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This certificate is proudly presented to

Nguyen Ngoc Son Hai, Nguyen Ngoc Nong, Peter Sanderson & Ravi Naidu

for the outstanding poster titled

"Evaluation of Heavy Metals (As, Cd, Cu, Pb, Zn) Accumulation in Native Plants Growing on Contaminated Thai Nguyen Sites, Vietnam"

VEST 2021 SYMPOSIUM

organized by

Master's Program in Environmental Engineering - Vietnam Japan University

Hanoi, Vietnam, 20 December, 2021

TRƯỜNG ĐẠI HỌC VIỆT NHẬT

Dr. Nguyen Thi An Hang
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VEST 2021 Symposium

Prof. Furuta Motoo
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EVALUATION OF HEAVY METALS (As, Cd, Cu, Pb, Zn) ACCUMULATION IN NATIVE PLANTS GROWING ON CONTAMINATED THAI NGUYEN SITES, VIETNAM

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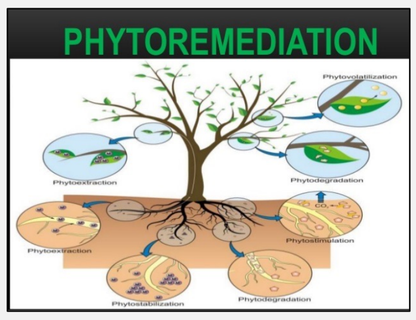
INTRODUCTION

Phytoremediation is a green remediation technology, a cost-effective and aesthetic solution for remediation of contaminated soil.

(a)



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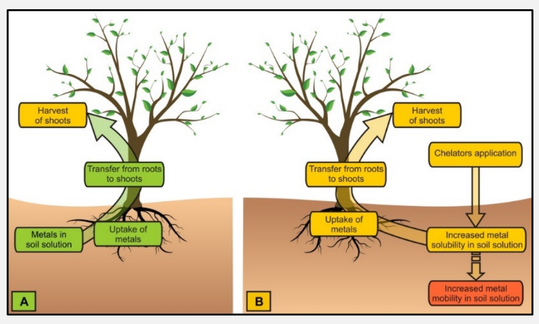


Figure 1. *(a) Phytoremediation (b) Schematic representation of the processes of natural (A) and assisted (B) phytoextraction (Paulo et al., 2004)*

One of the strategies of phytoremediation in metal-contaminated soil is phytoextraction through uptake and accumulation of metals into harvestable biomass of plants (i.e., shoots), which can then be harvested and removed from the site.

Another application of phytoremediation is phytostabilization, where certain plant species are used to immobilize the metals in the soil and could be considered as an integral part of risk management (Bolan et al., 2014).

This study evaluated the potential of most common native plants (2 species) including lau plant EA (*Erianthus arundinaceus (Retz.)* and reed plant PA, *Phragmites australis (Cav.),* growing on three selected contaminated sites in Thai Nguyen province, northern region of Vietnam.

(a)

(b)

Figure 2. *(a) EA (b) PA in mining sites in Thai Nguyen, Vietnam*

OBJECTIVES

- To characterize contaminated soils, in the three selected mining sites (lead-zine mine, tin mine and iron mine).
- To study bioaccumulation of heavy metals (HMs) in the plants and potential relationship between total metals in soil and plants (root, stem and leaves) of EA and PA growing in the different mining sites.

METHODS

- 36 contaminated soil samples (0-20 cm and 20-40 cm) from the point of sampling, 28 EA and PA were taken from 6 different locations in the 3 mining sites.
- Soil and plant sample were analyzed total metal contents by ICP-MS.
- Appropriate QA/QC was maintained: Montana Soil 2711A and spinach leaves (2511A) from National Institute of Standards and Technology.
- Soil samples analysed using SEM and EDS, XRD
- Statistical analyses were conducted using IBM SPSS Statistics 26.0

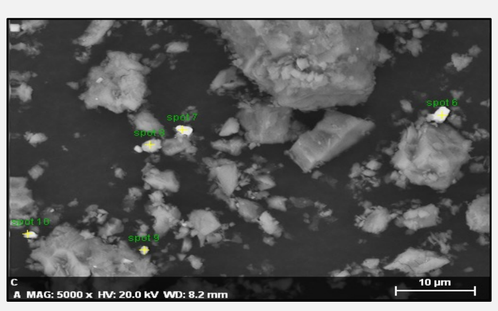
RESULTS

Table 1 – Soil properties

Average	Ha Thuong (HT) Tin mine	Hich Village (LH) Lead-zine mine	Trai Cau (TC) Iron mine
pH	5.00 (4.12-5.95)	8.28 (7.43 – 8.72)	6.96 (6.01 – 7.74)
EC um	102.11 (15.09 – 320.00)	227.74 (97.85 – 850.50)	166.13 (26.00 – 355.00)
CEC meq/100g	2.44 (1.74 – 3.29)	2.71 (1.20 – 4.67)	9.51 (2.68 – 17.95)
Sand (%)	53.75 (42.50 – 67.50)	66.88 (47.50 – 87.50)	29.17 (10.00 – 50.00)
Silt (%)	25.29 (18.75 – 30.00)	16.67 (7.50 – 26.25)	34.25 (24.25 – 43.75)
Clay (%)	20.96 (7.50 – 35.00)	16.46 (5.00 - 32.50)	36.58 (22.50 – 52.50)
As (mg kg^{-1})	1515.91 (**430.49–2604.62**)	44.35 (0.95–184.02)	43.31 (3.89–242.79)
Cd (mg kg^{-1})	2.93 (0.00-10.20)	36.87 (0.00–123.71)	2.52 (0.00–7.65)
Cu (mg kg^{-1})	292.90 (151.39-602.95)	18.67 (3.18-36.04)	208.67 (146.37-312.33)
Pb (mg kg^{-1})	1224.35 (270.13–4140.86)	1801.40 (53.60–5007.99)	720.91(238.28–2092.32)
Zn(mg kg^{-1})	1853.36 (46.69–7863.29)	7099.33 (63.93–31788.38)	1463.74 (566.69–2962.55)

Table 1. *The soil properties of contaminated soils collected in selected mining sites in Thai Nguyen province, Vietnam (Hai et al. 2020)*

(a)



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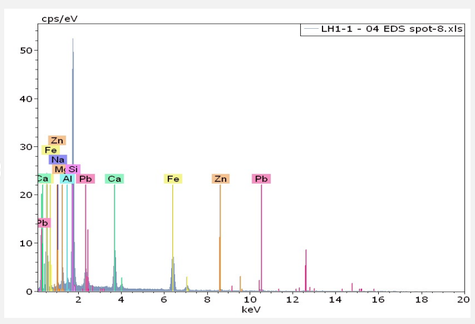

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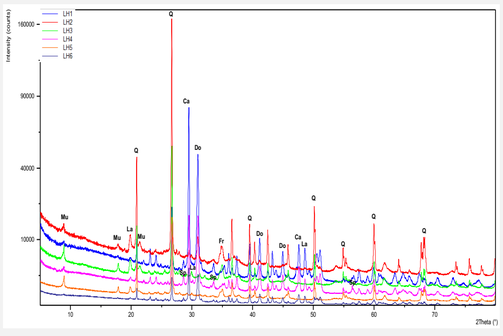

Figure 3. *Result analysis of soil samples in Hich Village (LH) Lead-zince mine (a) SEM (b) EDS (c) XRD*

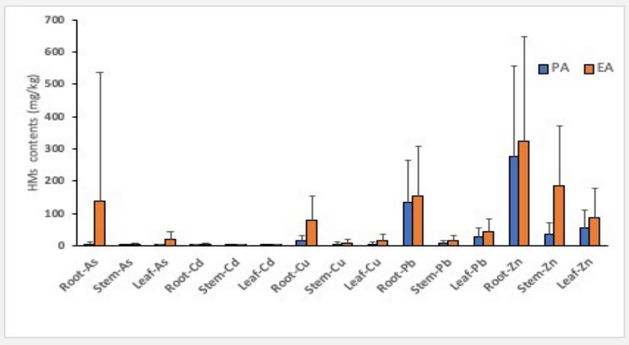

Figure 4. *The average contents of HMs in root, steam and leaves of EA and PA*

Table 2. The Bioconcentration factor (BCF), Translocation factor (TF), and Enrichment factor (EF) of RP and LP

