Development of N-Ce-AC-TiO_2 Composite via Sol-Gel Assisted Microwave Irradiation for the Adsorption-Photodegradation of Antibiotics

by

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LIST OF ABBREVIATIONS

AC	Activated carbon
AC-TiO_2	Activated carbon doped titanium dioxide
Alg	Alginate
AMX	Amoxicillin
ANOVA	Analysis of variance
AP	Adeq precision
Av	Aloe vera
BEN	Bentonite
BET	Brunauer-Emmett-Teller
Bi	Bismuth
C	Carbon
C-LDH	Concrete-based hydrotalcites
C-N=O	Nitroso
C_3N_4	Carbon nitride
CB	Conduction band
CCD	Central composite design
Ce	Cerium
Ce-AC-TiO_2	Cerium doped AC-TiO_2
Ce_2O_3	Cerium (III) oxide
Ce^{3+}	Cerium ion
Ce^{4+}	Cerium ion
CeO_2	Ceric oxide
Cl	Chlorine
CO_2	Carbon dioxide
Cu	Copper
DOE	Design of Experiment
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy dispersive X-ray
EPs	Emerging pollutants
et al.,	And others
eV	Electron volt
F	Fluorine

Fe	Iron
FTIR	Fourier transform infrared
FWHM	Full width at half maximum
H	Hydrogen
H_2O	Water
H_2O_2	Hydrogen peroxide
H_3PO_4	Phosphorus acid
HCl	Hydrochloric acid
HDTMA	Hexadecyltrimethylammonium
HO-C=O	Carboxyl
hv	Having energy
I	Iodine
IPA	Isopropyl alcohol
JCPDS	Joint Committee on Powder Diffraction Standards
K	Potassium
KBr	Potassium bromide
KOH	Potassium hydroxide
MBC	Biochar
min	Minute
Mo	Molybdenum
MWNTs	Multi-Walled Carbon Nanotubes
N	Nitrogen
N-AC-TiO_2	Nitrogen doped AC-TiO_2
N-Ce-AC-TiO_2	Nitrogen-Cerium co-doped AC-TiO_2
NaOH	Sodium hydroxide
Ni	Nickle
No.	Number
O	Oxygen
P	Phosphorus
pBQ	p-Benzoquinone
Pc	Phthalocyanine
Pd	Palladium
PFO	Pseudo-first order
PPCPs	Pharmaceutical and personal care products

PSO	Pseudo-second order
PVFD	Polyvinylidene fluoride
RE	Rare earth
RSM	Response surface methodology
S	Sulfur
SEM	Scanning electron microscope
TC	Tetracycline
TD	Triazine dendrimer
Ti	Titanium
TiO_2	Titanium dioxide
TTIP	Titanium (IV) isopropoxide
UV	Ultraviolet
UV-vis-NIR	Ultraviolet vis near infrared region
V	Vanadium
V	Visible li
VB	Valence band
VL	Visible light
Vo	Oxygen vacancies
Xe	Xenon lamp
XRD	X-ray diffraction
Zn	Zinc
$ZnCl_2$	Zinc chloride
ZnO	Zinc oxide

LIST OF SYMBOLS

b_i	Linear coefficient
b_{ii}	Quadratic coefficient
b_{ij}	Interaction coefficient
b_o	Constant coefficient
B_t	Boyd's equation
C_{BL}	Boundary layer thickness
C_e	Final antibiotic concentration
C_t	Antibiotic concentration at time t
C_θ	Initial antibiotic concentration
D_i	Diffusion coefficient
e^-	Electrons
e_{CB}^-	Electron on conduction band
E_g	Energy band gap
h^+	Holes
h_{VB}^+	Holes on valence band
HO_2^-	Hydroperoxide ion
k_2	Equilibrium rate constant
k_{eq}	Equilibrium constant
N_A	Avogadro Number
n_m	Monolayer activity
$\frac{P}{P_o}$	Relative pressure
P_o	Pressure at equilibrium phase
q_e	Amount of antibiotic adsorbed on photocatalyst surface
q_t	Amount of antibiotic adsorbed on photocatalyst surface at time t
S_{BET}	Specific surface area
x_1	Urea dose
x_2	Cerium (III) nitrate hexahydrate dose
x_3	Activated carbon dose
x_4	Microwave power
X_i	Factor variable and response
X_j	Independent factor
α'	Initial adsorption rate

