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DO THI HAI

STUDY AND USE AGRICULTURAL BY - PRODUCTS COMBINED WITH CONSTRUCTED WETLANDS TO TREAT HEAVY METALS Fe, Mn IN COAL MINE WASTWATER

Major: Environmental Engineering

Code: 9 52 03 20

SUMMARY OF ENVIRONMENTAL ENGINEERING DOCTORAL THESIS

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Supervisor 1: Prof. Dr. Bui Thi Kim Anh

Supervisor 2: Prof. Dr. Le Thanh Son

Reviewer 1: …

Reviewer 2: …

Reviewer 3: ….

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INTRODUCTION

1. The urgency of the thesis

Coal mining is a crucial industry in many countries worldwide, including Vietnam, providing fuel for thermal power plants, metallurgy, and chemical industries. However, the environmental and social impacts of coal mining activities are significant and cannot be ignored. Coal mine wastewater is one of the major contributors to environmental pollution and adversely affects the health of people living in nearby areas. Therefore, there is an urgent need to develop effective and sustainable solutions to prevent, treat, and minimize the impacts of coal mine wastewater.

Coal mine wastewater typically contains high levels of heavy metals such as iron and manganese, as well as total suspended solids (TSS) and low pH levels ranging from 1 to 3. Currently, the most commonly used methods to treat Fe and Mn pollution in coal mine wastewater are chemical-physical methods such as chemical precipitation, oxidation-reduction, ion exchange, flocculation, adsorption, electrochemical treatment, and membrane filtration. Although these methods are efficient, they are costly and generate a significant amount of metal precipitation and residual chemicals, leading to secondary pollution.

To address this issue, recent studies have focused on developing low-cost and eco-friendly methods for wastewater treatment. One of the innovative and promising approaches is using natural biological materials derived from agricultural by-products (VLSH) as a biological transformation agent combined with constructed wetlands (CW) to treat Fe and Mn pollution in coal mine wastewater. This method is highly efficient, adaptable, and environmentally friendly, making it a suitable candidate for large-scale implementation. Furthermore, it is simple, easy to operate, and does not require electricity or chemicals, leading to low treatment costs.

The dissertation titled ***"Study and Use of Agricultural By-Products Combined with Constructed Wetlands to Treat Heavy Metals Fe, Mn in Coal Mine Wastewater"*** aims to investigate the feasibility of this approach for treating coal mine wastewater in Vietnam.

2. Purpose and research contents of the thesis

Establishing a technological process for treating coal mine wastewater with high levels of Fe and Mn using some agricultural by-products through hydrolysis combined with constructed wetlands.

3. Scientific and practical significance

The research results provide important scientific data and basis for addressing the problem of coal mine wastewater pollution using environmentally friendly methods with low treatment costs and easy operation.

The established technology process for treating coal mine wastewater with high levels of Fe and Mn using agricultural by-products combined with constructed wetlands can be applied practically to coal mines of different scales or for similar types of wastewater.

4. The main research contents of thesis

(1) Conduct a survey, assess and evaluate the quality of coal mine wastewater in Quang Ninh and Thai Nguyen provinces;

(2) Study the ability to treat heavy metals Fe and Mn in wastewater using some agricultural by-products that have undergone hydrolysis on a laboratory scale;

(3) Study the ability to treat heavy metals Fe and Mn in wastewater using some aquatic plants;

(4) Establish a technological process for treating coal mine wastewater contaminated with heavy metals Fe and Mn using some

hydrolyzed agricultural by-products in combination with constructed wetlands.

CHAPTER1. GENERAL INFORMATION ABOUT RESEARCH

1.1. Overview of coal mine wastewater and treatment methods

1.1.1. Overview of coal mine wastewater

Coal mine wastewater is a type of water generated during the coal mining process. Wastewater often has a large volume and various origins. Coal mine wastewater is acidic (low pH), has a high concentration of suspended solids (TSS), and high levels of heavy metal ions (mainly Fe, Mn). In addition, it also contains organic compounds, sulfate ions, nitrate ions, ammonium ions, etc. which are generated from coal mining activities. If untreated, this wastewater can affect the lives of aquatic organisms, as well as human health through the food chain.

1.1.2. Coal mine wastewater treatment methods

1.1.2.1. Treatment of wastewater by physical-chemical methods

The physical-chemical method is currently widely used for wastewater treatment. This method is divided into two forms: aeration and the use of chemicals to neutralize acidic wastewater and precipitate heavy metals such as Fe and Mn.

1.1.2.2. Treatment of wastewater by biological methods

a) Adsorption and bioremediation method Adsorption and bioremediation of metals by plants (algae, duckweed, water spinach, watercress, etc.) or VLSH (microbial biomass of fungi, algae, bacteria and industrial waste on fermentation, processing seafood, agricultural production...) are used.

b) Biodegradation method Biodegradation: a process of reducing high-valence, toxic heavy metal ions into stable metal salts through direct reaction with enzymes or indirect reaction with metabolic products produced by specific microorganisms [6, 20].

1.1.2.3. Wastewater treatment using constructed wetlands

The use of constructed wetlands (CW) to improve mine wastewater has been studied both nationally and internationally. Wastewater passing through CWs shows a significant improvement in water quality, with decreased Fe, Mn, Ca, Mg, SO_4^{2-}, and increased pH. The CW system may be suitable for treating polluted coal mine wastewater.

1.1.2.4. Wastewater treatment using an anoxic limestone drain (ALD)

ALD is a pretreatment method where wastewater must flow through an anoxic system to transform dissolved metals. The design and size of the subsequent treatment system depend on the metals present in the water and can be a settling pond or CW [31].

1.1.3. Status of coal mine wastewater treatment in the world and Vietnam

Treatment of coal mine wastewater has been a concern since the 1990s in the US, where ALDs were constructed, followed by Europe and other places. Skousen, Jeffrey, 1991reported that there were about 50 ALDs constructed in the Appalachian region of the US by 1991.