Metals	Reed plant PA (*Phragmites australis (Cav.)*			Lau plant EA (*Erianthus arundinaceus (Retz.)*		
	Bioconcentration Factor (BCF)	Translocation Factor (TF)	Enrichment Factor (EF)	Bioconcentration Factor (BCF)	Translocation Factor (TF)	Enrichment Factor (EF)
As	0.15 ± 0.11 (0.04 – 0.35)	0.24 ± 0.18 (0.04 - 0.66)	0.03 ± 0.02 (0.00-0.07)	0.20 ± 0.27 (0.00 - 0.85)	1.39 ± 3.54 (0.02 - 13.63)	0.06 ± 0.14 (0.00 - 0.60)
Cd	0.20 ± 0.27 (0.00 – 0.81)	0.29 ± 0.29 (0.05 – 1.04)	0.03 ± 0.04 (0.00 – 0.13)	6.45 ± 23.38 (0.00 - 99.50)	0.74 ± 0.58 (0.01 - 1.86)	4.76 ± 17.00 (0.00 - 72)
Cu	0.37 ± 0.45 (0.04 – 1.19)	0.52 ± 0.18 (0.34 - 0.82)	0.22 ± 0.30 (0.02 – 0.95)	0.64 ± 0.91 (0.04 - 2.97)	0.48 ± 0.32 (0.02 - 1.59)	0.27 ± 0.49 (0.01 - 2.09)
Pb	0.28 ± 0.41 (0.02 – 1.13)	0.30 ± 0.30 (0.05 – 1.05)	0.05 ± 0.05 (0.00 – 0.14)	0.21 ± 0.48 (0.00 - 2.04)	0.56 ± 1.25 (0.01 - 5.45)	0.04 ± 0.06 (0.00 - 0.22)
Zn	0.22 ± 0.28 (0.03 – 0.81)	0.34 ± 0.18 (0.06 - 0.56)	0.08 ± 0.13 (0.01 – 0.44)	0.44 ± 0.99 (0.01 - 4.33)	0.64 ± 0.44 (0.03 – 1.56)	0.19 ± 0.41 (0.01 - 1.79)

- Native EA species have high BCF (6.45) and low TF (0.74) in terms of Cd indicating the EA has the potential for phytostabilization of Cd contaminated sites.

FINDINGS

- High concentration of HMs (As. Cd, Cu, Pb and Zn) in most soil samples.
- EA has much higher tolerance for multiple HMs concentration in soil environment compared with PA especially for As.
- HMs accumulated by EA much higher than PA, especially As.
- EA has the potential for phytostabilization of Cd contaminated sites.
- The phytoextraction capacity of EA and PA is relatively low; however their larger biomass results in much greater total accumulation of HMs.

FUTURE RESEARCH

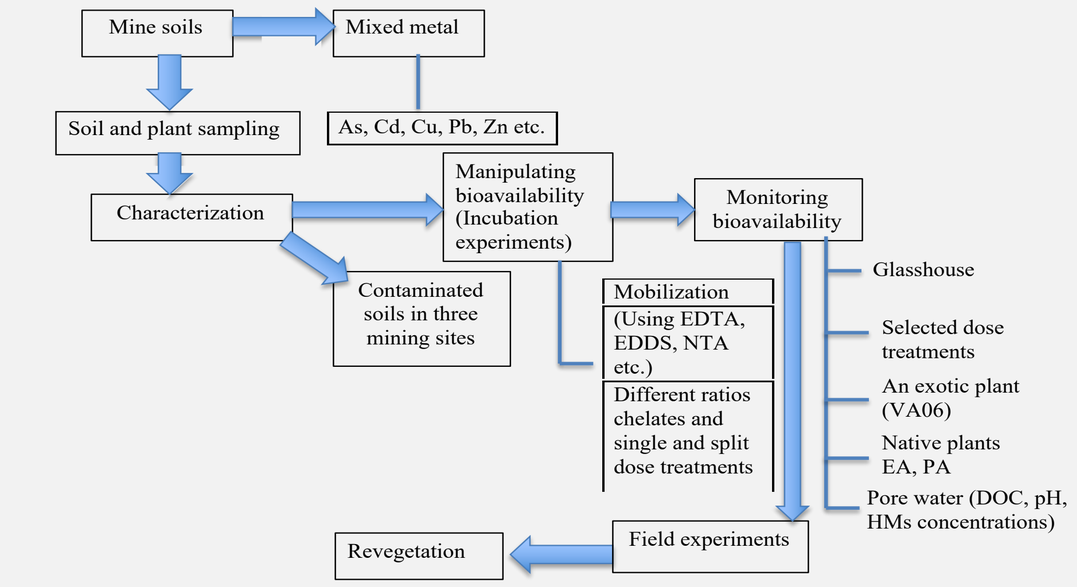

Figure 5. *Overview of research methodologies*

CONCLUSIONS

- EA and PA species growing on contaminated sites have the potential for phytoremediation to remediate metal-contaminated sites.
- EA and PA might not be appropriate for extracting HMs in the contaminated soils, however EA could be used to stabilize Cd in soil especially in extremely high concentrations of multiple HMs (As, Cd, Cu, Pb, Zn), thereby reducing offsite pollution in the mining areas.

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Rector
Vietnam Japan University

Characterization of ESBL-producing *Escherichia coli* in different wastewater treatment plants in Vietnam

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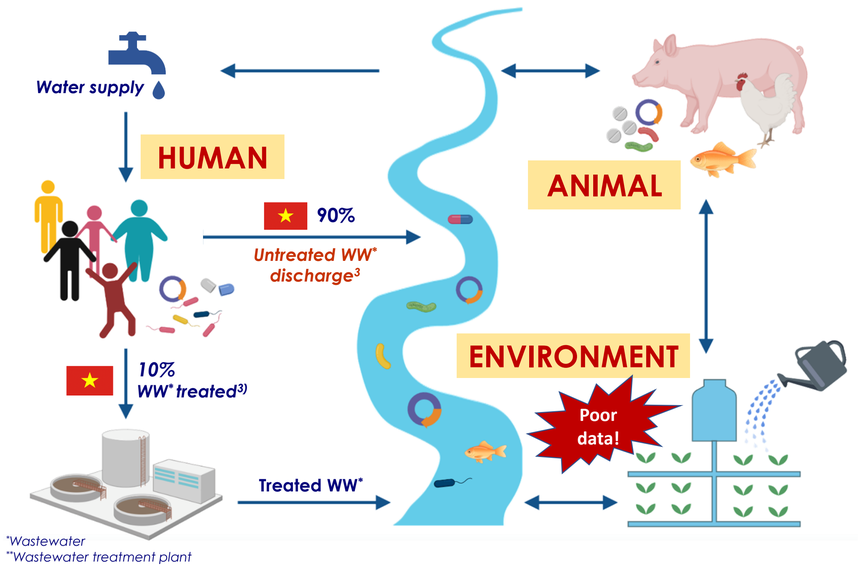
Introduction

Antimicrobial resistance (AMR)

- AMR is the ability of bacteria to be resistant to antibiotics.
- Global spread of AMR makes antibiotic treatment ineffective, resulting in incurable infections.
- In 2050, annual death by AMR would be 10 million[1].

One Health concept[2]: transmission of AMR



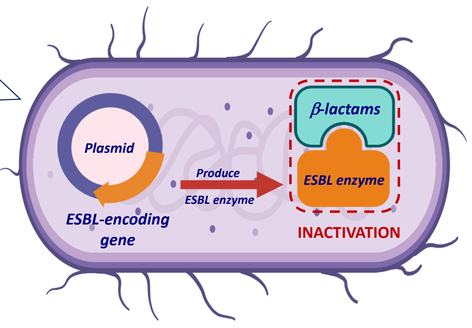
WHO Tricycle Project

AMR surveillance targeting ESBL *E. coli* in One Health (**human**, **animal** and **environment**)

ESBL *E. coli*

(Extended-spectrum β-lactamase-producing *E. coli*)

Inactivating β-lactam antibiotics by producing ESBL enzyme



β-lactam antibiotics

- Broad spectrum class containing a beta-lactam ring such as penicillin and cephalosporins.
- They can inhibit synthesis of bacterial cell wall.

Largest proportion of antibiotics used worldwide[4]

76% of antibiotics use before hospital[5]

Research Objectives

- Investigate the prevalence and characteristics of ESBL *E. coli* in urban wastewater
- Assess the removal of ESBL *E. coli* by wastewater treatment plants (WWTP)

Methods

Sampling sites

Samples:
Urban WWTPs (n=10)
- *Influent*
- *Effluent*

Sampling time:
September 2020 – March 2021

Southern Vietnam
- ✓ *Hanoi – Yen So*
- ✓ *Bac Ninh*
- ✓ *Hanoi – Bay Mau*
- ✓ *Hai Phong*

Central Vietnam
- ✓ *Vinh*
- ✓ *Hoi An*
- ✓ *Dak Lak*

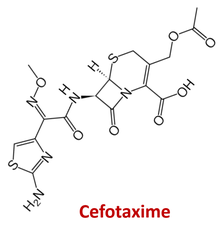
Northern Vietnam
- ✓ *Ho Chi Minh City – Binh Hung*
- ✓ *Ho Chi Minh City – Binh Hung Hoa*
- ✓ *Can Tho*

1. Occurrence of ESBL *E. coli*

Total *E. coli:* TBX agar

ESBL *E. coli:* TBX agar supplemented with cefotaxime (4mg/L)

- *E. coli* forms a blue-green colony on TBX agar.