β'	Elovich desorption constant
β	Beta
ε	Error
°	Degree
λ	X-ray wavelength
β	Full width at half maximum
θ	Bragg angle
&	And
%	Percentage
℃	Celcius
ΔG	Gibbs free energy
ΔH	Enthalphy
ΔS	Entropy
$\cdot HO_2$	Hydroperoxyl radicals
$\cdot O_2^-$	Superoxide radicals or radical species
·OH	Hydroxyl radicals
2θ	2 thetha
2D	Two-dimensional object
3D	Three-dimensional object
a	Section area of molecule adsorbed by adsorbent
A	Initial adsorption rate or desorption constant
A_T	Temkin constant for heat adsorption
B	Elovich constant
B_{DR}	Dubinin-Radushkevich constant
B_T	Temkin constant for adsorption potential
C	BET constant
cm	Centimeter
Cu Kα	Copper K-alpha
D	Crystalline sizes
df	Degree of freedom
E	Adsorption energy
$F(R)$	Kubelka-Munk function
g	Gram
GHz	Gigahertz
h	Hour
h	Initial adsorption rate

h+	Holes
k	Constant
K	Absorption coefficient
K	Kelvin
K_F	Freundlich constant
kJ	Kilojoule
K_L	Langmuir constant
kV	Kilovolt
L	Liter
m^2	Square meter
mA	Miliampere
mg	Miligram
mL	Mililiter
mm	Milimeter
mol	Mole
n	Nucleophile donates lone-pair
n_f	Heterogeneity factor
nm	Nanometer
P	Pressure in gas phase
pH_{pzc}	Isoelectric point
Q_{DR}	Amount of antibiotic adsorbed by photocatalyst
Q_m	Saturation capcity
R	Reflectance
R	Universal gas constant
R_L	Separation factor
rpm	Rotation per minute
S	Scattering coefficient
s	Second
t	Time
T	Temperature
W	Watt
W	Volume of gas adsorbed at relative pressure
wt	Weight
Y	Quadratic regression response
π	Pi

Pembangunan Komposit N-Ce-AC-TiO_2 Melalui Pendekatan Sol-Gel Dengan Bantuan Radiasi Gelombang Mikro Dalam Penjerapan-Fotodegradasi Antibiotik

