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The treatment efficiency of Iron and Manganese in wastewater by *Phragmites australis* combines limestone and rice husk

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Abstract

Mine wastewater includes rainwater, surface water and groundwater generated from dry-out and drainage operations during coal mining. In mine wastewater, Iron and Manganese are common metals with total concentration often exceed the National technical regulation on Industrial Wastewater (QCVN 40: 2011/BTNMT). Improperly treated wastewater will adversely affect the environment and human health.

Removal of iron and manganese in water sources has been attracting the awareness and attention of scientists. In this study, the authors used the reed species Phragmites australis with limestone and rice husk to remove iron and manganese in coal mine wastewater. Results of heavy metal removal were promising when iron and manganese treatment efficiency reaches 82 ÷ 98% and 70 ÷ 98%, respectively. In high pollutant concentration condition, the treatment efficiency proved better than the low pollution input.

Keywords: mine wastewater, Phragmites australis, limestone, rice husk.

I. Introduction

The reed species *Phragmites australis* is a large plant belonging to the *Poaceae* family, distributed in wetlands in both tropical and temperate regions of the world. When appropriate growing condition meets, it can achieve average height of 5m and even higher in with stems that grow vertically and root branches generate at regular intervals. Reed body can grow taller from 2 to 6m with vertical root. In areas with fertile soil and hot/humid summers, reed grows taller. The leaves of reeds are wide compared to grass species, from 20 to 50 cm long and 2-3 cm wide. Flowers have a dense purple-colored oval shape, 20 to 50 cm in length [wikipedia.org, 2019].

Phragmites australis naturally grows fast, regenerating using roots, stems, etc. Many studies have pointed out that reed is one of the aquatic plants having the ability to purify water and treat wastewater through its roots. The reed root is the home for many microorganisms that can decompose organic matter and absorb heavy metals in medical, domestic wastewater and wastewater.

Figure 1.1. Phragmites australis reed

Rice husk also play a very important role in the treatment of iron (Fe) and manganese

(Mn) in wastewater since it mainly composed of cellulose and silicon dioxide. Microorganisms hydrolyze cellulose into glucose, then continue to break it down into short carbon organic compounds such as ethyl alcohol, methanol, acetic acid, etc. Microorganisms use short-circuit carbon compounds from rice husk and organic carbon from plants root as a source of electron supply for the reaction that reduce sulfate to sulfide, nitrate to nitrogen. Thereby, the formed sulfide ion eliminates heavy metal (Fe, Mn). Using rice husks in pollution treatment will reduce organic waste, partly contribute to reducing greenhouse gas effects caused by the burning process.

Limestone has the effect of increasing the pH of waste water by the reaction of $CaCO_3$ with water. In addition, because limestone has the ability to precipitate some types of valence 2 and 3 heavy metals, it reduces the load for the rice husk and plant surfaces in the treatment system. Limestone also acts as the basement for microbial membrane to develope [1].

Therefore, in this study, we tried to combine reed species *Phragmites australis* with limestone and rice husk to treat iron and manganese in coal mine wastewater to limit their influence on with environment and people.

2. Research Methods

2.2.1. Data collection and analysis

Collect the materials related to the composition and nature of coal mine wastewater such as annual environmental monitoring reports from Vietnam Coal and Mineral Industries, mine wastewater treatment technology, environmental regulations and regulations field related to mine waste water quality. We also collect the documents and data on the ability of heavy metal absorption by reed, method of treating metal containing wastewater by natural biological materials, plants and other necessary documents.

2.2.2. Field survey, measurement, sampling

Field surveys were organized in some typical coal mines in Quang Ninh, measurement of field parameters (temperature, pH, DO, TDS, turbidity ...) in mine wastewater samples in the study area according to National standards: TCVN 6663-1: 2011 (ISO 5667-1: 2006) - Water quality - Part 1: Guidance on making sampling programs and sampling techniques; TCVN 6663-3: 2008 (ISO 5667-3: 2003) - Water quality - Sampling. Instructions for preservation and handling of samples.

