Reusability of Fe-modified MMT nanomembranes and the retrieval of the adsorbed mercury metal

M J Lodo¹,³ and L J Diaz²,³

1 Environmental Engineering Program
2 Composite Materials Laboratory, Department of Mining, Metallurgical and Materials Engineering
3 University of the Philippines, Diliman, Quezon City, Philippines
E-mail: mllodo@upd.edu.ph

Abstract. Determining the applicability of a wastewater treatment procedure is dependent on its efficiency and cost-effectivity. The main objective of this study is to establish the reusability of Fe-modified MMT nanomembrane when utilized as adsorbent material for wastewaters containing mercury in complex with cyanide in aqueous solutions. Three cycles of adsorption-elution runs were done on the nanomembranes and the mercury (Hg) concentrations in the wastewaters (initial, after adsorption, after elution) were analyzed using HD XRF. Results showed that there was no substantial difference in the adsorption efficiencies for the first two (2) cycles (37.61% and 35.69%). Using 0.01M acetic acid as eluate, the nanomembranes were observed to be reusable twice before the nanomembranes become extensively degraded. In addition, precipitation was employed to retrieve the Hg from the eluates. One (1) g as-received and grinded (150–500 µm) sodium thiosulfate (Na₂S₂O₃) precipitants were used and it was established that, after 24 h, the precipitant with finer particle sizes was able to retrieve higher amounts of Hg (as-received:59% vs grinded:87.27%). Moreover, increasing the amount of the grinded Na₂S₂O₃ to 5g resulted to better Hg recovery (89.47%). Further analysis on the derived precipitates also confirmed the presence of Hg (19.90ppm for red precipitates; 24.73ppm for black precipitates).

1. Introduction
The use of the mercury amalgamation technique in the extraction of metals, especially for gold (Au) and silver (Ag), is highly practiced in artisanal and small scale mining due to the ease of use and the availability of the said metal. However, different studies have proven that this method resulted to various health and environmental adverse effects. Previous mine workers were found to suffer from neurologic complaints, had elevated liver function tests and abnormal findings for pterydium, gingivitis and gum bleeding [1,2]. In addition, different tests confirmed the presence of elevated total mercury (T-Hg) and methyl mercury (Me-Hg) on the mining sites’ surrounding areas and nearby residents [1,2,3]. Another alternative technique is cyanidation, where miners use cyanide solutions for the extraction of Au from the ore. However, regardless of the method used, both of these processes pose harmful risks, not only to the contaminated environment but to the miners as well, especially if rudimentary and unsafe practices are done. Mercury (Hg) and cyanide can further form complexes either by 1) using cyanidation on more complex ores that contain significant amounts of Hg, 2) cyanidation of previously amalgamated tailings and 3) combination of Hg and CN releases to the nearby environment, especially on bodies of water. The presence of mercury cyanide complexes creates high risks of pollution on the nearby biota.
Different methods to reduce the associated issues have been done and various wastewater treatment technologies have already been developed to address these concerns [4]. Assessing the applicability of the different procedures on small scale mining, adsorption can be considered as one of the best technologies to adopt since it can be employed and is more practical for smaller scale systems. In this area, the use of nanotechnology has been widely utilized due to its ability to enable modification of different materials. One area that has been explored is the use of Fe-modified montmorillonite (Fe-modified MMT) dispersed in a polycaprolactone-dichloromethane (PCL-DCM) solution to create an adsorbent membrane. This was found to be an effective adsorbent for aqueous arsenic [5]. However, after an adsorption process, the next issue is the handling of the spent material and adsorbed contaminants. One way to reduce the amount of materials that will have to be disposed is to reuse and utilize them in another treatment cycle. This can be done through the regeneration or removal of the adsorbed substances by elution, without causing any irreversible changes in the adsorbent surface. Employing this process does not only ensure that utilization of the adsorbent is optimized and less energy and expenditures for procurement and production is achieved, but environmentally friendly procedures are implemented as well. With better recyclability comes less disposal needs for the resources used in the process. In addition, the retrievability of the adsorbed heavy metal can present potential for further mercury reuse, thereby lessening disposal and consequently, contamination issues. This study aims to determine the reusability of Fe-modified MMT adsorbent nanomembrane when used to treat mercury from synthetic wastewater, i.e. aqueous solution, containing mercury cyanide complexes. Recyclability tests were done to estimate the useful life of the adsorbent materials by subjecting them to repeated adsorption and elution runs. The physical condition of the nanomembranes and the adsorption efficiency were the main determining factors for the continued reusability. Mercury retrieval from the eluates using sodium thiosulfate as the precipitating agent was also tested.