In Vietnam, before 2009, almost all coal mine wastewater was untreated and directly discharged into the environment. Some highly polluted coal mines were treated with simple methods such as neutralization with lime and settling, resulting in treated water quality that did not meet standards before being discharged [3, 8, 12]. Since 2009, coal mine wastewater treatment plants using physicochemical technologies have been constructed, and there are monitoring stations to assess wastewater quality before discharge into the environment.

1.2. Overview of agricultural waste

Agricultural waste or by-products (AWB) are various types of waste generated during agricultural activities. The sources of AWB include the cultivation of industrial crops, cereals, fruits, and food production. The main types of AWB include corn cob, corn husk, coconut husk, straw, hay, rice husk, sawdust, bagasse, soybean hull, and manure [51].

1.2.1. Origin, composition and properties of agricultural waste

Based on their sources, AWB can be divided into two types: direct AWB and processing AWB. Most natural materials in agriculture have high fiber content, such as straw containing 34% fiber, and sugarcane leaves containing 43% fiber. These materials are difficult to biodegrade naturally.

1.2.2. Hydrolysis process of agricultural residues

Agricultural residues primarily composed of cellulose are mainly degraded by cellulolytic microorganisms. Enzymes attached to the cell wall or cell membrane are responsible for breaking down cellulose. During degradation, anaerobic bacteria predominantly cleave cellulose, hemicellulose, and lignin into short-chain soluble carbon compounds that are then used by anaerobic, facultative, and aerobic cellulolytic microorganisms to increase their biomass.

1.2.3. Research and use of agricultural residues for heavy metal pollution remediation in water environments

Numerous studies worldwide have been conducted on the use of bio-based materials from agricultural residues to remove heavy metals from wastewater, such as those by Srivastava, 2007 [54], Liu, 2009 [55], El-Said [56], Avinash, 2015 [58], Pablo Garcia, 2020 [61].

In Vietnam, the use of hydrolyzed agricultural residues as adsorbents for heavy metal ions in environmental treatment is still an underexplored topic. Most studies have focused on modifying agricultural residues for pollution removal. Some studies have utilized hydrolyzed agricultural residues for pollution treatment, such as those by P.T. Binh, L.H. Thieng, N.B. Tuan and T.T.C. Loan [62-70].

1.3. Treatment of wastewater using constructed wetlands

1.3.1. Types of constructed wetlands and vegetation used in wastewater treatment

Constructed wetlands (CW) use natural processes combined with a system of filter materials, vegetation beds, and a subsurface flow system to treat wastewater [73,74]. The most commonly used classification of CW is based on the direction of water flow and the type of vegetation used. It can also be based on the path of flow through the CW system. According to Vymazal, 1998 [75], CW is classified into two main types of flow: (i) surface flow; and (ii) subsurface flow.

1.3.2. Mechanisms for removing heavy metals from water using constructed wetlands

When heavy metals dissolve in wastewater and flow into the constructed wetland system, the following mechanisms can remove them: Precipitation and settling as insoluble hydroxides in the anaerobic zone, as metal sulfides in the anoxic zone of the filter material layer;
Adsorption onto the oxyhydroxide precipitates of Fe and Mn in the anaerobic zone; Combination with dead plants and soil; Absorption by roots, stems, and leaves of plants in the CW system.

1.3.3. Research and application of constructed wetlands in treating wastewater containing heavy metals

Constructed wetlands were first implemented in Germany in the 1950s, in the United States in the 1960s and 1970s, and later became widespread worldwide. In Vietnam, CW has been and is being researched to treat pollutants in various types of wastewater. Studies have been conducted by Tran Hieu Nhue, Vi Thi Mai Huong, Bui Thi Kim Anh, Le Sy Chinh, Vu Thi Phuong Thao, Nguyen Viet Anh.

1.4. Shortcomings and limitations that need to be addressed

Coal mine wastewater is a type of water generated during the coal mining process with a large flow rate. The wastewater is often acidic (low pH), with high TSS and Fe, Mn content. The main technology for treating Fe, Mn polluted coal mine wastewater is the physicochemical method, which usually has a fast treatment rate for pollutants but is quite expensive due to the use of many expensive chemicals and materials, while also creating a large amount of metal precipitate and residual chemicals causing secondary pollution to the environment. The method of treating Fe, Mn in coal mine wastewater using some agricultural combined with CW is one of the important and feasible solutions because of its effectiveness, adaptability, and environmental friendliness. It also utilizes agricultural waste, improving the landscape and ecological environment of the area. However, the CW-based treatment system has the main disadvantage of requiring a relatively large area for construction, so it needs to be researched and considered for application in specific areas.

CHAPTER 2. OBJECT AND RESEARCH METHOD

2.1. Object and Scope of Study

- Untreated coal mine wastewater polluted with heavy metals Fe, Mn in Thai Nguyen and Quang Ninh province.

- Simulated wastewater prepared in the laboratory.

- Agricultural residues including rice husk, coconut fiber, sugarcane bagasse, corn cob, sawdust, tea waste, coffee waste, and peanut shell. Inorganic material: Green limestone with a size of 2x3cm.

- Aquatic plants including *Chlorophytum bicheti, Dracaena sanderiana, Phragmites australis, Cyperus involucratus, and Caladium bicolor*.

Scope of study: The research was carried out at the laboratory scale and pilot scale at the Institute of Environmental Technology and Hanoi University of Mining and Geology.

2.2. Materials, Chemicals and Equipment Used

2.2.1. Chemicals and Equipment

The main chemicals used in the study include: H_2SO_4, $AgNO_3$; $FeSO_4.7H_2O$; $MnSO_4.H_2O$; $K_2S_2O_8$, HCl, $K_2Cr_2O_7$, NaOH; Citric acid, which have a purity of >99%, originated from Merck (Germany) and Sigma-Aldrich (USA) companies. Equipment in the laboratory was used to analyze and evaluate the research results.

