOM	Extracellular organic matter
Extra MC-LReq	Extracellular microcystin-LR equivalents
FBR	Floc blanket reactor
FT	Feed Tank
GAC	Granular activated carbon
HF	Hollow-fibre
HPLC	High performance liquid chromatography
HPSEC	Size exclusion chromatography
HRT	Hydraulic retention time
Intra MC-LReq	Intracellular microcystin-LR equivalents
IOM	Intracellular organic matter
IS	Ionic strength
LD ₅₀	Lethal dose (50%)
M	Month
MC	Microcystin

ABBREVIATIONS AND SYMBOLS

MC-LA	Microcystin-LA
MC-LF	Microcystin-LF
MC-LR	Microcystin-LR
MC-LR _{eq}	Microcystin-LR equivalents
MC-LW	Microcystin-LW
MC-LY	Microcystin-LY
MIB	Methylisoborneol
MW	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
NOM	Natural organic matter
PAC	Powdered activated carbon
PAC/UF	Powdered activated carbon adsorption/ultrafiltration
PDA	Photo diode array
PFR	Plug flow reactor
pH _{zc}	pH of zero charge
PSS	Polystyrene sulphonate standards
RT	Recirculating tank
SA	Salicylic acid
SUVA	Specific ultraviolet absorbance
TA	Tannic acid
TCE	Trichloroethylene
TCW	Tavira's clarified water
THM	Trihalomethanes
TMP	Transmembrane pressure
TOC	Total organic carbon
TOW	Tavira's ozonated water
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WRR	Water recovery rate
WTP	Water treatment plant

ABBREVIATIONS AND SYMBOLS

SYMBOLS

b	Langmuir energy of adsorption parameter
Bt	Boyd values
C/C_0	Normalised concentration
C_e	Equilibrium aqueous concentration
h	Initial adsorption rate
J_1	Pure water flux after backwashing
J_0	Initial pure water flux
J/J_0	Normalised flux
K	Freundlich unity-capacity parameter
k_1	Equilibrium rate constant
k_i	Intraparticle diffusion rate constant
n	Freundlich site-energy distribution parameter
Q_{\max}	Langmuir maximum capacity parameter
q_t	Surface concentration at a specific time
q_e	Surface concentration at equilibrium

ABBREVIATIONS AND SYMBOLS

UNIVERSIDADE DO ALGARVE

FACULDADE DE CIÊNCIAS DO MAR E DO AMBIENTE

REMOVAL OF CYANOBACTERIA AND CYANOTOXINS FROM DRINKING WATER BY POWDERED ACTIVATED CARBON ADSORPTION/ULTRAFILTRATION

(Tese para a obtenção do grau de doutor no ramo de Ciências e Tecnologias do Ambiente,
especialidade de Tecnologias do Ambiente)

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“Humanity needs practical men, who get the most out of their work, and, without forgetting the general good, safeguard their own interests. But humanity also needs dreamers, for whom the disinterested development of an enterprise is so captivating that it becomes impossible for them to devote their care to their own material profit”.

Marie Curie

Para o Nuno e os meus pais

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Removal of cyanobacteria and cyanotoxins from drinking water by powdered activated carbon adsorption/ultrafiltration

ABSTRACT

PAC/UF was investigated to remove the cyanobacterium *Microcystis aeruginosa* and microcystins, focusing on toxins adsorption onto PAC and the combined effect of the water organic and inorganic matrices, the cells removal and lysis by UF, and PAC contribution to membrane fouling control and microcystins removal by PAC/UF.

The fine-grade mesoporous PAC presented high capacity and fast kinetics for microcystins adsorption from ultrapure-water. In model and natural waters, NOM size governed microcystins-NOM competition, and inorganics contribution was crucial. Main competitor was NOM of closer size, hindering microcystins adsorption through a pore-blocking mechanism. Ionic strength induced the competition of larger compounds and diminished the competition of similar-sized compounds. Kinetic models confirmed the competing mechanisms proposed based on kinetic and isotherm data.

UF ensured absolute removal of *M. aeruginosa* single-cells, although lysis was detected, particularly with cell ageing. However, AOM-driven microcystins rejection attenuated/avoided the permeate degradation. While not affecting the reversible fouling, PAC improved the permeate quality and membrane irreversible-fouling, minimising the chemical cleaning. The worst flux impairment was associated to polysaccharide-like AOM in background inorganics, for which PAC was apparently ineffective.

PAC/UF performed better than PAC+C/F/S. For the usual concentrations of dissolved microcystins in natural waters, 10-15 mgPAC/L achieved the WHO guideline-value.

Key-Words: PAC adsorption, ultrafiltration, cyanobacteria, microcystins, NOM, drinking water.

