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**SUSTAINABLE WATER AND SANITATION SERVICES  
FOR ALL IN A FAST CHANGING WORLD**

**Potential reuse of coal mine wastewater:  
a case study in Quang Ninh, Vietnam**

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*In Vietnam, the local regulation and environmental impact are driving coal mining industry to reuse the large volume of wastewater it produces. The co-research project between National University of Civil Engineering (NUCE) and Mitsubishi Rayon Corporation (MRC) has started early 2013 to evaluate if the MRC membranes could be a great tool for treatment of coal mine wastewater for reuse. The experiment were conducted at one of coal mine plants in Quang Ninh province, Vietnam. It was found that pre-treatment of coal mine wastewater was an important part in the treatment process. The MRC membrane was a significant barrier to maintain stable and high quality effluent to meet the requirement of Vietnam national technical standard for domestic use.*

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## **Introduction**

Coalmine effluent has always been of concern in wastewater management. The wastewater from coalmines often called "Acid mine drainage" (AMD) is formed in underground workings (groundwater) of deep mines, and usually has low pH, high specific conductivity, high concentrations of iron, aluminum, manganese, high suspended solids and low concentrations of toxic heavy metals (Akcil and Koldas, 2006). The most common and conventional AMD treatment method is precipitation with different types of coagulants/oxidants (Silveira et al., 2009). Of the chemical oxidants such as hydrogen peroxide, calcium peroxide and ozone, ozone appeared to be the best to achieve rapid and complete oxidation; however, capital costs of the process need to be assessed (Rao et al., 1995). In addition to precipitation, biological method which employs different types of micro-organisms (bacteria, protozoa) for metal recovery have also been studied in many researches (Battaglia-Brunet et al., 2002; Johnson, 1995; Huisman et al., 2006). The biological technique was proved to be cheaper than other treatment technologies; however the application in large-scale industry seemed to be not so feasible due to some uncertainties in biological route under varying environmental conditions (Rao et al., 1995). Therefore, other technologies for the treatment of AMD are of interest such as electro dialysis (ED), microfiltration, reverse osmosis and ion exchange (Ali, 2011).

While the sustainable approach in wastewater management is to treat wastewater and reuse for different purposes such as toilet flushing, plant watering, road cleaning, fire fighting, underground water recharging, the AMD could also be treated to reuse for dust removal in coal mines, for domestic use (i.e., showering and washing for miners).

In Vietnam, coalmines are located mostly in Quang Ninh province, which contributes 90% of country's coal production. Coal mining brings about economic and social benefits to the communities in Quang Ninh but also has an environmental impact on these communities. It was reported by Quang Ninh Department of Resources and Environment that the total treated AMD from coal industry was 71,021 m<sup>3</sup>/d, accounting for 40.5% of total wastewater generated. Due to the pressure of environmental protection from water pollution, most of coal processing plants have AMD treatment systems. However, AMD treatment at open mines and closed mines is significantly low with 8.3% and 18.2% respectively. In order to achieve 100% of plants having AMD treatment before discharge, based on the Action Plan towards 2015, the Vietnam National Coal-Mineral Industries holding corporation limited (Vinacomin) has to invest about 50 treatment systems (Vinacomin report, 2009). In 2012, Vinacomin has started the construction of new 18 AMD treatment plants, of which four are for open mines and 14 are for closed mines. The two main treatment processes are:

- Settling by gravity in sedimentation ponds at Mao Khe mine, Vang Danh and Hon Gai coal process plants.
- Neutralization/Coagulation with limestone  $\text{CaCO}_3$  at Vang Danh coal mine, with  $\text{Ca(OH)}_2$  at Na Duong and Mao Khe coal mines, with  $\text{Ca(OH)}_2$  and polime A101 and followed by sedimentation tank/pond at Ha Lam and Khe Tam coal mines, Cua Ong coal process plant, etc.

According to Vinacomin report in 2011, most of AMD treatment systems were not working effectively. Because most treatment technologies are inadequate, quite commonly, significant AMD is left untreated. For a few plants working properly, the effluent quality only met QCVN 40:2011/BTNMT- type B (which is the criteria for discharging into non-drinking water sources). No reuse for domestic or manufacture application has been conducted even though the water shortage for domestic use is emerging in many coal mines. In fact, the treated AMD can be reused for dust removal in coal mines, providing water for miners washing and showering after each work shift, for toilet flushing and plant watering. This required amount of water could be as significant as 75,600 m<sup>3</sup>/d based on the wastewater discharge daily.