2. Experimental details

2.1. Preparation of the mercury cyanide wastewater
The wastewater used for all the experiments were synthesized in the laboratory. This was done by preparing a cyanide stock solution where cyanide salt was added to 1 M NaOH. Elemental mercury was then mixed into the solution and the mixture was subjected to sonication for two (2) hours to facilitate dissolution of mercury and formation of the complex. The final wastewater was derived by performing vacuum filtration thereafter for the removal of undissolved mercury. It must be noted that concentrations of Hg produced from this process is variable and therefore initial concentrations were always measured before every run.

2.2. Preparation of the Fe-modified MMT nanomembrane
The nanomembrane was obtained by dispersing Fe-MMT clay in a PCL-DCM solution using sonication following the procedure of Araño, et. Al [6]. Afterwards, electrospinning was done to create suspensions of the said solution, resulting to the creation of the membranes. The final products were cut into disks having diameters of 2.5”.

2.3. Establishment of the recyclability of the adsorbent and mercury retrieval procedures
Three (3) cycles, having three (3) replicates each, of adsorption-elution runs were done to test the nanomembranes. A batch set up was performed for both adsorption and elution runs. For the adsorption process, 490 mL of the synthesized wastewater was continuously fed for three (3) hours to the adsorption column with the nanomembrane, using 25 to 30 mL min⁻¹ flow rate, and a submersible pump to facilitate recirculation. The initial and post-adsorption Hg concentrations were analyzed using high definition x-ray fluorescence (HD XRF). Adsorption efficiency was calculated using Equation 1, where \( C_0 \) (mg L⁻¹) is the initial Hg concentration and \( C_f \) (mg L⁻¹) is the final Hg concentration in the wastewater before and after adsorption, respectively.

\[
\% \text{Adsorbed} = 100\% \left[ \frac{(C_0 - C_f)}{C_0} \right]
\] (1)
The nanomembranes were allowed to dry in the desiccator for two (2) days before subjecting them to the elution tests, where 0.01 M acetic acid was used as the eluent and five (5) hours contact time with the mercury-loaded adsorbent membrane was done. The elution conditions (i.e type and concentration of eluents, contact time) were derived from the preliminary tests done on this study. HD XRF was also used to detect the amount of Hg in the eluate and elution efficiency was determined using Equation 2, where \( C_d \) (mg L\(^{-1}\)) is the metal concentration in the eluate, \( V_a \) (in L) is the amount of wastewater used during adsorption, and \( V_d \) (in L) is the amount of eluent.

\[
\% \text{Elution} = 100\% \frac{C_dV_d}{(C_0-C_f)V_a} \quad (2)
\]

After each adsorption-elution run, the spent nanomembranes were evaluated if further use can still be done. If significant Hg adsorption was still achieved and the nanomembrane was not yet torn, it was subjected to another cycle. Otherwise, it was prepared for disposal. The derived eluates, on the other hand, underwent feasibility tests for precipitation of mercury using sodium thiosulfate as the precipitant. Varying concentrations (1 g and 5 g per 50 mL eluate) and particle sizes (ground and as-received) of the precipitant were mixed with the eluates containing Hg. After the set time, Hg concentrations of the solutions were tested using HD XRF and the retrieval percentage of Hg was computed using Equation 3, where \( C_f \) (mg L\(^{-1}\)) is the Hg concentration after the set contact time with the precipitant and \( C_0 \) (mg L\(^{-1}\)) is the initial concentration. The resulting precipitates were also analyzed for the presence of the expected metal (i.e. Hg), using the same equipment.

\[
\% \text{Retrieval} = 100\% \times \frac{(C_f - C_0)}{C_0} \quad (3)
\]

3. Results and discussion

3.1. Recyclability of the nanomembranes

The nanomembranes were subjected to three (3) cycles of adsorption-elution runs using initial Hg concentrations of 21.03 to 121 mg L\(^{-1}\) and the efficiencies after each run are shown in figure 1. It can be observed that the amount of adsorbed Hg from the first cycle did not largely vary from the second cycle. However, the third cycle obtained a negative value, suggesting an increase of Hg in the solution after adsorption. A decrease in the desorbed percentage after each round was also observed.