2.2.2. Aquatic plants

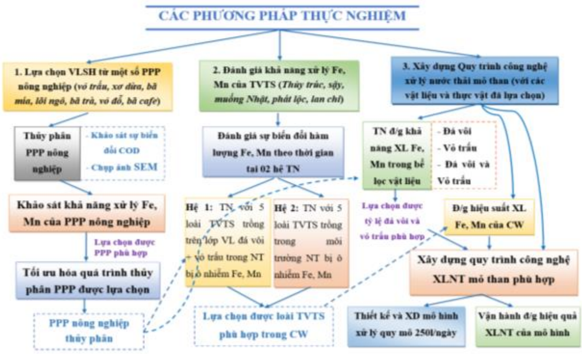
Five aquatic plants were studied, including Chlorophytum bicheti, Dracaena sanderiana, Phragmites australis, Cyperus involucratus, and Caladium bicolor. These plants have the ability to grow and develop in water environments that are polluted with KLN and lacking in nutrients.

2.2.3. Limestone

The limestone used in the study was 2x3cm in size [19], and was a type of green-colored stone commonly used in construction. It was sourced from the Quang Hanh limestone mine in Cam Pha city, Quang Ninh province.

2.3. Research methods

2.4. Field experiment methods



Hình 2.9. Sơ đồ bố trí các phương pháp thực nghiệm

CHAPTER 3. RESULTS AND DISCUSSION

3.1. Current Status of Coal Mine Wastewater Environment

The quality of untreated coal mine wastewater (NT1) in Khanh Hoa and Thai Nguyen provinces mostly meets the permissible limits specified by the Vietnamese Standard for Industrial Wastewater (QCVN 40:2011/BTNMT). However, certain parameters such as pH = 5.14 ± 0.4, TSS = 145 ± 5.2 mg/L, Fe = 10.72 ± 1.4 mg/L, and Mn = 2.83 ± 0.7 mg/L exceeded the permissible limits. In some coal mines in

Quang Ninh, the monitoring results showed that the wastewater had low pH values, high levels of total suspended solids (TSS), iron (Fe), and manganese (Mn), which mostly exceeded the limits specified in column B of QCVN 40:2011/BTNMT for industrial wastewater quality.

3.2. Results of Selecting Agricultural Waste Byproducts for Treating Fe and Mn in Coal Mine Wastewater

3.2.1. Evaluation of Agricultural Waste Byproduct Hydrolysis Process

Various agricultural waste byproducts such as coconut fiber, sugarcane bagasse, rice husk, soybean hull, corn cob, sawdust, tea waste, and coffee waste were hydrolyzed to produce biochar. The resulting biochar exhibited clear changes in color and properties, as shown in Figure 3.1.

Figure 3.1. Images of agricultural waste byproducts after hydrolysis

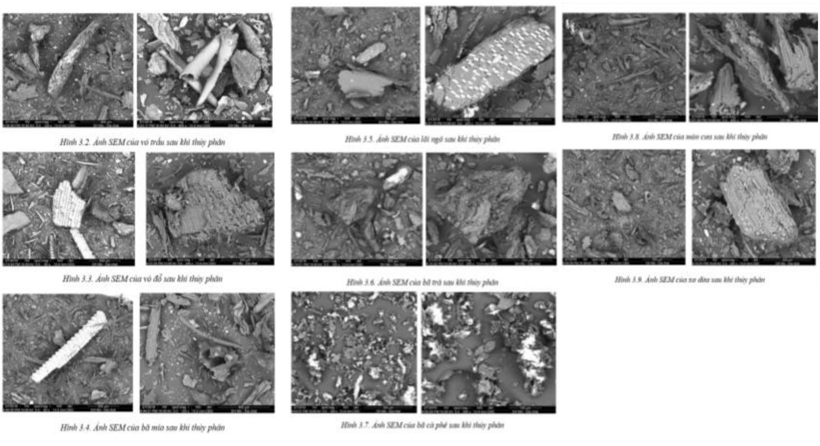
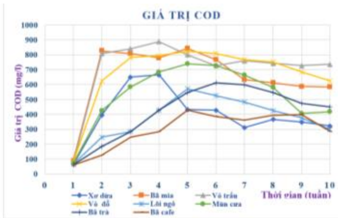


Figure 3.2. SEM images of the materials after hydrolysis

The SEM images of the eight types of resulting biochar indicated that they had porous surfaces with non-uniform distribution among the different types of biochar, such as rice husk and soybean hulls with corn cobs and soybean hulls, respectively. The surface roughness and pore density of the biochar also varied, resulting in different abilities to convert Fe and Mn in coal mine wastewater through biological transformation and adsorption.

3.2.2. Evaluation of changes in COD values during hydrolysis of AWB

The COD values increased rapidly during the first two weeks and then tended to decrease over the following time intervals. After four weeks, the COD values increased to a maximum and then showed a slight decreasing trend in the subsequent weeks. The hydrolysis of agricultural byproducts including rice husk, sugarcane bagasse, and soybean hulls resulted in the fastest decomposition rate. Specifically, the rice husk had the highest COD value of 888mg/l after four weeks of the experiment, while the sugarcane bagasse, soybean hulls, and sawdust had the highest COD values of 842mg/l, 824mg/l, and 686mg/l, respectively, after five weeks.

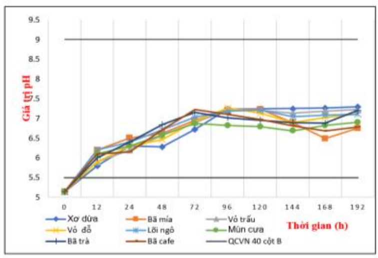


Hình 3.10. Diễn biến giá trị COD theo thời gian thủy phân các PPP nông nghiệp

3.2.3. Evaluation of pollution removal potential of AWB through hydrolysis in a constructed wetland system

3.2.3.1. pH variation assessment of wastewater

With an initial pH value of 5.13 that did not meet the Vietnamese national technical regulation for industrial wastewater quality after 12 hours of experimentation, the pH value of all trials (pH = 5.6-6.4) met QCVN standards. After 192 hours, the pH value of the effluent had significantly



Hình 3.11. Sự thay đổi giá trị pH trong nước thải ở các thí nghiệm chứa VLSH khác nhau

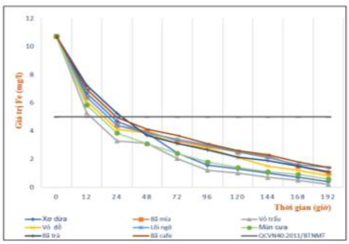
increased to 6.7-7.2. There was no significant difference in neutralization reaction among the different types of hydrolyzed AWB, and all met QCVN40 standards. The various types of agricultural waste products had little effect on the pH neutralization reaction in the wastewater.