So as to solve the water pollution at coalmines and enhance the water reuse for domestic application, it is necessary to conduct research and propose a proper and sustainable technology for AMD treatment in Vietnam in general and Quang Ninh province in particular. Within this research project (cooperated with Mitsubishi Rayon Corporation MRC), we have conducted the ADM treatment with membranes provided by MRC to evaluate the potential of reusing treated AMD wastewater for domestic purposes.

## Materials and method

### Membranes

The membranes tested were provided by Mitsubishi Rayon Corporation. Membrane specification is provided in Table 1. The membranes were rinsed with distilled water thoroughly before testing.

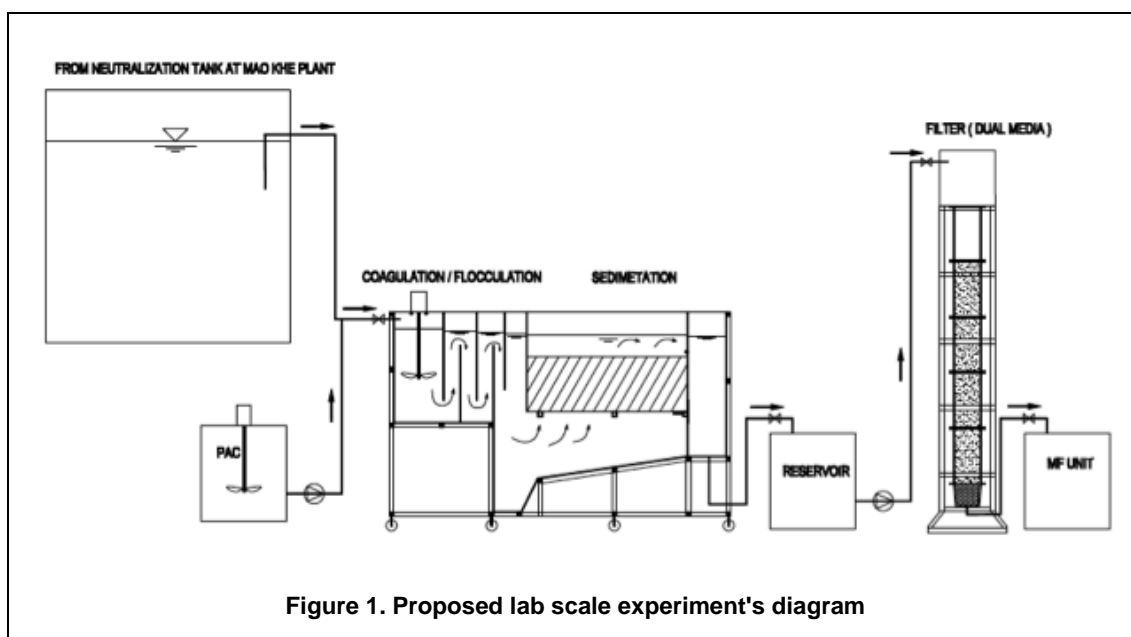
Item	Unit	Specification
Membrane material	-	PVDF
Nominal pore size	µm	0.4
Nominal membrane surface area/element	m <sup>2</sup>	0.07
Filtration mode	-	outside in
Nominal transmembrane pressure (TMP)	kPa	Initial TMP + 15 kPa or below
Nominal temperature	°C	5 - 40
pH range of raw water	-	6- 9

### Feed wastewater

The coal mining wastewater from Mao Khe (closed mine) was selected for testing this time. This site represents the coal mining wastewater in Vietnam with low pH, high Fe and Mn, high suspended solids, etc.

### Experimental set-up and protocol

The proposed lab scale experimental set-up was illustrated in Figure 1. The volume flowrates through MF was about 20 L/d. The wastewater (after being neutralized to pH 7-8) was be pumped into coagulation and flocculation tanks where 30 mg/L of PAC and 1mL/L of  $\text{Ca(OH)}_2$  were added. After settling in lamella clarifier, the water was stored in a reservoir before pumping to media filter, then to MF unit (see Figure 1 for details). Samples prior and after MF were collected once per week and analyzed in terms of Fe, Mn, Ca, Mg, pH, TSS, SO<sub>4</sub>. While flowrate, temperature, pH, TDS and hardness were analyzed daily. Duration of the test was 3.5 months (from August to November of 2013). It should be noted that the MF lab-scale set up was in fact brought to Mao Khe plant for testing to guarantee enough and continuous feed water supply.



Further on filtration test, the fouled membranes were analyzed to find out the major types of foulants on membranes after being used for coal mine WW treatment. After that they were under cleaning study in which different types of chemicals were tried to obtain the best cleaning solution.