2.2.3. Laboratory experiment

Water pH indicator was measured by the HANA 211 pH meter, the iron and manganese concentration were determined by photometric method on spectrophotometer (UV-Vis Spectrometer Shimadzu UV-2450 of Shimadzu firm).

- Iron is determined by photometric method when reacting with reagent 1.10 - phenantrolin in acidic environment, compound with red orange color, with maximum absorption intensity at wavelength of 510 nm (TCVN 6177: 1996) .

- Manganese determined by photometric method when reacting with fomaldoxim reagent in alkaline environment, compound with reddish brown color, with maximum absorption intensity at wavelength of 450 nm (TCVN 6002: 1995).

2.2.4. Field experiment

Field experimental has been prepared to evaluate the effectiveness of iron and manganese treatment in mine wastewater using *Phragmites australis* combined with decomposed rice husk and limestone system. Sample of wastewater is prepared in the laboratory environemnt at different concentrations of pollutants to evaluate *Phragmites australis* with the best treatment capacity in any concentration range. Removal efficiency of Fe and Mn was analyzed and evaluated in 120 hours of experiment, after each experimental period: 0h, 6h, 18h, 24h, 48h, 72h, 96h and 120h will take samples and measure pH, stool Fe, Mn content of each module at different concentrations (C1, C2, C3, C4, C5).

2.2.5. Data processing methods

Use some software such as Word, Excel for data processing. The results of waste water quality and experimental models are shown in the form of tables, diagrams, charts ... and then analyzed, synthesized and evaluated.

3. Research results and discussion

3.1. Characteristics of coal mine waste water

According to the results of the authors' research in August 2018 and January 2019 and monitoring results of the Vietnam National Coal and Mineral Industries Group (TKV) in Vietnam, the pH value in coal mining wastewater is usually low, normally at pH = 2.34 ÷ 5.7 in the dry season and pH = 3 ÷ 6.5 in the rainy season, high concentration of Fe ranges from 2 to 47.6 ppm (in dry season) and 0.5 to 11.16 ppm (in the rainy season), Mn concentration ranges from 1.5 to 13.5 ppm (in dry season) and 0.5 to 9.7 ppm (in the rainy season), total suspended solids (TSS) ranges from 50 to 670 ppm in the dry season and from 150 to 900 ppm in the rainy season. These values exceed QCVN 40:2011/BTNMT for multiple source water type B [4].

3.2. Field experiment set up

The experiment was implemented on a rectangular mica tank of 50x35x20cm in size and with a tap to guide wastewater into underground streams. Each mica tank contains 22kg of limestone, 669g of rice husk, divided into three layers, the bottom layer is limestone (2x3cm in size) with a thickness of 5cm, the next layer is hydrolyzed rice husk 5cm thick and top layer is 5 cm thick limestone, *Phragmites australis* was grown on the top limestone layer with 6 reed groups

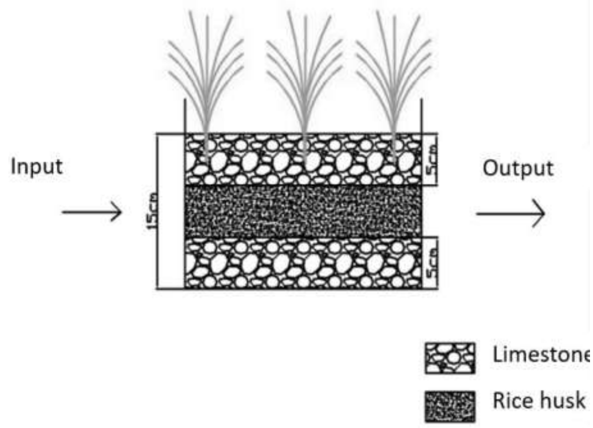

Figure 3.1. Simulation module for experimental modules

Table 3.1. Initial concentrations of Fe and Mn in experimental modules

No.	Fe (mg/l)	Mn (mg/l)	Modular symbols
1	5	1	C1
2	10	2	C2
3	15	3	C3
4	20	4	C4
5	25	5	C5

distanced in 15cm x 15cm wide. The water volume of each tank is 10 liters.