3.2.3.2. Investigation of the impact of agricultural PPPs on COD values in wastewater

The initial COD value was 145mg/L, after passing through CW with the addition of 8 different agricultural PPPs (coconut fiber, sugarcane bagasse, rice bran, bean husk, corn cob, sawdust, tea waste, and coffee waste) that underwent hydrolysis and lime treatment, the COD value changed significantly. The general trend in all treatments showed an increase in COD value during the first 12-24 hours and then gradually decreased. This may be explained by the addition of agricultural AWB, which increased the organic matter content in the wastewater. In the following period, with no additional source, the treatment processes in the CW system caused the COD value to decrease over time. Substrates containing rice bran, sugarcane bagasse, and bean husk had higher treatment efficiency and speed compared to other substrates.

3.2.3.3. Evaluation of the ability of agricultural AWBs to treat Fe in constructed wetland systems

The efficiency of this process was relatively high, ranging from 51% to 69%, and the Fe values met the QCVN40 standard in all treatments. However, three types of filter media, namely rice husk, coconut fiber, and sawdust, showed significantly better treatment efficiency. Among them, the treatment with rice husk had the highest removal efficiency, reaching 69% after 24 hours, while the treatments with coconut fiber and sawdust had lower removal efficiency, with treatment efficiencies of

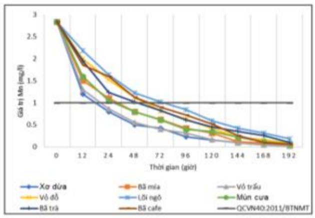


Hình 3.13. Sự thay đổi giá trị Fe trong nước thải ở các TN chứa PPP nông nghiệp khác nhau

62% and 61%, respectively. The treatment efficiency of Fe increased to 87-98% after 192 hours. Therefore, agricultural waste products can be arranged in the following order for treating Fe: rice husk, coconut fiber, sawdust > bean shell, tea waste, corn core > sugarcane bagasse, coffee waste. This provides a basis for selecting appropriate filter media from agricultural waste products for Fe treatment in mine wastewater using constructed wetlands in future studies.

3.2.3.4. Evaluation of the ability of agricultural AWBs to treat Mn

Figure 3.14 shows the general trend of Mn concentration change in the experiments, which decreased rapidly in the early stages and then slowly decreased. The use of agricultural PPPs such as coconut fiber and rice husk had a rapid Mn removal rate in the 24-hour experiment, with treatment efficiencies of 71.3% and 69.6%, respectively, and the effluent Mn concentration met QCVN40 column B. Bagasse and sawdust VLSH met the standard after 48 hours, and most other materials met the standard after 72 hours except for the use of corn core material. After 192 hours, rice husk and hydrolyzed coconut fiber VLSH could remove Mn in the wastewater with a high efficiency of 98.2% and 98.9%, respectively.



Hình 3.14. Sự thay đổi hàm lượng Mn trong nước thải trong các thí nghiệm với các loại PPP nông nghiệp khác nhau

Therefore, the appropriate material order for treating Mn can be arranged as follows: Coconut fiber, rice husk > Bagasse, oak bark, sawdust, tea waste, coffee waste > Corn core This is the basis for selecting VLSH from agricultural waste products for Mn treatment in mine wastewater using artificial plant filter systems.

3.2.3.5. Selection of suitable agricultural by-products for treating Fe, Mn in coal mine wastewater

The selection of suitable VLSH from agricultural by-products to supplement the CW system for treating Fe and Mn in wastewater needs to meet the following criteria: agricultural by-products suitable for the characteristics of the wastewater source; high treatment efficiency; low replacement frequency; no secondary pollution; a favorable substrate for plants and microorganisms; low material costs. The agricultural by-products selected in this study are all inexpensive, readily available, and environmentally friendly materials. From the above studies, it can be seen that rice husks have the ability to treat pollutants well, especially KLN pollutants. This is an inexpensive material, readily available in Vietnam and entirely suitable for application in CW systems for treating Fe and Mn in coal mine wastewater. Therefore, the rice husk hydrolysis process needs to be optimized for future research.

3.2.3.6. Study of rice husk hydrolysis using available bioproducts or cow manure in the filtration system

Results in Table 3.3 show that several main products are generated during the process of rice husk hydrolysis, such as glucose, lactate, acetate, methanol, and ethanol. These products act as a carbon source for the activity of micro organisms and as reducing agents during the sulfate reduction process.

Table 3.3. Analysis results of metabolites in the metabolic exchange process

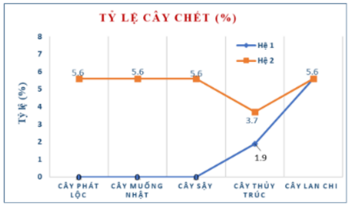
Sample	**Concentration before hydrolisis (mg/ml)**					**Concentration after hydrolisis (mg/ml)**				
	Đ/C	*TN1*	*TN2*	*TN3*	*TN4*	*Đ/C*	*TN1*	*TN2*	*TN3*	*TN4*
Glucose	-	-	-	4,35	6,12	-	-	-	-	4,8
Lactate	-	-	5,29	5,83	8,35	-	-	-	2,07	1,12
Acetate	-	-	1,49	1,02	7,73	-	-	-	-	1,08
Methanol	-	-	-	1,25	1,40	0,27	1,29	1,42	-	3,03
Ethanol	-	-	4,77	5,29	0,00	1,58	7,67	6,27	8,02	6,69
Total	-	-	**11,55**	**17,74**	**23,6**	**1,85**	**8,96**	**7,69**	**10,09**	**16,72**

The use of micro organisms products for rice husk hydrolysis showed higher efficiency compared to the process without the products. The total amount of short-chain carbon compounds produced was highest when both isolated cellulose-hydrolyzing micro organisms and cow manure were used (highest value reached approximately 16.72 mg/ml in experiment (TN4). Based on the experimental results, the optimal formula for rice husk hydrolysis on a larger scale was determined to be 300g of rice husk, 2 liters of water, 15 ml of a mixture of micro organisms hydrolyzed from rice husk, and 15g of cow manure.