For cleaning study, two cleaning mechanisms were applied (Table 2). Fouled and cleaned membranes were run with ultra pure water to determine the permeation flux for recovery assessment.

Table 2. Cleaning protocols	
Cleaning mechanism 1	Cleaning mechanism 2
A) 0.3%NaClO for 2hrs	E) 0.3%NaClO+1.5%Surfactant for 2hrs
B) 0.3%NaClO for 24hrs after A)	F) 0.3%NaClO+1.5%Surfactant for 24hrs after E)
C) 2% Citric acid for 2 hours after B)	G) 2% Citric acid for 2hrs after F)
D) 2% Citric acid for 24hr after C)	H) 2% Citric acid for 24hr after G)

The fouled and cleaned membranes were analyzed by Scanning electronic microscopy SEM (Model:SU-1500, Hitachi High-Technologies, Japan) and X-ray micro analyzer XMA(Model:S-3400N, Hitachi High-Technologies, Japan).

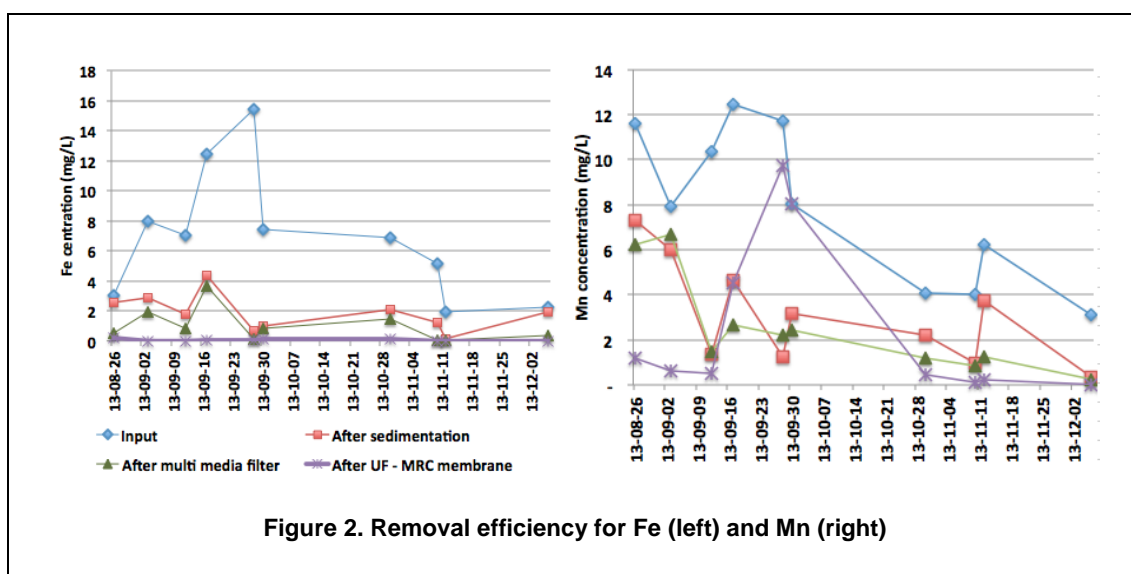
## Results and discussions

### Contaminant removal efficiency

Comparison of treated water with MF membranes and the national criteria is present in Table 3. In fact, there has not been any national criteria for water reuse, thus, we refer the national criteria for domestic water supply by Ministry of Health. It was found from Table 3 that with the input of TSS of 200 - 450 mg/L, reducing to about 45 mg/L after pre-treatment, the TSS effluent after membranes was consistently below 2 mg/L. The total hardness decreased remarkably from nearly 900 mg as CaCO<sub>3</sub>/L to averagely 200 mg as CaCO<sub>3</sub>/L.

Table 3. Result comparison (based on average numbers from over 3 month run)				
Parameters	Input	After media filter	After membrane unit	QCVN 02:2009/BTY criteria (for domestic use)
Fe	6.962	0.984	0.058	0.5
Mn	7.95	2.52	0.45 (2.55)*	0.3
TSS	280.5	44.3	1.7	N/A
Total hardness	866.8	457.7	203.5	350

\* The number in bracket was taken into account the "high Mn values" at the end of September.



In terms of Mn and Fe removal, it was noted that in both graphs of Figure 2, there was a big change after September 30, 2013. It was due to (1) membrane cleaning and (2) change of filter media. The reason of cleaning membranes and replacing regular sand by Mn-coated sand was because of decreasing removal efficiency of Mn at the end of September (after 1 month). It was found that the Mn removal efficiency clearly improved after this modification and consistently lower than 0.1 mg/L during the last month.