Wastewater was prepared with iron and manganese content assumed from $FeSO_4.7H_2O$ and $MnSO_4.H_2O$ with the ratio 5:1, respectively. The initial concentration of iron and manganese in the experiment is presented in Table 3.1.

Experimental modules were repeated twice for each concentration (10 tanks). Adjust the pH value of the water sample in the range of 2.5÷5 according to the acid characteristics of the mine wastewater. Carrying out and analyzing the parameters of pH, Fe, Mn at the modules at 6h, 18h, 24h, 48h, 72h, 96h and 120h intervals.

3.2. pH value

Experimental results show that input wastewater has a relatively low pH of about 2.5 ÷ 3.5, after the first 6 hours, the pH value increases very rapidly to 6.5 and reaches 7.2 after 18h. After about 24 hours to 120 hours of experiment, pH was somewhat stable, increasing slowly, reaching about 7.8 at 120 h. With wastewater with a pH of 6.5 ÷ 8, it is suitable for the development of sulfate reducing microorganisms that exist in the microbiota of hydrolyzed rice husk and reed.

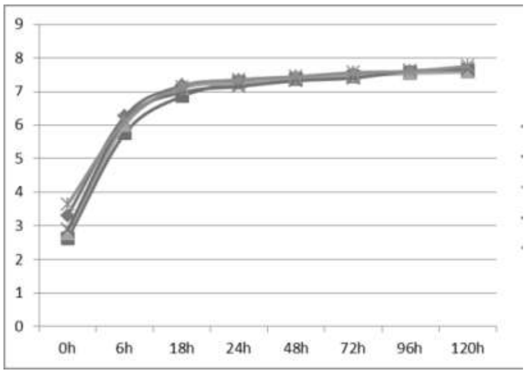

Figure 3.2. Variation pH over 120 hours of experiment

3.3. Effect of reed Phragmites australis on treatment efficiency of Fe and Mn in wastewater

Ability to handle Iron and Manganese in wastewater

The concentration of Iron decreases with time and varies in the input concentration ranges (C1, C2, C3, C4, C5). Specifically, the concentration of Iron decreased the fastest after the first 6 hours, only about 0.91 ÷ 3.05mg/l. After 18 ÷ 120 hours of experiment, the concentration decreased slowly, ranging from 0.81 ÷ 2.10 mg l at 18 hours, 0.45 ÷ 1.34 mg l at 24 hours and only 0, 1 ÷ 0.42 mg/l after 120 hours.

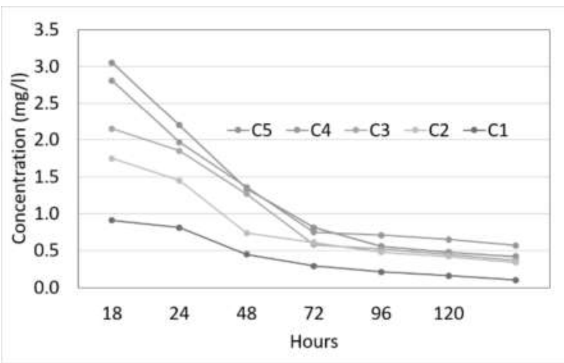

Figure 3.3. Iron concentration decreases through time

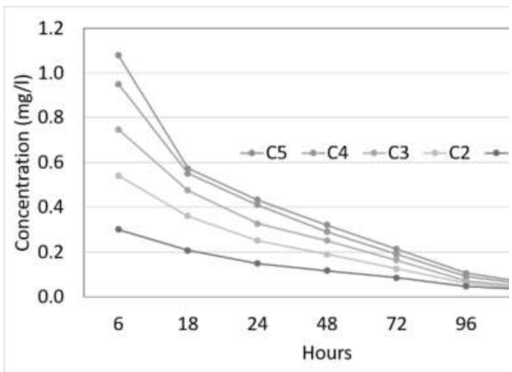

Figure 3.4. Manganese concentration decreases through time

The concentration of Manganese in mixed contaminated wastewater is slightly more variable than that of only Mn-contaminated wastewater and varies in input concentration ranges (C1, C2, C3, C4, C5). Specifically, Manganese concentration decreased sharply, only 0.30 ÷1.08 mg/l after the first 6 hours. After 15 hours, Manganese concentration ranged from 0.1 ÷ 0.67 mg/l. Later, Mn concentration decreased slowly, only about 0.17 ÷ 0.39 mg/l after 24 hours and 0.06 ÷ 0.11 mg/l after 48 hours of experiment. The concentrations of Manganese in the experimental output meet the permitted limits specified in column B of QCVN 40: 2011/BTNMT.