3.3. Evaluation of the ability of aquatic plants (AP) to treat Fe, Mn

3.3.1. Assessment of the adaptability of AP species in experimental systems

In system 2, the highest mortality rate was observed in water hyacinth, Japanese water spinach, lotus, and water fern (5.6%), while the lowest mortality rate was observed in water bamboo (3.7%). However, in system 1, the mortality rate was much lower, with water fern, Japanese water spinach, and water hyacinth showing the best adaptation when grown on a filter material supplemented with natural VLSH, and no plant deaths occurred during the TN process. The mortality rate of water bamboo was 1.9%, while that of lotus was the highest (5.6%). This suggests that the selection of AP species such as water fern, Japanese water spinach, and water hyacinth grown in KLN-polluted NT on a filter medium with natural VLSH hydrolyzed (system 1) is suitable for treating Fe and Mn in coal mine wastewater.



Hình 3.17. Tỷ lệ cây chết của TVTS trồng trong 02 hệ thí nghiệm

3.3.2. Evaluation of Fe, Mn removal ability of aquatic plants

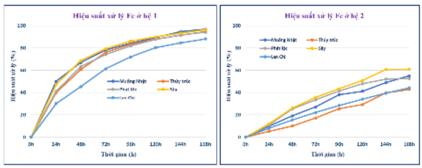
The effectiveness of Fe, Mn removal by five species of aquatic plants in experimental systems (System 1 - planting aquatic plants in constructed wetlands on filter media and System 2 - planting aquatic plants in pure hydroponic environment with additional Fe = 15mg/l, Mn = 5mg/l) was synthesized in Table 3.5.

From Figure 3.23, it can be seen that the Fe removal efficiency in System 1 (a) of the species E. crassipes and P. stratiotes was 96.5% and 96.8% after 168 hours of the experiment and reached QCVN 40 after only 48 hours with a removal efficiency of 68.7% and 67%.

Table 3.5. Fe and Mn removal efficiency of aquatic plants

No	Tree type	Treatment productivity (after 168 hrs)				Time to reseach allowable concentration (hr)			
		Fe		***Mn***		***Fe***		***Mn***	
		System 1	System 2	System 1	System 2	System 1	System 2	System 1	System 2
1	*Dracaena sanderiana*	94,3%	52,6%	94,7%	54,4%	72h	-	96h	-
2	*Caladium bicolor*	96,8%	54,9%	97,9%	59,6%	48h	-	96h	-
3	*Phragmites australis*	96,5%	61,0%	96,5%	57,9%	48h	-	96h	-
4	*Cyperus involucratus*	94,8%	42,8%	95,1%	59,1%	72h	-	96h	-
5	*Chlorophytum bicheti*	88,1%	44,2%	87,4%	44,2%	72h	-	96h	-

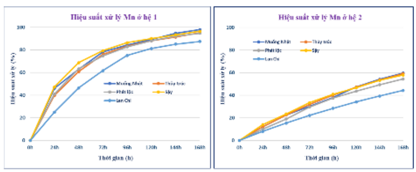
Meanwhile, the Fe removal efficiency of H. dubia, T. latifolia, and L. minor was lower, achieving 88.1-94.8% after 168 hours of the experiment and reaching QCVN after 72 hours. The ability to remove Fe in System 2 (b) when planting aquatic plants in a pure wastewater environment showed low removal efficiencies, ranging only from 44.2 to 61% after 168 experiments, with Fe levels not meeting the allowed standard.



(a) (b)

Hình 3.23. Hiệu suất xử lý Fe của các loại TVTS ở hai hệ (a. Hệ 1, b. Hệ 2)

From Figure 3.24, the Mn removal efficiency in System 1 and System 2 also showed a significant difference. The Mn removal efficiency of all species after 168 hours of the experiment in System 1 ranged from 87.4 to 97.9%, while in System 2, it ranged only from 44.2 to 59.6%. The best Mn removal efficiency in System 1 was observed in P. stratiotes and E. crassipes, achieving 97.9% and 96.5%, respectively, while the worst was observed in T. latifolia, achieving 87.4%. In System 2, the highest Mn removal efficiency was observed in P. stratiotes, T. latifolia, and E. crassipes, and the lowest was observed in H. dubia, but none of them met the allowed standard after 168 hours of the experiment.



(a) (b)

Hình 3.24. Hiệu suất xử lý Mn của các loại TVTS ở hai hệ (a. Hệ 1, b. Hệ 2)

3.3.3. Selection of Suitable Wetland Plant Species for Treating Fe, Mn in Coal Mine Wastewater

In the constructed wetland (CW) system using wetland plants combined with limestone and hydrolyzed rice husks as substrate, it was found that *Phragmites australis* and *Caladium bicolor* had good resistance to pollutants in Fe and Mn contaminated wastewater and high removal efficiency for Fe and Mn with a short retention time. This model can be applied for treating Fe and Mn pollutants in coal mine wastewater. However, plants such as *bamboo*, *orchids*, and *peace lilies* also had good resistance in polluted water, but their efficiency in Fe and Mn removal was not high enough to be selected for treating pollutants in coal mine wastewater.