ABSTRAK

Pencemaran antibiotik yang merebak secara meluas di dalam persekitaran telah menyebabkan munculnya cabaran global disebabkan oleh kesan negatifnya kepada ekologi, kesihatan dan kesejahteraan manusia. Oleh itu, fotodegradasi menjadi kaedah yang baik bagi menyingkirkan bahan cemar ini dalam merawat pencemaran air. Dengan itu, kajian ini bertujuan untuk mensistesis N-Ce-AC-TiO_2 fotomangkin melalui pendekatan sol-gel dengan bantuan radiasi gelombang mikro dalam penjerapan-fotodegradasi *amoxicillin* (AMX) dan *tetracycline* (TC). Kaedah Rangsangan Permukaan (RSM) digunakan bagi menentukan kondisi optimum dalam proses penyediaan fotomangkin. N-Ce-AC-TiO_2 menunjukkan fasa anatase yang stabil dengan size kristal 5.48 nm, kawasan permukaan Brunauer-Emmett-Teller (BET) yang bagus iaitu 278.87 m^2 g^{-1} dan jurang tenaga yang rendah yang mana signifikasinya dikurangkan daripada TiO_2 asli 3.20 eV kepada 2.16 eV. Daripada kajian pengoptimuman, N-Ce-AC-TiO_2 yang disintesis dengan 0.02 g nitrogen, 0.20 g cerium, 0.50 g karbon teraktif dan diaktifkan dengan 600 W sinaran kuasa gelombang mikro dalam masa 15 minit dapat mencapai tahap degradasi maksimum bagi TC dan AMX pada nilai 93% ± 0.23 dan 96% ± 0.16 dalam masa 100 minit dibawah sinaran UV, bagi tahap kepekatan pemula 10 mg L^{-1}, pada suhu 30 ℃, dengan larutan pH 7 bagi TC, dan pH 6 bagi AMX. Spesis aktif yang paling menyumbang kepada proses fotodegradasi adalah lohong (h^+) dan radikal superoksid ($\cdot O_2^-$). Degradasi TC mematuhi isoterma Langmuir, model kinetik pseudo-tertib pertama (PFO) (R^2: 0.999), dan Langmuir-Hinshelwood (R^2: 0.988). Manakala AMX mematuhi isoterma Langmuir, model kinetik pseudo-tertib pertama (PFO) (R^2: 0.999), dan Langmuir-Hinshelwood (R^2: 0.976). Perubahan pada entalpi (ΔH) (TC: 27.65 kJ mol^{-1}, AMX: 15.50 kJ mol^{-1}), entropi (ΔS) (TC: 0.09 kJ mol^{-1}, AMX: 0.05 kJ mol^{-1}), dan tenaga pengaktifan bebas Gibbs (ΔG) (TC: -1.05 kepada -3.88 kJ mol^{-1}, AMX: -1.16 kepada -2.80 kJ mol^{-1}) mencadangkan proses penjerapan adalah endoterma, bersesuaian dan spontan bagi kedua-dua antibiotik. Antara interaksi yang berkemungkinan terlibat diantara TC dan AMX dengan N-Ce-AC-TiO_2 termasuk $kation - \pi$, interaksi elektrostatik, ikatan hidrogen, $n - \pi$, dan $\pi - \pi$. Selain itu, kestabilan N-Ce-AC-TiO_2 disahkan melalui 80% kecekapan penyingkiran selepas kitaran yang ke-empat (AMX) dan ke-lima (TC). Secara asasnya, hasil kerja ini menawarkan perspektif baru dalam mencipta fotomangkin yang efektif, boleh diulang pakai, dan ditambah baik, menggunakan pendekatan sintesis dengan bantuan gelombang mikro untuk penyahlumusan antibiotik.

Development of N-Ce-AC-TiO_2 Composite via Sol-Gel Assisted Microwave Irradiation for the Adsorption-Photodegradation of Antibiotics

ABSTRACT

The widespread antibiotic pollution in the environment has emerge as a global challenge due to its adverse impacts on ecology, human health, and well-being. Hence, photodegradation is the promising method to remove this pollutant in polluted water treatment. Therefore, this study aims to synthesize N-Ce-AC-TiO_2 photocatalyst via the sol-gel approach with microwave irradiation assistance in the adsorption-photodegradation of amoxicillin (AMX) and tetracycline (TC). Response surface methodology (RSM) was used to determine the optimum conditions in preparing the photocatalyst. N-Ce-AC-TiO_2 showed a stable anatase phase with a crystallite size of 5.48 nm, a good Brunauer-Emmett-Teller (BET) surface area of 278.87 m^2 g^{-1} and a low band gap energy, which was reduced significantly from 3.20 eV of pristine TiO_2 to 2.16 eV. From the optimization studies, N-Ce-AC-TiO_2 synthesized with 0.02 g nitrogen, 0.20 g cerium, 0.50 g activated carbon, and activated with irradiation power of 600 W in 15 mins achieved maximum degradation for TC and AMX at 93% ± 0.23 and 96% ± 0.16 within 100 min under UV light irradiation for an initial concentration of 10 mg L^{-1}, at 30 ℃, with solution pH 7 for TC and pH 6 for AMX. Active species that contribute to the photodegradation process the most are holes (h^+) and superoxide radicals ($\cdot O_2^-$). The TC degradation was appropriately obeyed by Langmuir isotherms, pseudo-first order (R^2: 0.999), and Langmuir-Hinshelwood (R^2: 0.988) kinetic models. The AMX degradation obeyed Langmuir isotherms, pseudo-first order (R^2: 0.999), and Langmuir-Hinshelwood (R^2: 0.976) kinetic models. The change in enthalpy (ΔH) (TC: 27.65 kJ mol^{-1}, AMX: 15.50 kJ mol^{-1}), entropy (ΔS) (TC: 0.09 kJ mol^{-1}, AMX: 0.05 kJ mol^{-1}), and Gibbs free energy (ΔG) (TC: -1.05 to -3.88 kJ mol^{-1}, AMX: -1.16 to -2.80 kJ mol^{-1}) suggested that the adsorption process was endothermic, favourable, and spontaneous for both antibiotics. Possible interactions involved between TC and AMX with N-Ce-AC-TiO_2 include $cationic - \pi$, electrostatic interaction, hydrogen bonding, $n - \pi$, and $\pi - \pi$ interactions. Additionally, N-Ce-AC-TiO_2 stability was confirmed through 80% removal efficiency after the fourth (AMX) and fifth (TC) cycles. In essence, this work offers new perspectives on creating effective, reusable, and improved photocatalysts using a convenient microwave-assisted synthesis approach for antibiotic decontamination.