Cefotaxime
β-lactam class

$$\Rightarrow \quad \text{Resistance ratio} = \frac{\text{ESBL } E.coli}{\text{Total } E.coli}$$

2. Removal of *E. coli* by WWTPs

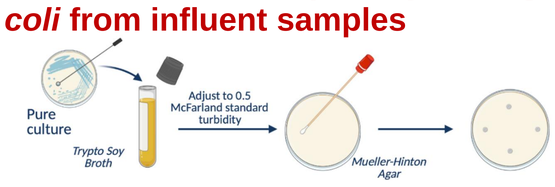
$$\text{Log Removal Value (LRV) of ESBL } E.coli = \log\left(\frac{\text{ESBL} E.coli_{\,influent}}{\text{ESBL } E.coli_{\,effluent}}\right)$$

$$\text{Log Removal Value (LRV) of total } E.coli = \log\left(\frac{total\ E.coli_{\,influent}}{total\ E.coli_{\,effluent}}\right)$$

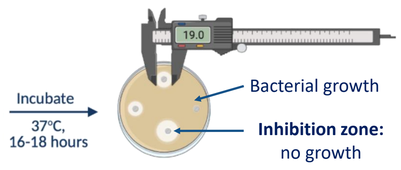
3. Genotyping of ESBL-encoding bla_{CTX-M} genes in *E. coli* from influent samples

		Primers	PCR product size (bp)
Multiplex PCR[6]	bla_{CTX-M} group1	MultiCTXMGp1_for	688
		MultiCTXMGp1-2_rev	
	bla_{CTX-M} group2	MultiCTXMGp2_for	404
		MultiCTXMGp1-2_rev	
	bla_{CTX-M} group9	MultiCTXMGp9_for	561
		MultiCTXMGp9_rev	
Monoplex PCR[6]	bla_{CTX-M} Group8/Group25	CTX-Mg8/25_for	326
		CTX-Mg8/25_rev	

4. Antimicrobial susceptibility testing of ESBL *E. coli* from influent samples



Prepare liquid culture — Spread evenly — Place antibiotic disks



Measure inhibition zone diameter

Susceptibility Judgement

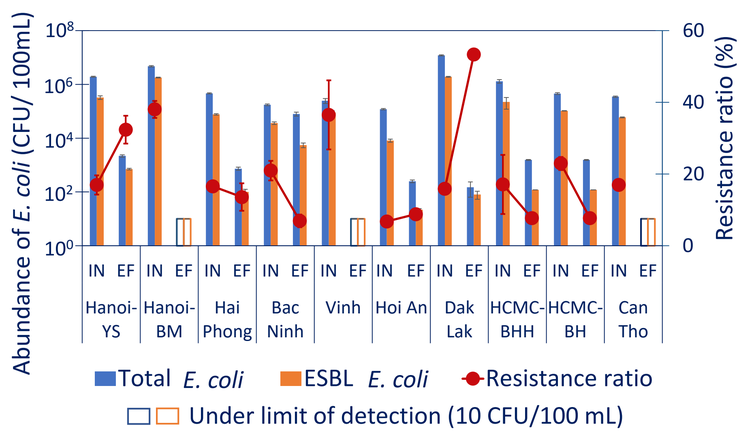
Based on the diameter (d) of inhibition zone *(CLSI)*
- **Resistant** (CTX: d≤22mm)
- **Intermediate** (CTX: 23 mm ≤d≤ 25mm)
- **Sensitive** (CTX: d≥26mm)

Tested antibiotics

Beta-lactams		Tetracyclines	Quinolones
Cephalosporins	**Broad-spectrum penicillins**	*Tetracycline **(TC)***	*Levofloxacin **(LVX)***
3rd generation:	*Chloramphenicols **(CP)***	*Tigecycline **(TGC)***	
*Cefotaxime **(CTX)***	**Aminopenicilins**	**Aminoglycosides**	
*Ceftazidime **(CAZ)***	*Ampicillin **(APB)***	*Gentamycin **(GC)***	*Kanamycin **(KC)***
*Cefdinir **(CFN)***	**Carbapenems**	**Sulfonamides/Trimethoprim**	
4th generation:	*Imipenem **(IPM)***	*Sulfamethoxazole +Trimethoprim **(ST)***	
*Cefpirome **(CPR)***	*Meropenem **(MPM)***		

Results and Discussion

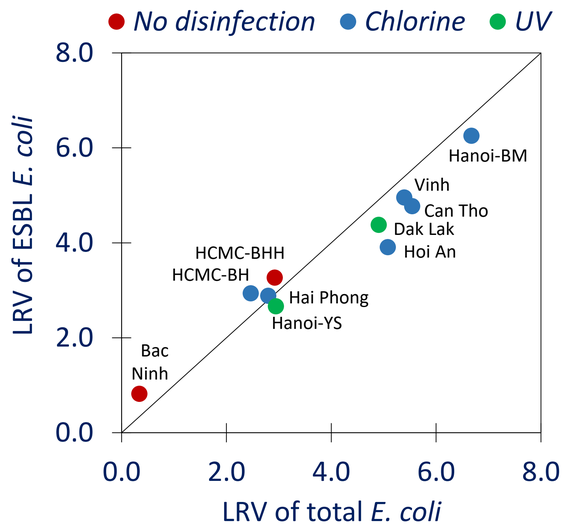
1. Occurrence of ESBL *E. coli*



- ESBL *E. coli* in the influent and effluent ranged from 8.1×10^3–1.9×10^6 and 0–5.5×10^3 CFU/100 mL, respectively.
- The resistance ratio in the influent and the effluent varied among cities, from 15.9–38.0 and 6.9–53.3%, respectively. Except for Hanoi–YS, Hoi An and Dak Lak, resistance ratios decreased to 3–38% after treatment.

2. Removal of *E. coli* by WWTPs

Log removal values (LRV) by different disinfection techniques



- LRV of total *E. coli* and ESBL *E. coli* varied from 0.3-6.7 to 0.8-6.3
- No significant difference among LRV of *E. coli* and ESBL *E. coli* (paired *t*-test, p>0.05)

⇒ Reduction of ESBL *E. coli* is equivalent to total *E. coli*.

3. Genotyping of bla_{CTX-M} genes of ESBL *E. coli* from influent samples

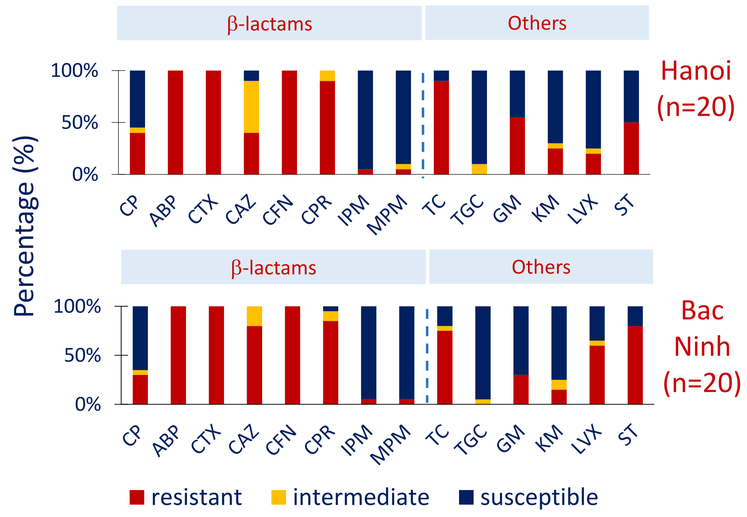
ESBL-encoding genes pattern of ESBL *E. coli* (in influents)

Source	Total (n)	Any bla_{CTX-M}	bla_{CTX-M} group 1	bla_{CTX-M} group 2	bla_{CTX-M} group 9	bla_{CTX-M} group 8/25
		%	%	%	%	%
Hanoi	**46**	*91*	*52*	*0*	*39*	*0*
Hai Phong	**14**	*100*	*50*	*0*	*50*	*0*
Bac Ninh	**19**	*84*	*53*	*0*	*32*	*0*

- bla_{CTX-M} (group 1 and group 9) is the most prevalent ESBL-encoding genes in *E. coli* from the urban wastewater. Similar finding was also observed in the effluent samples in Japan[7].
- These groups also dominates in ESBL *E. coli* isolates from human and animal in Vietnam[8].

4. Antimicrobial susceptibility testing of ESBL *E. coli* from influent samples

AMR profile of ESBL *E. coli* isolates (in influents)



- Similar patterns of AMR in Hanoi and Bac Ninh isolates.
- Most of ESBL *E. coli* were resistant to almost all β–lactams.
- They were mostly sensitive to carbapenems (IPM and MPM), which are last-resort drugs.
- Resistance to other antibiotics suggested the co-existence of other AMR genes.