To understand further the negative efficiencies, the amount (in mg) of mercury in the solutions in each stage of the process was also determined as shown in figure 2. For the first two (2) cycles, Hg in the wastewater decreased, indicating removal of the ions from the wastewater solution. For the third cycle, however, there was an apparent increase of Hg in the solution, signifying a transfer of the previously adsorbed ions back into the solution. The amount of desorbed Hg, on the other hand, is highest from the third cycle, thereby suggesting that an increase of Hg in the adsorbent corresponded to an increase in the desorbed amount induced by higher concentration gradients.

![Figure 1. Adsorption and elution efficiencies after each cycle.](image-url)
Figure 2. Comparison of the Hg concentrations: Initial Hg in wastewater; Hg in wastewater after adsorption, Hg in eluent after elution.

3.2. Characterization of the nanofiber membrane

The condition or state of the adsorbent membrane after each stage of the adsorption-elution cycle was also monitored, as shown in figure 3. As the membrane gets exposed to more adsorption and elution cycles, physical changes become more apparent. Fragility of the nanomembrane increases after each process, causing it to be more susceptible to tears during handling and transfers. A visible accumulation of gray and white deposits after each adsorption process is also noticeable in figure 3. A subsequent clearing or reduction of the deposits can then be seen after elution as shown in figure 4. Furthermore, it can be observed that after the third cycle, the membrane was already torn.

Figure 3. Nanomembrane after adsorption: a) first cycle, b) second cycle, c) third cycle.

Figure 4. Nanomembrane after elution: a) first cycle, b) second cycle, c) third cycle.

In order to identify the causes of the observed physical alterations, characterization of the nanofiber membrane was done using scanning electron microscopy (SEM). Figure 5.a shows the presence of
fibers and “beads” or clumps of clay in the unused adsorbent, which are typical features expected in an
electrospun membrane [6]. Observing the membrane under an increased magnification of 10,000x
(figure 5.b) shows the circular morphology of the fibers, ranging from 50 – 500 nm in diameter. After
three (3) cycles of adsorption-elution treatments (figure 5.c), it can be observed from the images that
the adsorbent membrane’s fibrous network has changed into something that looks like formation of
lumps. Observation under higher magnification (figure 5.d) shows that the fibers are either broken into
fragments, or became coated with deposits or residues from the adsorption-elution stages. It can also
be noted that some portions or fragments along a fiber is missing, which could have been removed and
transferred back into the solution. This could be the reason behind the increase in Hg concentration in
the solution after the third cycle of adsorption-elution cycle.

![Figure 5](image_url)

**Figure 5.** SEM images for: a) unused membrane at 500x, b) unused membrane at
10000x, c) spent material at 500x, d) spent material at 10000x.

The Hg concentration in the original as well as the spent adsorbent material after three (3) cycles were
analyzed using HD XRF. The initial concentration of Hg in the nanomembrane was determined to be
below the detection limit (less than 0.9 ppm), signifying no prior contamination of the said metal on
the adsorbent. The presence of Hg in the spent nanomembrane (13,679 ppm) indicates that Hg from
the wastewater was adsorbed. However, this also shows that the elution process was not efficient
enough to remove all of the adsorbates.