CHAPTER 1 : INTRODUCTION

1.1 Background

Antibiotics are a type of medicine that is used to fight or treat bacterial infection. It is widely used in human medicine, agriculture, and livestock. However, due to uncontrolled usage of antibiotics worldwide, it led to pollution that contributed to the potential harm in the ecological environment and raised concern when discussing on maintaining environmental sustainability (Coronado-Apodaca et al., 2023; Noorani et al., 2024; Suhan et al., 2023). Antibiotic pollution usually originates from the pharmaceutical industry (Ranjan et al., 2022), excretion of incomplete metabolism of antibiotics in humans or animals from bodies after consumption (Haffiez et al., 2022), hospital waste (Barathe et al., 2024), and pharmaceutical and personal care products (PPCPs) from daily use (Gautam et al., 2024). Antibiotic traces can be found in sediment, wastewater, and water surfaces (Aguilar-Aguilar et al., 2023; Ahmad et al., 2022; Lu et al., 2023).

Antibiotics like amoxicillin (AMX) (Al-Musawi et al., 2023; Palacio et al., 2021), ciprofloxacin (Rodríguez-González et al., 2022; Thuan et al., 2022), erythromycin (Low et al., 2021), and tetracycline (TC) (Leichtweis et al., 2022; Zhang et al., 2024) are the most common antibiotics associated with the pollutants found in the environment. It was reported that 80-90% of consumed antibiotics were discharged into the environment in their original form (Obayomi et al., 2023). Improper management can lead to resistance development, which can affect our ecology (Domingo-Torner et al., 2023), wildlife and aquatic systems, and bring negative impacts on human health and well-being (Zhao et al., 2024). The increase in detection of antibiotics is challenging due to the lack specific established regulations to monitor their removal and treatment process. Therefore, the

development of plausible methods for managing antibiotic traces in polluted water is a crucial matter for environmental sustainability.

There are several established methods used to remove excess antibiotics in water, such as membrane treatment (Hassan et al., 2021), advanced oxidation process (Akbari et al., 2021), reverse osmosis (Zare et al., 2021), membrane separation (Wang et al., 2023), biological treatment (Pu et al., 2022), adsorption (Stylianou et al., 2021), constructed wetlands (Zhao et al., 2023), and photocatalytic (Marinho et al., 2022). However, these methods have shortcomings such as high cost, long treatment duration, fouling, low removal rates, and incomplete degradation of antibiotics (Wu et al., 2023; Chin et al., 2023). Currently, a combination of adsorption and photodegradation techniques is the best alternative method due to its simple operation, low energy consumption, and high efficiency in antibiotic removal (Ammar et al., 2024; Lan et al., 2024). Degradation of antibiotics using adsorption and photodegradation was observed in the removal of AMX (Wahyuni et al., 2024), ciprofloxacin (Ammar et al., 2024), norfloxacin (Lan et al., 2024), TC (Khanmohammadi et al., 2024), and quinolone antibiotics (Almasi Jaf et al., 2024).

Titanium dioxide (TiO_2) is widely used as a photocatalyst for its non-toxicity, stability, low cost, and high photocatalytic activity (Abdullah et al., 2023; Gloria et al., 2023; Negoescu et al., 2023). However, since TiO_2 is a non-porous material, it often has limitations in adsorption capacity and is prone to agglomeration the during catalytic process, hence reducing the photocatalyst degradation efficiency (Suhan et al., 2023). In order to overcome these drawbacks, carbon-based materials such as activated carbon (AC), biochar, carbon nanotubes, and graphene are among the materials used as TiO_2