Conclusion

- ESBL *E. coli* has already presented in the urban WW in Vietnam. Its abundances varied among cities. Group 1 and 9 of bla_{CTX-M} is the most prevalent ESBL-encoding genes. ESBL *E. coli* were also resistant to other class of antibiotics, suggesting the co-existence of other AMR genes.
- WWTPs reduced ESBL *E. coli* loads to the environment (LRV: 0.8–6.3). Disinfection should be applied to enhance the removal of ESBL *E. coli* before discharging effluents to the environment.

Acknowledgement: This research is partially supported by Japan Agency for Medical Research and Development (AMED) "*Development of Integrated Surveillance for Antimicrobial Resistance*" (PI: Sugai Motoyuki (NIID), Co-Investigator : Kasuga Ikuro (VJU) etc. 2020-2022).

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Assessment of total concentrations of heavy metals in industrial sludges from North region of Vietnam and their potential impact on ecosystem

Nguyen Thuy Chung, PhD[1]; Nguyen Van Thinh, PhD[2]; Luong Thi Mai Ly, PhD[3]
[1]Hanoi University of Science and Technology, [2]Kyushu University, Japan,
[3]University of Science, Vietnam National University (VNU)

Abstract

Industrial sludges from wastewater treatment plants in two industrial areas and a groundwater treatment plant in northern Vietnam were investigated in this study. The total concentrations and their sequences of heavy metals (As, Cd, Cu, Cr, Ni, Hg, Pb, Zn) and other toxic elements (Mn, Pd, Sb, V) in the sludges were measured using ICP-MS methods. In addition, the surface characteristics of the samples were analyzed using SEM-EDS and FTIR techniques. Based on Vietnam's current waste management regulation (MONRE 2013), the two industrial sludges were belonged to the hazardous waste category. In contrast, the sludges of the groundwater treatment plant showed a low content of heavy metals and toxic elements. The sequential extraction method revealed that the heavy metals in the industrial sludges exhibited higher immobilization forms than those in the sludges of the groundwater treatment plant. The mobilization ability of heavy metals would be related to the surface function groups of the sludges, which were dominated by (-COOH) and (-OH) groups. The potential ecological risk assessment calculations indicated that the industrial sludges had high potential risk, which was mainly affected by the content of Cd in the sludge samples.

Introduction

Heavy metals contamination of water bodies presents a significant threat to environment and public health because of theirtoxicity, accumulation in the food chain and persistence in nature. Strict regulations and guidelines have been imposed or recommended in many countries to restrict heavy metals contamination of natural water bodies

Industrial sludge containing high level of heavy metals is a potential source of contamination to the environment. In this study, concentrations of heavy metals (HMs – As, Cd, Cr, Cu, Hg, Pb, and Zn) in industrial sludge samples collected from different industrial zones in the North of Vietnam were analyzed using ICP-MS method. Apart from the sludge samples, some agricultural soil samples and certified reference material sample (CRM) were also analyzed and used as the comparative and control samples, respectively.

This study analysed the data for the spatial and seasonal distribution of the heavy metals. Our results indicated that, in general, the industrial sludges were rich in organic content, T-N and T-P. The possible sources of these toxic elements and their potential impact to ecosystem will be identified and assessed by conducting field surveys to obtain information about the types of industries presence in the studied industrial zones.

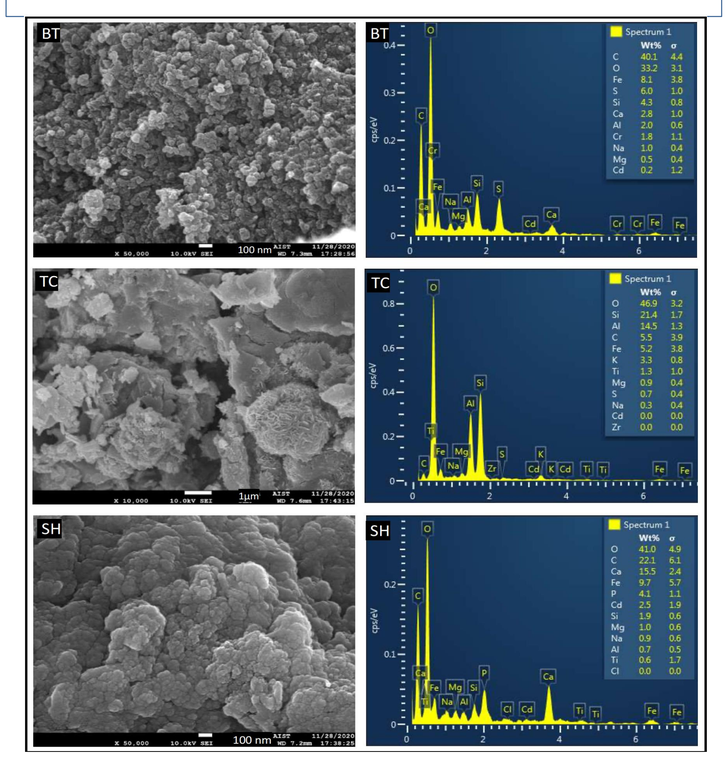

Figure 1. Some images of SEM and XRD of the sludges

Methods and Materials

Sampling sites

- 12 sludge samples were collected at the wasterwater treatment plant of Ba Thien Industrial Park (Vinh Phuc, Vietnam) for 4 seasons in 2020
- 16 other sludge samples were collected from Thanh Cong Cement company (Hai Duong) for 5 types of industrial activities)
- Control sample: natural soils nearby the industrial park

Sample pre-treatment and analysis

- Using Standard method (EPA Method 3050B)
- Characteristic of sludges
- Heavy metals analysed by ICP-MS equipment (12 elements: Cu, Pn, Zn, Fe, Mn, As, Hg, Ni, Cr,…)
- SEM, EDS samples were analysed by AIST-HUST
- Determining ecological risks of heavy metals using Hakanson method (1980)
- Statistical analysis was performed using SPSS Statistics

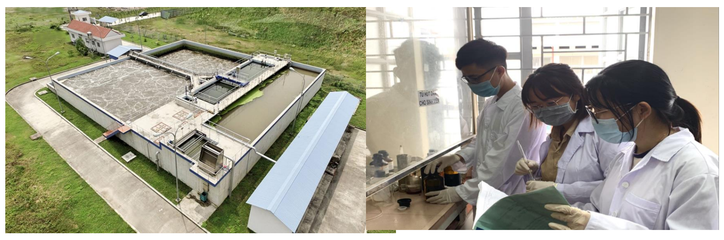

Figure 2. Sampling sites and analysis method.

Results and Discussion

Figure 1 shows SEM images of the industrial sludges. A surface morphology of sludge can be observed in the SEM photographs. The carbon coated surfaces were relatively homogenous. EDS data showed that the Fe and Si were dominant in the sludge.
Concentration variation in sludge samples were shown in Figure 4. The data presented that there is not much difference among seasons. Pb and Cu are the main pollutants in the sludge samples.
Some industrial activities (metallurgical, mechanical, chemistry and WWTP) sludges were compared in total heavy metal concentrations. The result showed that Cu, Pb was relatively higher in mechanical factory than other factory, while Vanadium was highest in metallurgical factory. It means each industrial activites had separate heavy metal release depending on producing process.
The ecological risk (RI) values calculated from Ba Thien and Thanh Cong sludges were all high and got the very high risk. It is reasonable and considered to be hazardous waste which could not be disposed freely into the environment (Table 2).