Seemingly, the MF membranes helped reduced the Fe and total hardness to successfully meet the national criteria for domestic use. However MF membranes seemed not to be effective in control the dissolved Mn, especially when Mn concentration was high. Only when Mn-coated sand was introduced in the media filter to lower the Mn concentration (by trapping  $\text{MnO}_2$  in the sand) prior to MF membrane unit, the Mn removal efficiency of membranes was increased.

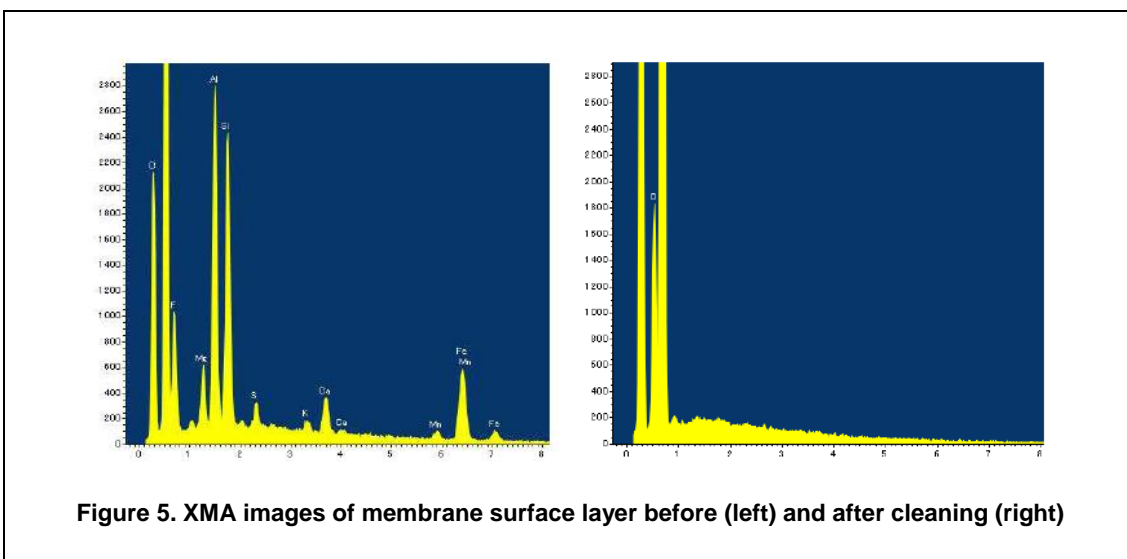
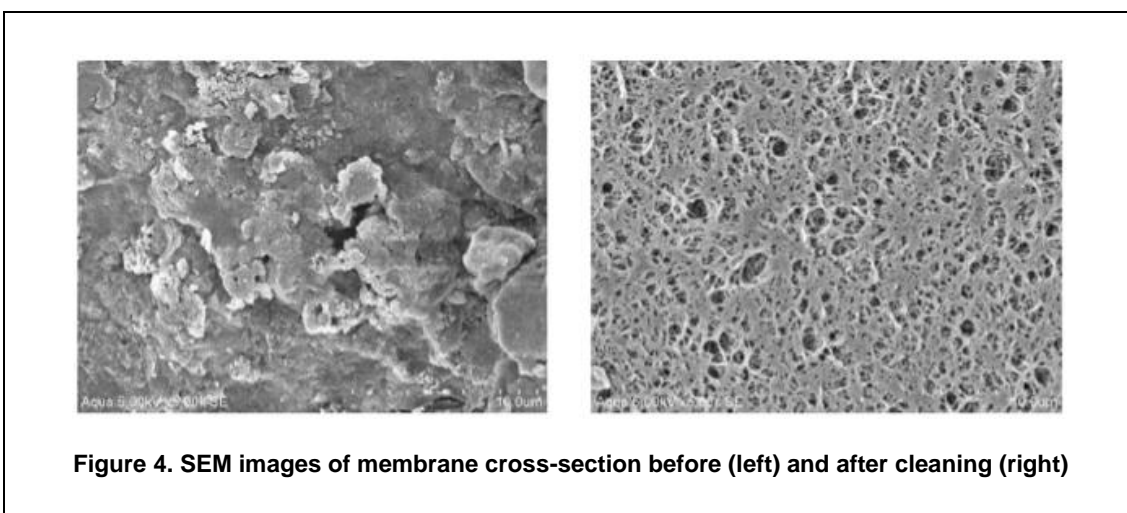
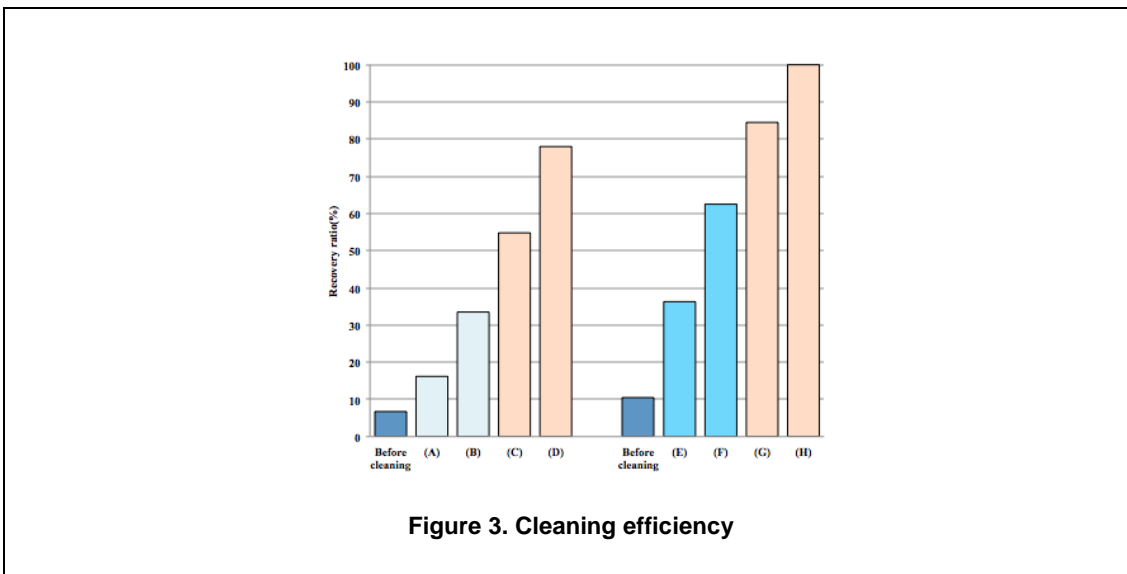
### Fouling analysis and cleaning study