3.4. Development of a technology process for treating Fe, Mn in coal mine wastewater

3.4.1. Technology process for treating Fe, Mn in coal mine wastewater at a scale of 250L/day

Based on the survey and analysis of the quality of coal mine wastewater at some mines in Thai Nguyen and Quang Ninh provinces, the main pollution characteristics of coal mine wastewater are low pH, high levels of Fe, Mn, TSS. The use of agricultural PPPs combined with constructed wetlands (CWs) is evaluated as suitable for the criteria set out, treating the pollution parameters effectively. Therefore, this process is chosen to apply in the technology process for treating high levels of Fe, Mn in coal mine wastewater. The designed wastewater flow rate is 250L/day to be closer to actual conditions.

Table 3.6. Waswater quality at Tay Lo Tri coal mine, Quang Ninh

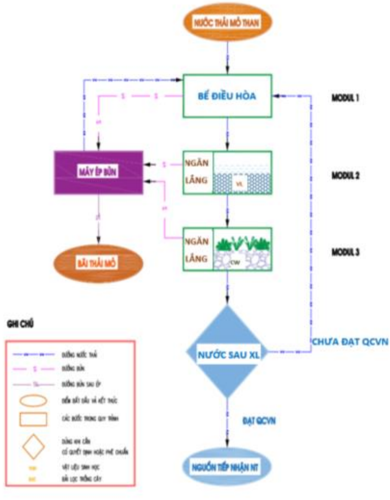
No	Indicator	Unit	Analysis method	Results	**QCVN 40**
1	pH	-	TCVN 6492:2011	4,23±0,3	**5,5 ÷ 9**
2	TSS	mg/l	TCVN 6625:2000	172±14	**100**
3	Fe	mg/l	TCVN 6177:1996	14,6±3,6	**5**
4	Mn	mg/l	TCVN 6002:1995	8,4±2,4	**1**

The process flow diagram for Fe and Mn treatment in coal mine wastewater is presented in Figure 3.25, which includes three main modules (regulation tank, filter media tank with lime and rice husk, and planted flow constructed wetland):

- Module 1: Regulation tank;

- Module 2: Filter media tank containing a mixture of lime and hydrolyzed rice husk;

- Module 3: Planted flow constructed wetland (CW) with horizontal subsurface flow technology .



Hình 3.25. Quy trình công nghệ xử lý nước thải mỏ than

The design of the modules in the system was calculated based on Fe (25mg/l) and Mn (15mg/l) concentrations. The settling tank has a retention time of 12 hours. The filter tank is expected to remove 60-80% of Fe, Mn, and pollutants after treatment in the hydrolyzed rice husk filter tank with COD ≤ 300 mg/l; Mn and Fe ≤ 10mg/l. The CW tank treats residual pollutants and pollutants after treatment according to QCVN 40 column B. Based on the calculations, the sizes of the tanks were determined as follows:

- Regulation tank (tank 1) with a volume of V1 = 0.25m^3;

- Filter media tank (tank 2) with a volume of V2 = 1.66m^3;

- Planted flow constructed wetland (CW) tank with a volume of V3 = 1.875m^3.

3.4.2. Evaluation of Fe and Mn removal efficiency in modules

3.4.2.1. Effectiveness of Fe and Mn removal using limestone and rice husk filter modules

a. Evaluation of Fe and Mn removal efficiency using limestone

Different masses of limestone (0kg, 5kg, 10kg, 15kg, 20kg, 25kg) were used to treat Fe and Mn. At TN1 with 5kg of limestone, the lowest treatment efficiency was observed, with only 42% removal after 144 hours. In contrast, higher masses of limestone (10kg, 15kg, 20kg, 25kg) showed over 80% removal efficiency. Particularly, at 25kg of limestone, the removal efficiency reached up to 95%, and the Mn concentration met the QCVN 40 column B standard after only 24 hours.

b. Removal ability of Fe and Mn using rice husk material

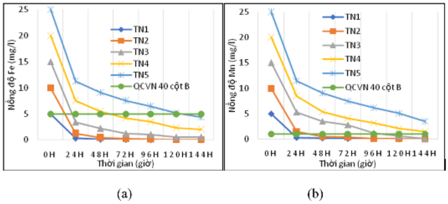
Wastewater containing Fe and Mn with the same initial concentration (10mg/l) was fed into the treatment system containing different masses of rice husk (0kg, 0.5kg, 1kg, 1.5kg, 2.0kg, 2.5kg). The removal of Fe occurred rapidly within approximately 24 hours, with the residual Fe in the wastewater being less than 0.3 mg/l and almost completely removed in all systems. The Mn removal efficiency at TN1 with 0.5kg of rice husk was the lowest, reaching only 76.2% in 24 hours. The higher the mass of rice husk used, the higher the removal efficiency. TN5 with 2.5kg of rice husk showed the highest removal efficiency, with over 85% removal after 24 hours. Rice husk was found to be more effective at removing Fe, while Mn was also significantly removed during the treatment process.

c. Evaluation of Fe and Mn removal efficiency in material filter bed module

The highest Fe and Mn removal efficiency after 144 hours was observed in TN6, with approximately 99.8% removal. The removal efficiency of Fe and Mn in TN7 (containing only rice husk) was much higher than in TN1 (containing only limestone). After 144 hours, Fe and Mn concentrations decreased by approximately 93% in TN7 and 75% in TN1. The initial pH in all experimental models was 4, and at the end of the experiment, the pH of the output in TN7 (without limestone) was 6.7, while the pH values in all other experimental models (TN1-TN6) ranged from 7.1 to 7.3. The results of this study provide a basis for selecting appropriate material ratios for filter beds containing limestone and rice husk in the treatment of coal mine wastewater according to TN6 (containing 5kg of limestone and 2.5kg of rice husk).