• *Evaluate the treatment efficiency of iron and manganese in wastewater*

The treatment efficiency of Iron reaches 82% ÷ 98%, while the processing efficiency of Manganese reaches 70 ÷ 98%. The processing efficiency of Iron and Manganese increases with time and varies in the input concentration ranges. In general, the processing efficiency for the large input concentration (C5) range is higher than the low input concentration (C1).

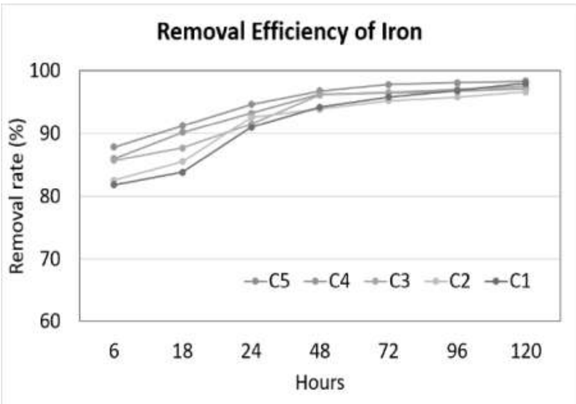

Figure 3.5. Removal rate of Iron

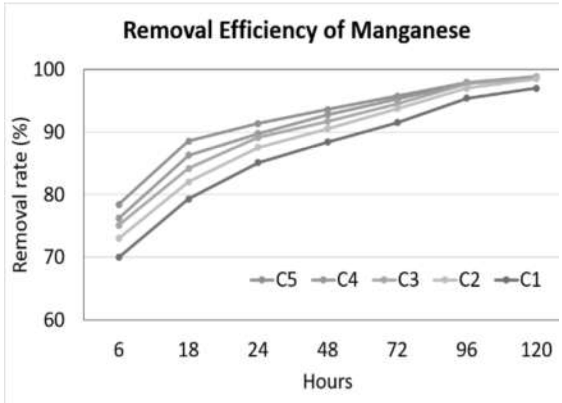

Figure 3.6. Removal rate of Manganese

Through the results of processing Iron and Manganese in the above experiments, showed that: the module uses aquatic systems in combination with limestone and rice husk hydrolyzate (limestone system - sawdust - The reed *Phragmites australis* in the laboratory) with efficiency higher and more thorough treatment of Iron and Manganese than limestone - reed in Hong Thai coal mine - Quang Ninh (efficiency of 82 ÷ 96% of experimental modules compared to 70 ÷ 84.3% of Hong Thai mine). Thus, rice husk is used in this experiment as an additional layer of material in artificial wetland systems to filter and adsorb precipitates, metals and suspended solids to increase cleaning ability wastewater.

4. Conclusions and recommendations

The pH value in coal mining wastewater is usually low, normally at pH = 2.34 ÷ 5.7 in the dry season and pH = 3 ÷ 6.5 in the rainy season, high concentration of Iron ranges from 2 to 47.6 ppm (in dry season) and 0.5 to 11.16 ppm (in the rainy season), Manganese concentration ranges from 1.5 to 13.5 ppm (in dry season) and 0.5 to 9.7 ppm (in the rainy season), total suspended solids (TSS) ranges from 50 to 670 ppm in the dry season and from 150 to 900 ppm in the rainy season.

The pH of the wastewater after the treatment system is from 6.5 ÷ 8, which is suitable for the development of sulfate reducing microorganisms that exist in the microbiota of hydrolyzed rice husk and reed *Phragmites australis*.