3.3. Precipitation tests
For the feasibility tests of precipitating the mercury in the eluate, 50 mL of the eluates were used.
Grinded and as-received sodium thiosulfate (Na$_2$S$_2$O$_3$) pellets were used. Initial solutions were clear
but after the addition of the precipitating agent, suspended solids were observed. After 24 h, some of
the suspended solids settled at the bottom of the containers.
The as-received pellets were added as is while the grinded ones were pounded and found to have 150–
500 μm particle sizes. Aside from the 5-g test which had 21 h, all other tests had 24 h contact time and
three (3) replicates. The initial and final Hg concentrations in the solutions were analyzed using HD
XRF. Prior to the analysis, the solutions were filtered using filter paper in order to separate the precipitates.
Table 1 shows that when the particle size of the precipitant was decreased, the extraction rate increased with increasing contact time, similar to the observations made by Han, et al. and Sandberg, et. al. on their precipitation studies [7,8]. After 24 h, no visible precipitates formed in the set-ups where 1 g as-received Na$_2$S$_2$O$_3$ pellets was added but the 59% reduction in the concentration indicates that some Hg ions were retrieved and some still remained in the eluent solution. On the other hand, 87.27% of the Hg was removed from the solutions with grinded Na$_2$S$_2$O$_3$. For those with higher initial Hg concentrations, visible black and red precipitates were observed. This emphasizes the significance of the original ion concentration when it comes to the development of larger agglomerates.

| Na$_2$S$_2$O$_3$ condition | Initial Hg concentration ppm | Final Hg concentration Ppm | Hg retrieved, mg | % Retrieved |
|---------------------------|-----------------------------|---------------------------|-----------------|-------------|
| as received pellets, 1g   | 1.85                        | 0.09                      | 0.73            | 0.04        | 0.06        | 59.00%       |
| Grinded, 1g               | 17.47                       | 0.87                      | 1.17            | 0.06        | 0.82        | 87.27%       |
| Grinded, 5g               | 1.90                        | 0.10                      | nd<0.2*         | 0.01        | 0.09        | 89.47%       |

* concentration was below the detection limit of 0.2 ppm

To further test the effect of the amount of the precipitant chemical, another set up where 5 g of grinded Na$_2$S$_2$O$_3$ was added was performed. The conducted preliminary tests indicate that increasing the concentration of Na$_2$S$_2$O$_3$ further enhances the retrieval rate of Hg ions. After 21 h, 89.47% removal was already achieved.

The positive results that exhibited the ability of sodium thiosulfate to remove Hg from the eluates is due to the low solubility of HgS compared to other Hg compounds. Thiosulfates form complexes with Hg and this eventually decomposes to solid HgS [9]. With this property, the formation of solid precipitates makes possible a less complicated retrieval of the target ions and the subsequent reduction of the concentration of the toxic adsorbate prior to the disposal of the effluent.

### 3.4. Hg concentrations of the precipitates

Two (2) test solutions were observed to have visible precipitates. Two (2) types were obtained – red and black. At room temperature, there are two possible forms of HgS – red cinnabar and black metacinnabar. Red cinnabar is more stable but metacinnabar is what is normally obtained during laboratory experiments [10]. Red HgS has a hexagonal form while black HgS has a cubic tetrahedral form. It should be noted though that the color of the precipitate is not an all-encompassing technique to determine the form.

The precipitates were analyzed through HD XRF where 19.90 ppm Hg concentration was obtained from the red precipitates while 24.73 ppm was attained from the black particles. These results substantiate the fact that Hg was removed from the eluate through the formation of the precipitates.

### 4. Conclusion

Fe-modified MMT nanomembranes were subjected to repeated adsorption and elution runs to determine the adsorbent’s reusability. Given the operational parameters used in the study (adsorption: 3 h contact time, 490 mL wastewater; elution: 5 h contact time, 0.01 M acetic acid), the derived adsorption efficiencies and resulting physical characteristics showed that the adsorbent can be reutilized twice, after which, the nanomembrane undergoes a substantial degradation that will affect its adsorption capability. This showed the recyclability potential of the nanomembrane. However, as the nanomembrane is subjected to more adsorption-elution cycles, the fibers become broken/thinned out/coagulated, which is manifested by the gradual fragility of the material. Further studies considering other experimental parameters and/or eluates may be done to determine if reusability of the nanomembrane can be increased.

Sodium thiosulfate was also verified to be an effective agent in the retrieval of Hg from 0.01M acetic acid eluate, with the highest recovery obtained using 5 g of grinded Na$_2$S$_2$O$_3$ (89.47% after 21 h).
This facilitates separation of the heavy metal ion, enabling possible Hg recycling and/or better disposal handling of Hg and the eluates.

5. References

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