Table 1. Summary of sludge characteristic

SLUDGE CHARACTERISTIC							
Para.	BT1	BT2	BT3	TC1	TC2	TC3	CON.
DO	11.2	10.5	10.7	11.4	13.5	17.6	12.8
ORP	203	192	182	199	189	173	266.3
TOC	729	839	203	687	605	302	365.1
T-N	611.3	953.4	1232.5	610.4	405.5	758.4	441.8
T-P	45.4	23.4	32.2	49	31.1	40	34.0

Table 2. Risk assessment values of the industrial sludges

BA THIEN INDUSTRIAL PARK								
SEASONS	As	Cr	Pb	Cu	Cd	Zn	RI	Degree Ecol. Risk
SPRING	19.1	29.6	21.9	106.1	128.7	16.6	323.3	Very high risk
SUMMER	21.1	24.0	44.3	130.3	96.6	21.7	338.0	Very high risk
AUTUMN	53.7	33.3	20.6	159.6	137.9	36.8	441.8	Very high risk
WINTER	18.4	26.4	147.0	147.0	156.3	21.0	381.4	Very high risk

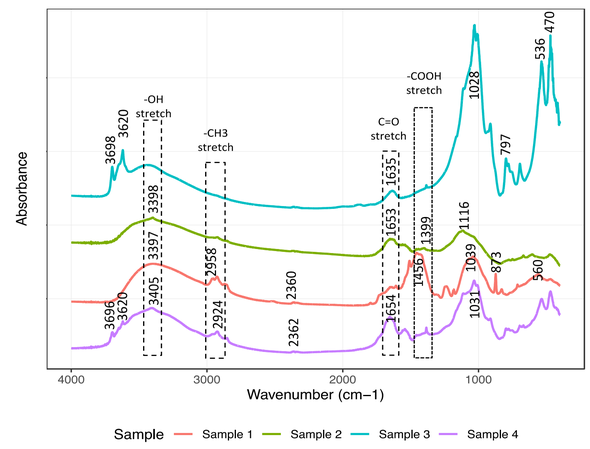

Figure 3. FTIR spectra of sludges from sampling sites

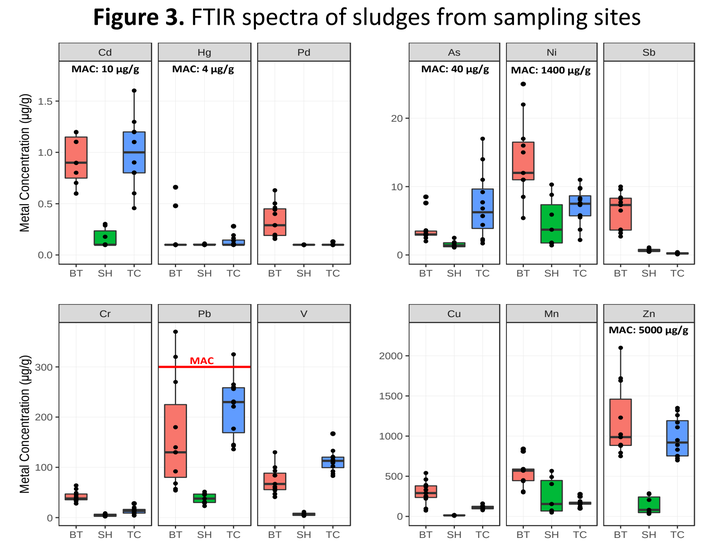

Figure 4. Heavy metal concentration in different kinds of industrial sludges

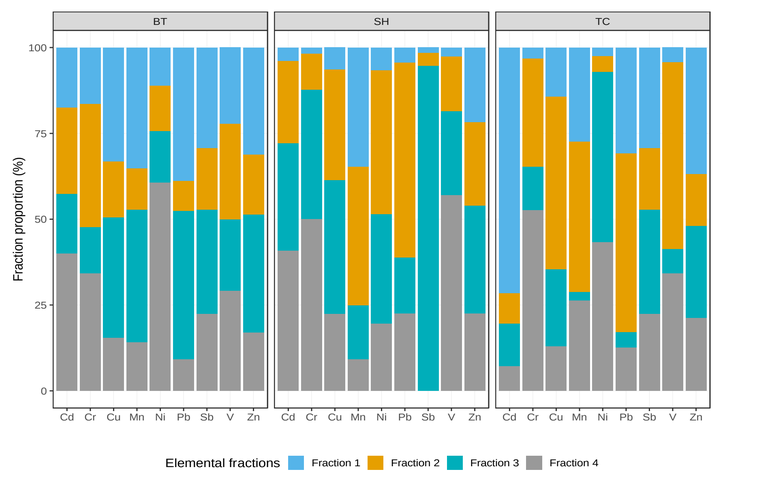

Figure 5. Heavy metals fractionation of industrial sludges

Conclusions

The result showed that concentrations of most heavy metals were lower than the national standard of industrial sludge (QCVN 50:2013/BTNMT) except for Pb, which had slightly exceeded the permitted values in some samples. The mean concentrations of all heavy metals were generally higher in sludges than those in agricultural soils, indicating that industrial and wastewater treatment activities have contributed to the accumulation of heavy metals in the sludges. In addition, the organic and total nitrogen and phosphorus were high in many sludge samples.

The ecological risk as assessed by Interim freshwater sediment quality guidelines (ISQG) was low to moderate in all industrial sludge samples. Our study provided evidence on pollution control effort of the industry in Vietnam but at the same time highlighted the potential of industrial sludge to become a polluting source of the soil or water resources (in case of landfill) if they are directly released to the environment without appropriate treatments.

The detailed characteristics of the sludges and species of heavy metals in the sludges from three water treatment plants (two of them are wastewater treatment systems) in northern Vietnam were investigated. The results suggested that despite multiple step treatment, sludges from industrial zones can still be hazardous due to exceeding the maximum allowable level of Pb in the sludge.

Contact

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for the outstanding poster titled

"Study on Photocatalytical Degradation of Organic Pollutant under Visible-Light using Z-Scheme Heterostructure CoWo4/G-C3N4"

VEST 2021 SYMPOSIUM

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Master's Program in Environmental Engineering - Vietnam Japan University

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Dr. Nguyen Thi An Hang
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The 1st Vietnam Symposium on Environment Science & Technology (VEST 2021)
Vietnam National University - Hanoi University of Science

Study on photocatalytical degradation of organic pollutant under visible-light using Z-scheme heterostructure CoWO4/g-C3N4

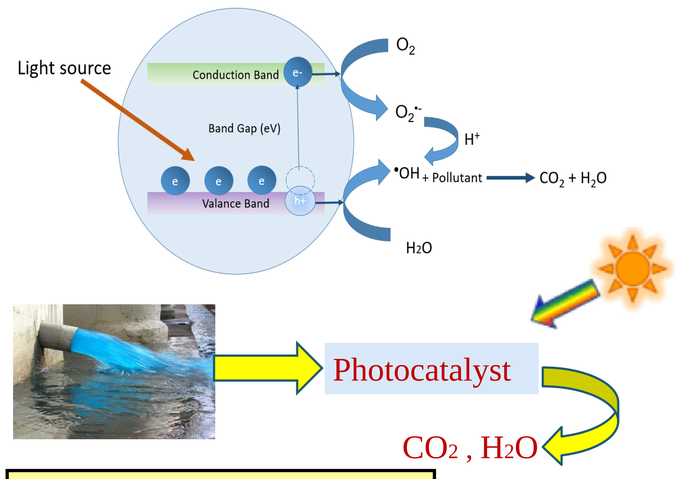
Pham Viet Hai, Nguyen Minh Phuong ,Nguyen Minh Viet, Tran Thi Viet Ha, Do Van Dang, Dang Nhat Minh

Abstract: In this study, direct Z–scheme heterostructure $CoWO_4$/g-C_3N_4 was synthesized by a facile hydrothermal method. The enhanced photocatalytic performance ascribed to interfacial contact between g-C_3N_4 and $CoWO_4$, thus further inhibiting the recombination of photo generated electron/hole pairs. The as-obtained $CoWO_4$/g-C_3N_4 exhibited enhanced photocatalytic activities under visible light irradiation with 92% Rhodamine B removal after 80 minutes irritation. It is anticipated that the construction of Z–scheme heterostructure is an effective strategy to develop high-performance photocatalysts for the degradation of organic pollutants in water.

Introduction

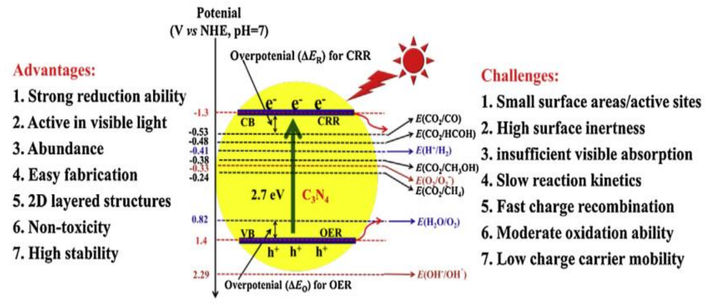
- With the rapid industrialization growth, various pollutants are being released into water bodies, Photocatalyst has received growing attention as a promising solution in wastewater treatment.