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DATA: 27 de Novembro de 2008

TÍTULO DA TESE:

Processo integrado de adsorção em carvão activado em pó e ultrafiltração para remoção de cianobactérias e cianotoxinas em água para consumo humano.

RESUMO

Investigou-se a remoção de *Microcystis aeruginosa* e microcistinas por PAC/UF, principalmente a adsorção das toxinas pelo carvão e o efeito da composição da água, a remoção e lise celular por ultrafiltração, e a contribuição do PAC no controlo da colmatação da membrana e remoção de microcistinas por PAC/UF.

O PAC revelou elevada capacidade e rápida adsorção de microcistinas em água pura. Em águas modelo e naturais, o tamanho da NOM determinou a competição microcistinas-NOM, sendo fundamental o efeito dos iões. Verificou-se maior competição de compostos idênticos, retardando a adsorção por bloqueio de poros. Os iões induziram a competição de compostos maiores e diminuíram a de semelhantes. Os modelos cinéticos confirmaram os mecanismos de competição.

UF removeu totalmente as células de *M. aeruginosa*, mas ocorreu lise especialmente das mais velhas. O material algógeno promoveu a rejeição de microcistinas, atenuando/evitando a degradação do permeado. PAC melhorou a qualidade do permeado e a colmatação irreversível da membrana, minimizando a limpeza química. O fluxo foi especialmente afectado por AOM polissacarídico (com iões), para o qual o PAC foi aparentemente ineficaz.

PAC/UF apresentou melhor desempenho que PAC+C/F/S e com 10-15 mgPAC/L atingiu-se o valor-guia da OMS, partindo de concentrações típicas de microcistinas em águas naturais.

Palavras-Chave: PAC, ultrafiltração, cianobactérias, microcistinas, NOM, água para consumo humano

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AHA	Aldrich humic acid
AOC	Assimilable organic matter
AOM	Algogenic organic matter
CF	Cross-flow
C/F/S	Coagulation/flocculation/sedimentation
CFV	Cross flow velocity
CSTR	Continuous stirred tank reactor
C ₀	Initial concentration
Chl-a	Chlorophyll-a
CP	Concentration polarization
CYN	Cylindrospermopsin
DAF	Dissolved air flotation
DE	Dead-end
DI	Deionised water
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EC	Electric conductivity
EOM	Extracellular organic matter
Extra MC-LReq	Extracellular microcystin-LR equivalents
FBR	Floc blanket reactor
FT	Feed Tank
GAC	Granular activated carbon
HF	Hollow-fibre
HPLC	High performance liquid chromatography
HPSEC	Size exclusion chromatography
HRT	Hydraulic retention time
Intra MC-LReq	Intracellular microcystin-LR equivalents
IOM	Intracellular organic matter
IS	Ionic strength
LD ₅₀	Lethal dose (50%)
M	Month
MC	Microcystin

ABBREVIATIONS AND SYMBOLS

MC-LA	Microcystin-LA
MC-LF	Microcystin-LF
MC-LR	Microcystin-LR
MC-LR _{eq}	Microcystin-LR equivalents
MC-LW	Microcystin-LW
MC-LY	Microcystin-LY
MIB	Methylisoborneol
MW	Molecular weight
MWCO	Molecular weight cut-off
NF	Nanofiltration
NOM	Natural organic matter
PAC	Powdered activated carbon
PAC/UF	Powdered activated carbon adsorption/ultrafiltration
PDA	Photo diode array
PFR	Plug flow reactor
pH _{zc}	pH of zero charge
PSS	Polystyrene sulphonate standards
RT	Recirculating tank
SA	Salicylic acid
SUVA	Specific ultraviolet absorbance
TA	Tannic acid
TCE	Trichloroethylene
TCW	Tavira's clarified water
THM	Trihalomethanes
TMP	Transmembrane pressure
TOC	Total organic carbon
TOW	Tavira's ozonated water
UF	Ultrafiltration
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WRR	Water recovery rate
WTP	Water treatment plant

ABBREVIATIONS AND SYMBOLS

SYMBOLS

b	Langmuir energy of adsorption parameter
Bt	Boyd values
C/C_0	Normalised concentration
C_e	Equilibrium aqueous concentration
h	Initial adsorption rate
J_1	Pure water flux after backwashing
J_0	Initial pure water flux
J/J_0	Normalised flux
K	Freundlich unity-capacity parameter
k_1	Equilibrium rate constant
k_i	Intraparticle diffusion rate constant
n	Freundlich site-energy distribution parameter
Q_{\max}	Langmuir maximum capacity parameter
q_t	Surface concentration at a specific time
q_e	Surface concentration at equilibrium

ABBREVIATIONS AND SYMBOLS