3.4.2.2. The effect of metal concentration on the efficiency of Fe and Mn treatment in the filter tank

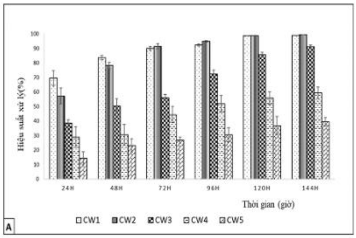
Within 24 hours, the concentration of Mn decreased significantly, with treatment efficiency ranging from 54% to 94%. At TN1, the Mn concentration reached QCVN40 after 24 hours, while at TN2, it took 48 hours to reach QCVN40 at higher concentrations of 20-25 mg/l. After 144 hours, the Mn concentration was only 1.5-3.5 mg/l, and the removal efficiency was 86-92.5%, but the quality of the treated water did not meet the QCVN 40 Column B standard. The research results indicate that the filter tank can treat Fe concentrations up to 15 mg/l and Mn concentrations up to 10 mg/l within 2 days, meeting the permissible standard.



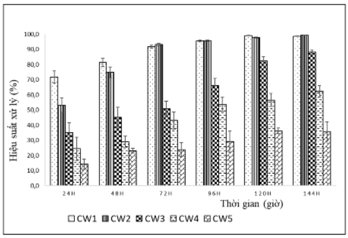
Hình 3.31. Sự thay đổi hàm lượng Mn, Fe theo thời gian (a. Fe, b. Mn)

3.4.2.3. Efficiency of Fe and Mn removal in the constructed wetland system

The research results demonstrated that the CW models effectively removed Fe and Mn. The highest removal efficiency of Fe (99%) and Mn (98.8%) was recorded in CW1 with initial Fe and Mn concentrations of 5 mg/l after 144 hours. In CW2, with initial Fe and Mn concentrations of 10 mg/l, the removal rate of Fe and Mn was approximately 99.5% after 144 hours. When the initial concentration of Fe and Mn was 15 mg/l (in CW3), the removal efficiency of Fe and Mn was about 91.1% and 88.4% respectively after 144 hours. However, when the initial concentration of Fe and Mn increased to 20 mg/l (in CW4), the removal efficiency of Fe and Mn decreased to only 59.5% and 62.5%, respectively. Similarly, when the initial concentration of Fe and Mn increased to 25 mg/l (in CW5), the removal efficiency of Fe and Mn was only 39.5% and 35.9% after 144 hours. Therefore, the CW system



Hình 3.32. Hiệu suất xử lý Fe của bãi lọc trồng cây



Hình 3.33. Hiệu suất xử lý Mn của bãi lọc trồng cây

with Japanese mint and water hyacinth grown on a substrate of limestone and acid-hydrolyzed rice husk was able to effectively treat Fe and Mn in wastewater, and could treat a Fe concentration of 15 mg/l within 96 hours and a Mn concentration of 10 mg/l within 72 hours, meeting the standard requirements. This provides a basis for selecting design parameters for constructed wetlands for wastewater treatment in practical applications.

3.4.3. Evaluation of Treatment Efficiency of the Technological Process

- The pH value of the input water sample (coal mine wastewater in Tay Lo Tri) ranged from 3.8 to 5.2 and did not meet QCVN standards. After going through the treatment system, the pH value of the output wastewater ranged from 6.7 to 7.5, meeting QCVN 40:2011/BTNMT column B.
- The input TSS value fluctuated between 153.2-176.4 mg/l, exceeding QCVN 40 by 1.5-1.8 times. After going through the treatment system, the TSS value was removed by settling in the settling tank, then filtered and settled in the filter tank and CW tank. The TSS value in the output wastewater was 38.2-46.3 mg/l, meeting QCVN 40:2011/BTNMT column B.
- The COD value in the input wastewater of the treatment system was about 200-280 mg/l. After going through the treatment system, the COD value decreased to only about 50-80 mg/l, meeting QCVN 40:2011/BTNMT column B.
- The results showed that at the output of the system, the concentration of Fe ions was only about 0.004-0.1 mg/l, and the Fe concentration in the output wastewater of the treatment system met QCVN 40:2011 /BTNMT column A.
- The results showed that the input Mn concentration ranged from 8.2-9.1 mg/l, and after going through the treatment system, the amount of Mn remaining in the wastewater was negligible. The removal efficiency of Mn by the treatment system was about 97-99%. The coal mine wastewater after going through the designed treatment system gradually removed environmental pollution indicators such as pH, TSS,

Fe, and Mn through each module. The treatment efficiency of pollutants through the 3 main modules is shown in Table 3.9 below.

Table 3.9. Treatment efficiency of pollutant parameters in each module.

No	Parameters	Treatment efficiency by each module (%)			
		Module 1	*Module 2*	*Module 3*	*Module ra*
1	pH	7,3	13,9	49,9	62,4
2	TSS	3,5	27,0	60,5	76,5
3	COD	1,1	(25,9)	33,0	72,1
4	Fe	8,2	18,5	82,5	98,8
5	Mn	6,9	14,0	85,2	98,6

Therefore, after 3 months of operating the wastewater treatment system according to the designed technology process, the quality of the treated water output from the wastewater treatment system consistently meets QCVN 40:2011/BTNMT Column B for COD, TSS, and meets QCVN 40 Column A for KLN Fe, Mn. The treatment system operates stably, and there are no blockages in the filter bed or CW; the plants in the CW grow well throughout the treatment process. The TN results provide a basis for applying the wastewater treatment technology process to larger-scale coal mine wastewater treatment.

CONCLUSION AND RECOMMENDATION

1. Conclusion

Several conclusions can be drawn from the research process:

- The results of the analysis of wastewater quality from some coal mines in Quang Ninh and Thai Nguyen provinces show that coal mine wastewater has main characteristic pollution parameters including pH, TSS, Fe, Mn, which exceed the QCVN 40:2011/BTNMT (column B) many times. The levels of these parameters vary as follows: pH = 3.82 to 5.34; TSS = 125 to 248 mg/l; Fe = 7.4 to 139.4 mg/l; Mn = 4.9 to 88.2 mg/l.

- The natural adsorbent material of rice husk was evaluated and selected from 08 types of agricultural residues (rice husk, coconut fiber, sugarcane bagasse, corn core, sawdust, tea waste, coffee waste, and peanut shell) used in the study. The removal efficiency of Fe and Mn after 24 hours of rice husk reached 69% and 69.6%, respectively. After 192 hours, the removal efficiency of Fe and Mn reached the highest values of 98.3% and 98.2%, respectively.