Photocatalyst



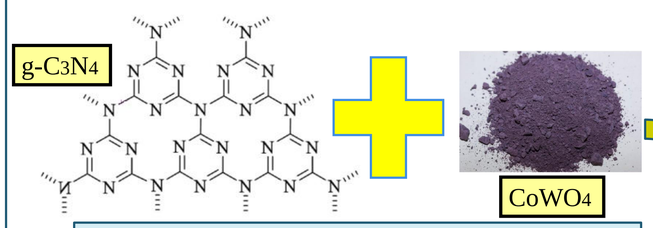
g- Carbon nitride (g-C_3N_4)

- n-type polymeric semiconductor
- Moderate energy band gap (2.7 eV)
- Received attentions since 2009



$CoWO_4$

- p-type polymeric semiconductor
- Low energy band gap (2.2 eV)
- Been applied in many fields

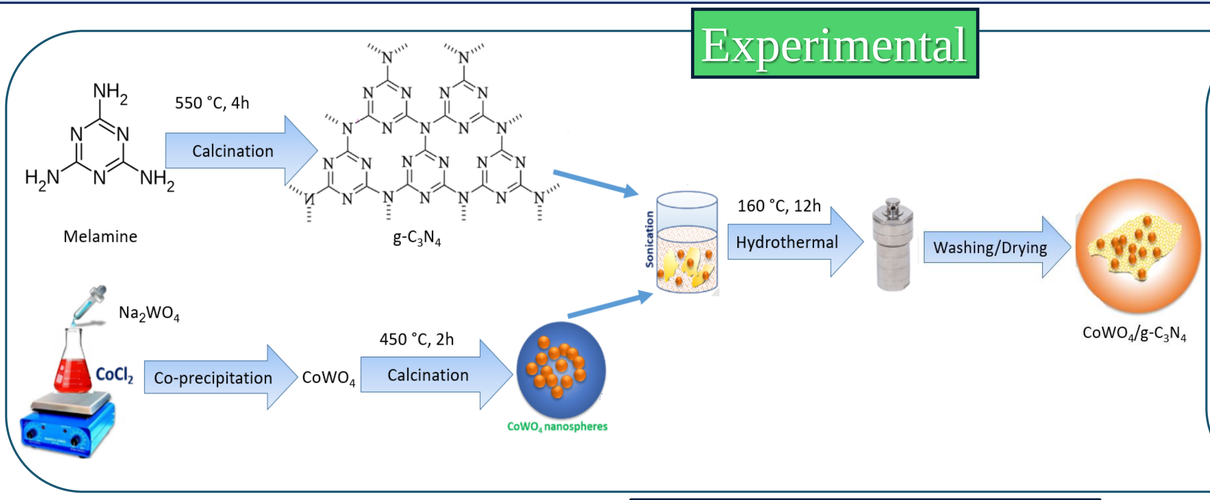


A photocatalyst with low charge recombination,strong oxidation/ reduce ability for removal of pollutant

OBJECTIVES

- ✓Synthesis, characterization of heterojunction $CoWO_4$/g-C_3N_4
- ✓Optimization of mass ratio between $CoWO_4$ and g-C_3N_4
- ✓Comparision of dye removal between the heterojunction and pristine components.

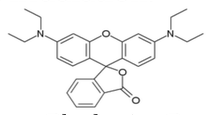
Experimental



Analysis

Material properties: XRD,UV-Vis DRS, FTIR,SEM,PL

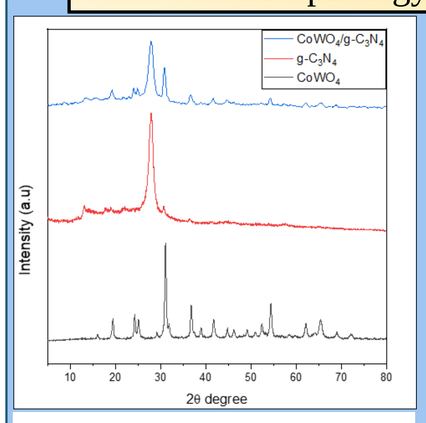
Photocatalytic activies: Measure Rhodamine B concentration under visible light irradiation.



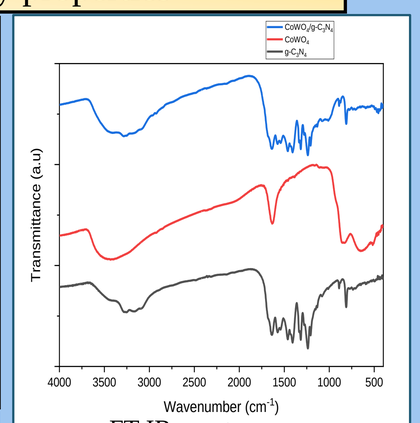
Rhodamine B

Results and discussion

Morphology properties



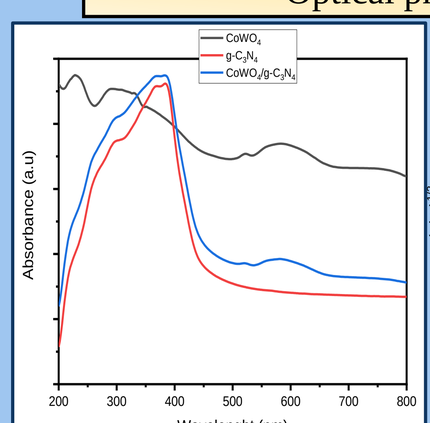
XRD spectra



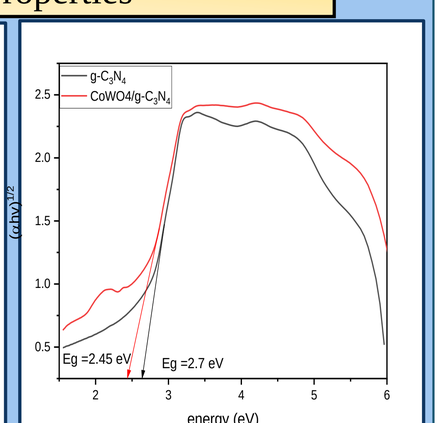
FT-IR spectra

- $CoWO_4$ have monoclinic crystal with wolframite structure g-C_3N_4 was shown to have the conjugated aromatic system .
- XRD and FT-IR results shows no significant change in structure of component after hydrothermal.

Optical properties



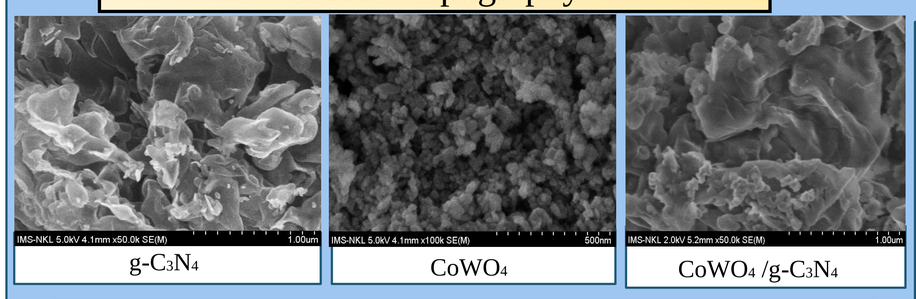
UV-vis spectra



Band-gap energy

- Pure g-C_3N_4 exhibits a clear absorption edge at ~400 nm while $CoWO_4$ at ~600 nm.
- The addition of $CoWO_4$ to g-C_3N_4 increases visible-light absorption intensity and reduces band-gap energy.

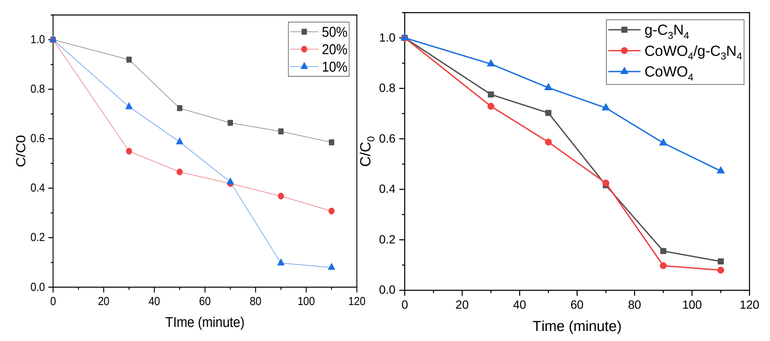
Surface topography



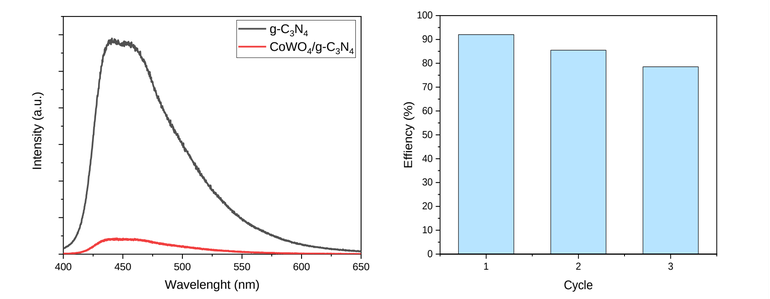
g-C_3N_4 | $CoWO_4$ | $CoWO_4$ /g-C_3N_4

- The SEM result of g-C_3N_4 shows a sheet-like structure.
- $CoWO_4$ exhibits great number of nanoclusters.
- $CoWO_4$ nanocrystals are well-anchored over the sheets of g-C_3N_4.