Results of cleaning study (Figure 3) revealed that the combination of NaOCl - surfactant and acid citric had better impact than NaOCl and acid citric (without surfactant). A 100% recovery can be achieved with combination of three chemicals. It might be due to the fact that there was some oil compounds in the coal mine wastewater, thus, the addition of surfactant help remove completely the polluted contaminants.

It can be seen, via SEM images, that the cross-section of fouled membranes showed agglomeration of foulants on and inside the pores. It was impossible to see the pores of membranes in this condition. However, the pores of cleaned membranes showed obviously in Figure 4. That proved the membranes were completely cleaned with chemicals recommended by MRC.

Via XMA analysis (Figure 5), it showed that there are peaks of Fe, Mn, Al, Si, S, K, O, F and Cd. It could be predicted that O and F are elements of PVDF polymer - based of MRC membranes. Al and Si could relate to PAC coagulants's residues from coagulation process. Peaks of Fe and Mn proved that there were a deposition of those ions on membranes, thus there was of decrease of Mn and Fe in the effluent. It is

interesting that there were no more peaks of Fe, Mn, Al, Si, S, K ions on membranes after cleaning. That's the reason why pores were shown and membrane permeability was recovered 100%.



### Learning points from this research

Over three month experiment with MF membranes for coal mine wastewater has shown some interesting findings as below:

- The pretreatment played important role in supporting MF membranes for solid and ions removal.
- The process of "neutralization+ coagulation/flocculation+sedimentation+media filter+membranes" has successfully treated coal mine wastewater to meet national criteria for domestic water supply.
- As membranes (provided by MRC company) are fouled, NaOCl+surfactant+citric acid solution is the best option for cleaning.
- MF membranes could be an option for application in coal mine wastewater treatment for domestic reuse in Vietnam. However, when the Mn concentration in the influent is high, it is recommended to have intensive Mn oxidation process ahead of membrane unit to lower the dissolved Mn and ensure the Mn removal efficiency of the membranes.
- Although energy was not analysed in this research, however, based on the membrane supplier report, the energy requirement is about 0.4kWh/m<sup>3</sup> for biological treatment and filtration in MBR. The O&M cost would not be so crucial as PVDF-base membranes have a life time of 7-10 years if proper cleaning with recommended chemicals are strictly followed.

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