The efficiency of Iron treatment is 82 ÷ 98%, higher than the Manganese processing efficiency reaching 70 ÷ 98%. The concentration of Iron and Manganese in the experimental output met the permitted limits specified in column B of QCVN 40: 2011/BTNMT. In general, the processing efficiency for the high input concentration (C5) range is better than the low input concentration (C1).

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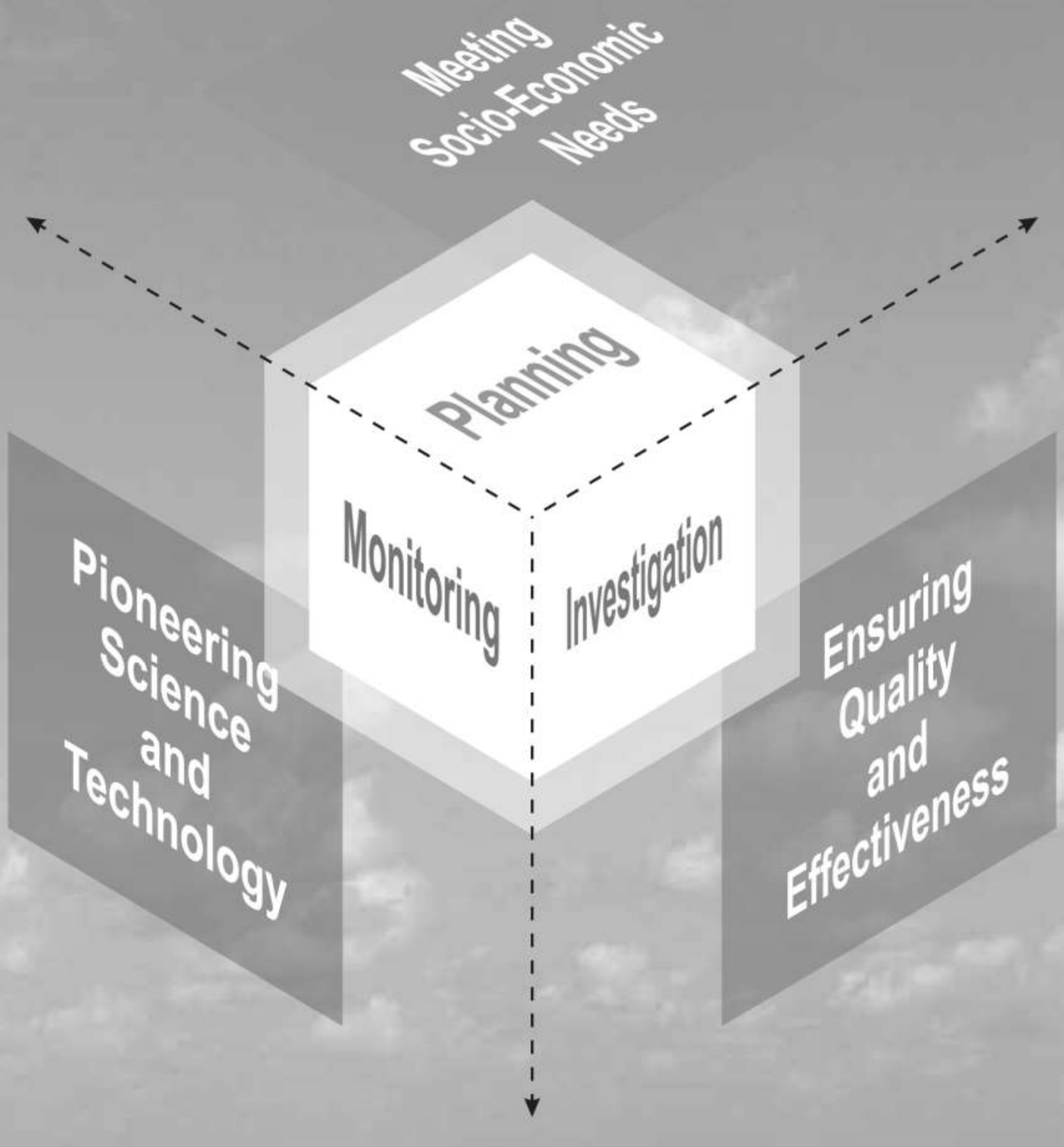

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