Photocatalytic activity



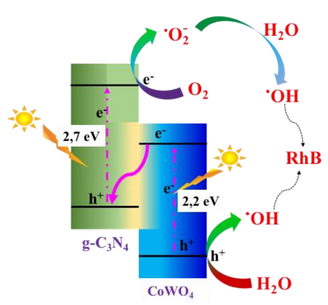
Optimized components ratio | Photodegradation of RhB



PL spectra | Recyclability

- The optimum ratio of $CoWO_4$: g-C_3N_4 is 10%.
- $CoWO_4$/g-C_3N_4 shows to have enhanced efficiency compares to pristine components with 92% RhB removal
- The PL spectra confirms the charge recombination have been significantly limited.

Proposed photocatalyst mechanism



$g\text{-}C_3N_4 + h\nu \rightarrow e^-_{CB}(g\text{-}C_3N_4) + h^+_{VB}(g\text{-}C_3N_4)$

$CoWO_4 + h\nu \rightarrow e^-_{CB}(CoWO_4) + h^+_{VB}(CoWO_4)$

$e^-_{CB}(g\text{-}C_3N_4) + O_2 \rightarrow O_2^{\bullet-}$

$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet}$

$e^- + HO_2^{\bullet} + H^+ \rightarrow H_2O_2$

$e^- + H_2O_2 \rightarrow {}^{\bullet}OH + {}^-OH$

$RhB + (h^+_{VB}, HO^{\bullet}) \rightarrow CO_2 + H_2O$

- The process follow Z-scheme mechanism.
- The photogenerated electron of g-C_3N_4 and hole of $CoWO_4$ are preserved during process.

Conclusion

- ✓Heterojunction $CoWO_4$/g-C_3N_4 was successfully synthesized by a facile hydro-thermal method. The component's morphology remained unchanged throughtout the process.
- ✓The material shows enhanced in light absorption and lowered band-gap energy.
- ✓The optimum ratio for $CoWO_4$/g-C_3N_4 = 10%.Material reached 92% Rhodamine B removal after 80 minutes irradiation,exceeded all the pristine components.
- ✓The construction of Z-type conjuction reduced significantly the recombination of electron-hole pairs.

Acknowledgement

This study was funded by the National Foundation for Science and Technology Development (NAFOSTED).

NAFOSTED
Quỹ Phát triển khoa học & công nghệ Quốc gia

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2. (Prabavathi, Govindan, Saravanakumar, Jang, & Muthuraj, 2019)
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Comparison of Nutrient Removal Using Hybrid Constructed Wetlands with Foamed Waste Glass

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1. Introduction

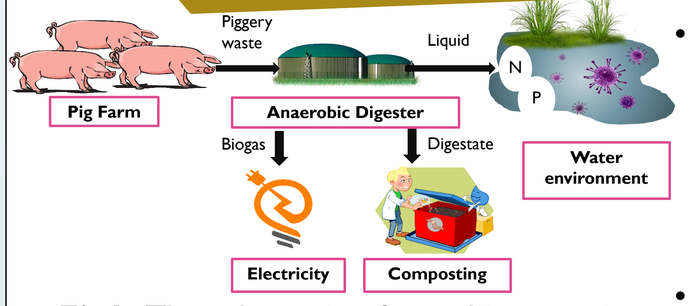


Fig1. The schematic of post-biogas swine wastewater[1,2]

- With the growing number of livestock farms, enormous amounts of solid waste and wastewater are generated. About 40% of small-scale farms discharges animal manure directly into receiving waters without proper treatment[4].
- Resulting in negative consequences and threatening human health.

Anaerobically treated swine wastewater needs **further treatment** before being discharged the environment

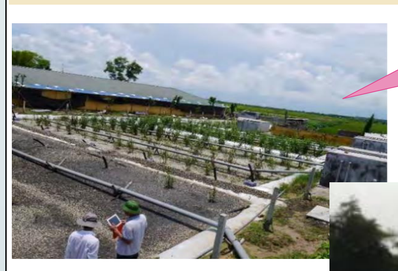


Fig2. The Hybrid CWs at Hai Duong and Thai Nguyen[3]

Advantages

- Green technology
- Low-cost
- Sufficient removal of BOD, SS

Issues and Challenges

- Land area requirement
- Design and construction expertise
- **Insufficient removal of nutrient**

Need to **nutrient removal** from anaerobically treated swine wastewater using **CWs**

Glass Waste

Recycling

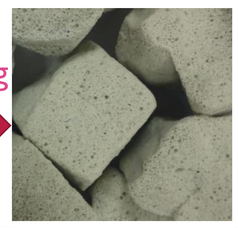


Fig3. Foamed Waste Glass (FWG)

Advantages

- Recycle from waste glass
- Excellent microorganism carrier
- Porous material
- High ability of P adsorption

Objective

Comparison of nutrient removal efficiency in CWs filled with different kinds of Foam Waste Glass (FWG).

2. Materials and Methods

2.1. Material

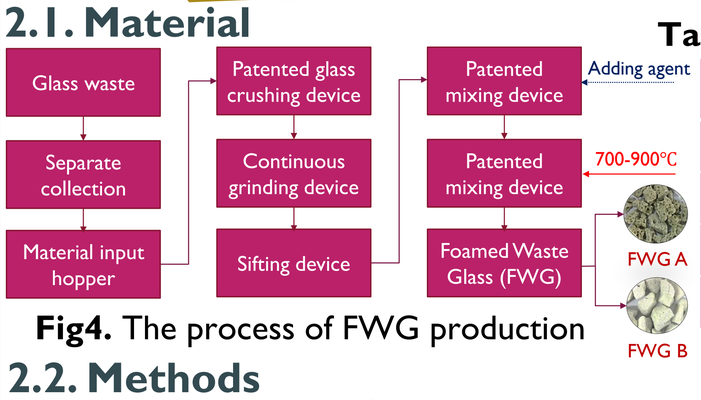


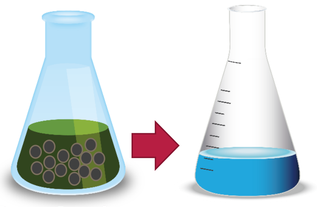
Fig4. The process of FWG production

Tab1. Properties of Synthetic Wastewater

Parameters	Concentration	Unit
pH	6.43 ± 0.25	-
COD	1279 ± 339.77	mg/L
NH_4^+	353.52 ± 52.03	mg/L
PO_4^{3-}	62.37 ± 11.21	mg/L

2.2. Methods

Adsorption experiment



P solution Before — P solution After

Fig5. Adsorption test

(1) Solution Volume: 75 mL, (2) Horizontal Shaking: 120 rpm, (3) Temp: Room (No control) (4) Initial P Conc: 50 mgP/L, (5) Contact Time: 24 h, (6) Mass: 3.0 g, (7) pH: 7.0

pH 3.0 - 11.0 → **Mass** 3.0 - 9.0 g → **Initial P Conc** 0 – 1,000 mgP/L → **Isotherm model**

Design and operation of Hybrid CWs

Hybrid CWs were designed as following:

- H x D = 66 cm x 15 cm
- Q (VF_{unsat}) = 2.6 (L/d)
- HLR (VF_{sat1}) = 0.036 (m/d)
- HLR (VF_{sat2}) = 0.034 (m/d)
- HLR (VF_{sat3}) = 0.039 (m/d)
- HRT = 7 days
- Duration: 15th May to 15th July, 2020