- Two species of macrophytes, including Phragmites australis and Caladium bicolor, were studied and selected among 05 species of macrophytes (Chlorophytum bicheti, Dracaena sanderiana, Phragmites australis, Cyperus involucratus, and Caladium bicolor), with the ability to treat Fe, Mn in coal mine wastewater, and grow well in the environment of KLN-polluted water with nutrient-poor soil. Both species of plants selected were capable of withstanding high levels of Fe and Mn in water environments. The survival rate of plants reached nearly 100% in system 1 and from 94.6% to 100% in system 2. The best Fe and Mn removal efficiency was achieved by Caladium bicolor (96.8% and 97.9%), followed by reed (96.5% and 96.5%) after 168 hours, meeting QCVN40:2011/BTNMT column B after 48 hours. The less efficient ability to treat Fe and Mn was found in Chlorophytum bicheti, Dracaena sanderiana and Cyperus involucratus.

- The technology process of treating Mn and Fe in coal mine wastewater with a flow rate of 250 L/day includes 3 main modules: module 1 is a settling/conditioning tank; module 2 is a material filter tank composed of a mixture of hydrolyzed rice husk and lime rock; module 3 is a constructed wetland (CW) filter bed. The efficiency of treating characteristic pollution parameters of coal mine wastewater according to this technology process reached from 62.4% to 98.8%. The experimental model operated stably for 3 months, and the quality of wastewater always met QCVN 40:2011/BTNMT column B for COD and QCVN 40:2011/BTNMT column A for Fe, Mn, and TSS. This technology process has potential for practical application in coal mine wastewater treatment.

2. Recommendations

The research results of the thesis need to be scaled up in the treatment of wastewater from open pit coal mines. However, for each application location, an overall evaluation is needed to choose a suitable design. In particular, for constructed wetlands (CWs), preliminary evaluations are needed for the adaptability of plant species to wastewater sources and environmental conditions.

In addition to studying the treatment of Fe and Mn in mine wastewater, further research on other indicators is also needed. The treatment model presented in this thesis can be considered for the treatment of similar wastewater sources.

NEW CONTRIBUTIONS OF THE THESIS

Research and selection of rice husk VLSHs with the most effective treatment of Fe and Mn in wastewater from coal mines among 8 common agricultural by-products in Vietnam *(rice husk, sawdust, coconut fiber, sugarcane bagasse, peanut shells, tea waste, coffee waste, corn cobs*).

Research and selection of two plant species, *Phragmites australis* and *Caladium bicolor* with good capability in treating Fe and Mn parameters in wastewater from coal mines. Both plant species have good growth and development in polluted and nutrient-poor wastewater environments.

The establishment of a technology process for treating mine wastewater containing high levels of Fe and Mn, with low pH levels using agricultural by-products that have been hydrolyzed, combined with constructed wetlands for plant growth.

LIST OF SCIENTIFIC PUBLICATIONS

1. **Do Thi Hai,** Bui Thi Kim Anh, Le Thanh Son. *Current status of wastewater in some coal mines in Vietnam. Solutions for management and treatment of mine wastewater through biological methods*. Proceeding & directory Vietnam international water week, VACI, 2018. Vietnam Cooperation Highlights. ISBN: 978-604-67-1059-2, 101-106.

2. **Do Thi Hai**, 2018. *Study on the effect of some natural biological materials on the treatment of Fe, Mn in mine wastewater by Wetland technology.* National Conference on Earth and Natural Resources with Sustainable Development (ERSD 2018). Transport Publishing House, ISBN: 978-604-76-1753-1, pp. 22-35.

3. **Hai Thi Do**, Anh Thi Kim Bui, Mai Hoa Nguyen, Quan Tran Anh, Thao P.T. Vu, Ha K.T. Tran, 2019. *The treatment efficiency of Iron and Manganese in wastewater by Phragmites australis combines limestone and rice husk. Innovative WaterSolutions for Vietnam and Region*. Vietnam National University Press, Ha Noi. ISBN 978-604-67-1216-9, Page 150-155.

4. Viet Anh Nguyen, Minh Phuong Nguyen, Karin Tonderski, **Hai Do Thi** and Anh Thi Kim Bui. *Design and performance of a coarse media, high hydraulic load polishing wetland for steel industry wastewater*. Water Science & Technology, IWA Publishing, UK, 2019, Vol 80, Issue 1, July. ISSN 0273-1223

5. **Hai Thi Do**, Anh Thi Kim Bui, Mai Hoa Nguyen, Quan Tran Anh, Thao P.T. Vu, Ha K.T. Tran, 2019. *Study on the capability of treating Fe, Mn in the wastewater of several aquatic plant species*. Journal of Mining and Earth Sciences, ISSN 1859-1469.

6. Bui Thi Kim Anh, Nguyen Van Thanh, **Do Thi Hai**. *Research and application of contruction wetlands to treat heavy metals, iron and manganese in wastewater*. Scientific Conference of Vietnam Academy of Science and Technology, October 2020.

7. Bui Thi Kim Anh, **Do Thi Hai**, Nguyen Hong Chuyen. Patent *"Useful solutions*" No. 2541 on Mine wastewater treatment process was granted by the National Office of Intellectual Property under Decision No. 17778w/QD-SHTT dated 13/11/2020.

8. **Do Thi Hai**, Bui Thi Kim Anh, Nguyen Van Thanh, Nguyen Van Binh. *Research and application of contruction wetlands to treat iron and manganese heavy metals in wastewater.* Environmental Magazine, thematic number 1, March 2021. ISSN: 2615-9597, Pages 52-55.

9. **Do Thi Hai**, Nguyen Minh Phuong, Nguyen Van Thanh, Bui Thi Kim Anh, 2022. *Iron and Manganese Removal from Wastewater by Constructed Wetlands Planted with Caladium bicolor*. VNU Journal of Science: Earth and Environmental Sciences, Vol. 38 (2022), 111-118.