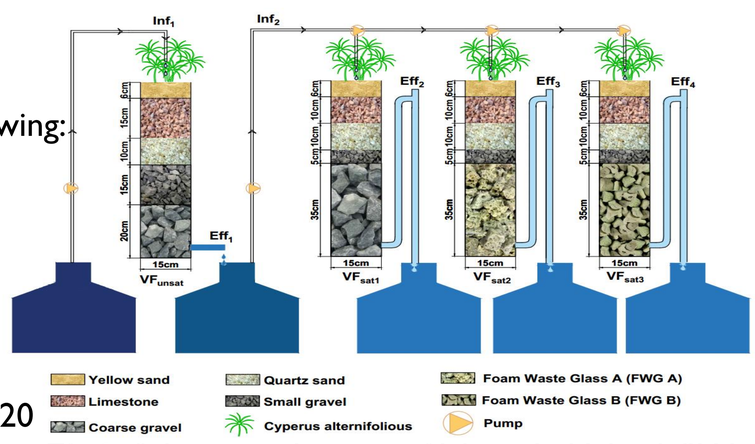


Fig6. Schematic diagram of lab-scale Hybrid CWs

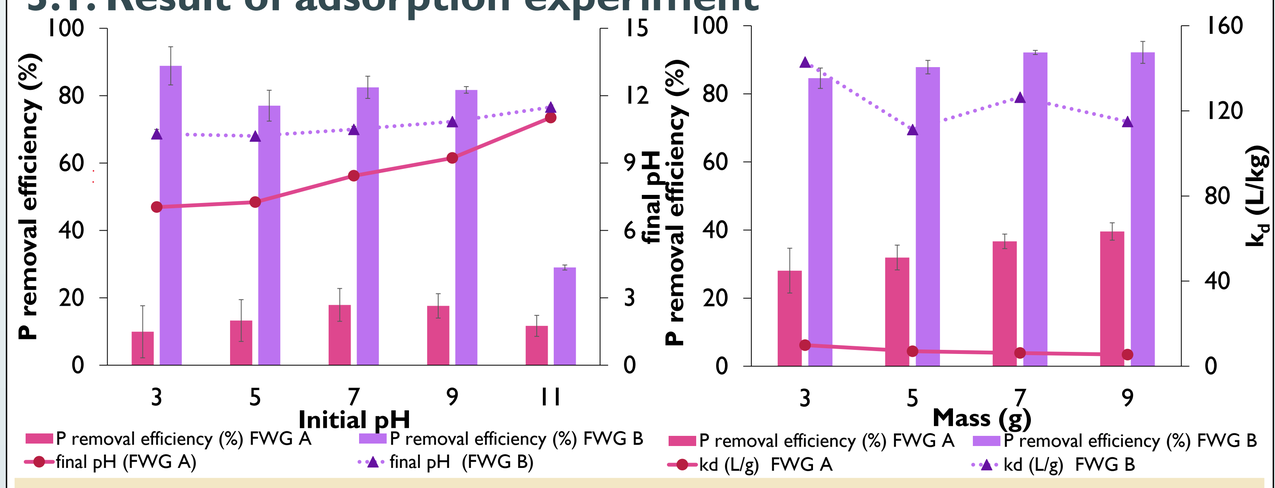
2.3. Calculation

$$R_e = \frac{C_{inf} - C_{eff}}{C_{inf}} \times 100\ (\%)$$

C_{inf} is the concentration of P or N in the influent (mg/L); C_{eff} is the concentration of P or N in the effluent (mg/L)

3. Results and Discussion

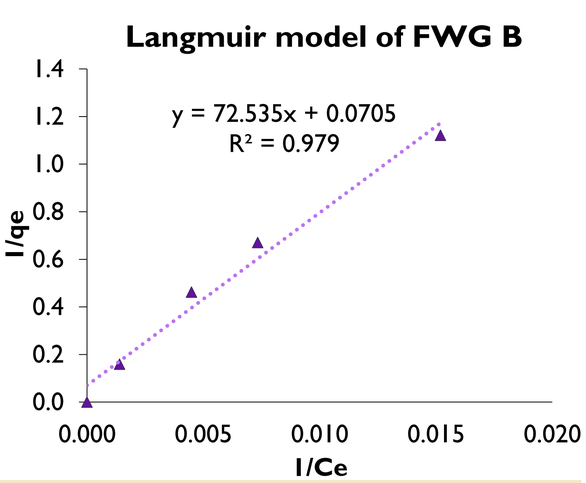
3.1. Result of adsorption experiment



pH =7, m = 3 g were the highest condition at Ci = 50 mg/L.

Tab2. Adsorption isotherm for phosphorus on FWG A and FWG B

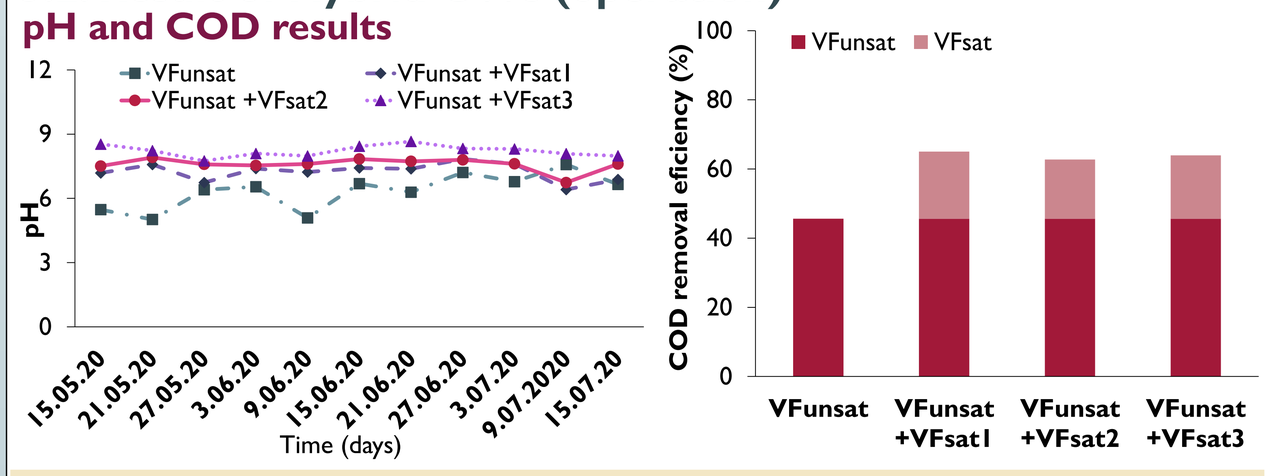
Type of isotherm	Parameter	FWG A	FWG B
Langmuir	q_{max} (mg/g)	11.95	14.18
	K_L (L/mg)	0.001	0.001
	R_L	0.977	0.954
	R^2	0.998	0.979
Freundlich	K_f	0.040	0.041
	1/n	0.610	0.718
	R^2	0.955	0.986



The Langmuir isotherm was appropriate for describing the adsorption process for FWG A while the Freundlich isotherm was appropriate for FWG B.

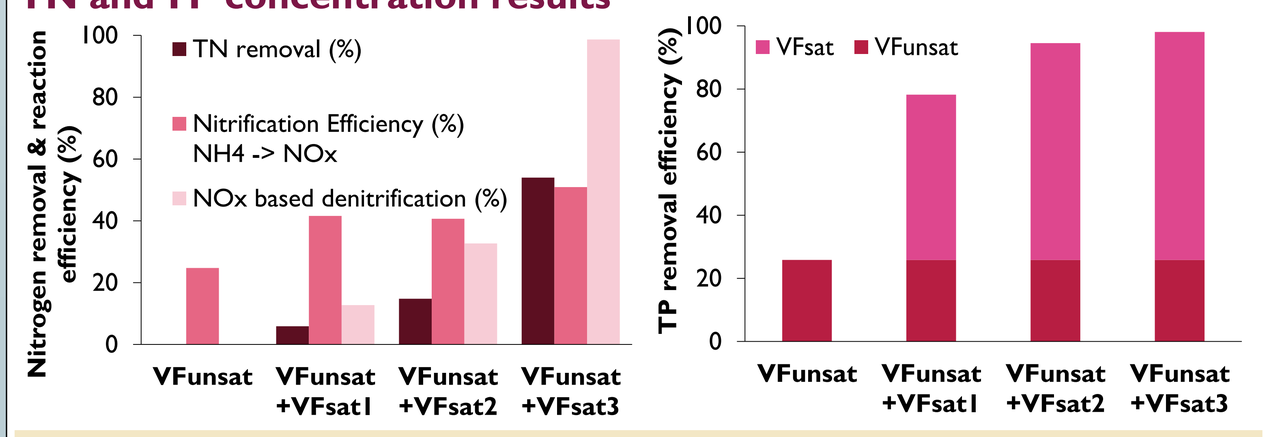
3.2. Result of Hybrid CWs (operation)

pH and COD results



pH of VF_{sat2} and VF_{sat3} achieved approximately 7 -9, respectively. COD removal efficiency of FWGs are similar with conventional material.

TN and TP concentration results



The nitrogen removal efficiencies were 6% for VF_{unsat}+VF_{sat1}, 15% for VF_{unsat}+VF_{sat2}, 54% in VF_{unsat}+ VF_{sat3}. The nitrification efficiency was 25% VF_{unsat}. Denitrification efficiencies from NOx were significantly different between VF_{sat3} (99%), while lower in VF_{sat1} (13%) and VF_{sat2} (33%). TP removal efficiency of FWGs in VF_{sat2} and VF_{sat3} are higher than VF_{sat1}.

4. Conclusion

- FWG B has higher and faster capacity and kinetic than FWG A.
- FWG B data fitted well with Freundlich isotherm model while FWG A data fitted well with Langmuir isotherm.
- TP removal efficiencies FWGs in VF_{unsat}+VF_{sat2} and VF_{unsat}+ VF_{sat3} were 92-97% while N removal efficiencies were 15% for VF_{unsat}+VF_{sat2}, 54% in VF_{unsat}+VF_{sat3}, respectively. In terms of nutrient removal efficiency and nutrient concentration, the use of Foamed Waste Glass, specially FWG B, as a filter material in Hybrid CWs was better than traditional material.

References: 1. Chinh, T.K.P (2020) Master thesis, Vietnam Japan University, 2. Chinh, T.K.P *et al.* (2020) WET 2020, p.61 [Poster], 3. Dinh *et al. 2017, 4.* Kato *et al.* (2019).

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