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Comparison of Phytoremediation and Filtration for Diamond-mine-tailings Water Treatment
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Comparison of Phytoremediation and

## Filtation

## Treatment

Hatidhuddin Noor ${ }^{1}$ Miiani Rahma ${ }^{2}$ Aurmad Gazali ${ }^{1}$ Nia Kania ${ }^{3}$ Aulia Rahma ${ }^{4}$ Erdina Lulu Atika Rampun ${ }^{4}$ Amal Engaar Prativi ${ }^{5}$ Muthia Elma ${ }^{5}$

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Abstract This work aims to treat a polluted diamond mine tailing ponds water located in South Kalimantan, Indonesia using phytoremediation and simple tiltration processes. Einchinimia Crassipes (water hyacinth) was employed as biomass during the
 diamond tailing water was poured into 5 reactors ( $40 \times 50 \times 30 \mathrm{~cm}$ in volume) and tested for 7 days in the phytoremediation process using batch method. It it observed that BOD and COD values of tailing raw water are much higher than national maximun
standard $(89$ and 22 mg $\mathrm{L}-1$ respectively) From the experiment it was found that phytoremediation process has ability increase $55 \%$ of DO better than the filtration process when using diamond mine tailings water. Also, BOD and COD values were increase $55 \%$ of Do better than the filtration process when using diamond mine tailings water. Also, BOD and COD values we
excellenty reduced from 25 to $80 \%$. Interestingly, during the phyytoremediation process, Fe, Mn and ammonia contents as metal ontents have greatly reduced as much
Keywords: phytoremediation process, simple filtration process, diamond mine tailings water
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J. Gao, H. Dang, L. Liu, L. Jiang, Desalin. Water Treat. 55 (2015) 381

# Comparison of Phytoremediation and Filtration for Diamond-mine-tailings Water Treatment 

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#### Abstract

The water pollution caused by diamond mine activities can kill aquatic life. In this work, we used phytoremediation and filtration to treat pond water polluted by the tailings of a diamond mine located in South Kalimantan, Indonesia. Einchhornia crassipes (water hyacinth) was utilized as the biomass for the phytoremediation process. Gravel (10-15 mm ) and sand ( $0.1-1 \mathrm{~mm}$ ) were used as filter media in the simple filtration setup, using an up-flow system (bottom to top). In the experiment, 16 L of diamond tailing water was poured into five phytoremediation reactors (each 60 L in volume), which were then tested over seven days. A pretreatment analysis of the tailings water showed that its biochemical oxygen demand (BOD) of $8.9 \mathrm{mg} \mathrm{L}^{-1}$ and chemical oxygen demand (COD) of $22 \mathrm{mg} \mathrm{L}^{-1}$ exceeded the national maximum standards of $2 \mathrm{mg} \mathrm{L}^{-1}$ and $10 \mathrm{mg} \mathrm{L}^{-1}$, respectively. The experimental results demonstrate that both phytoremediation and filtration could increase the dissolved oxygen concentration ( $4.7 \mathrm{mg} . \mathrm{L}^{-1}$ ) and reduce the BOD ( $3.2 \mathrm{mg} . \mathrm{L}^{-1}$ ), COD ( $6.5 \mathrm{mg} . \mathrm{L}^{-1}$ ), $\mathrm{Fe}\left(0.6 \mathrm{mg} . \mathrm{L}^{-1}\right)$, $\mathrm{Mn}\left(0.16 \mathrm{mg} . \mathrm{L}^{-1}\right.$ ), and ammonia ( $0.63 \mathrm{mg} . \mathrm{L}^{-1}$ ) concentrations from those measured in the raw diamond-mine-tailings water. The phytoremediation performance was better than that of filtration. The COD values were successfully reduced to the permissible limit, although the other parameters still failed to meet the government water quality regulation requirements.


#### Abstract

Abstrak Metode Perbandingan antara Proses Fitoremediasi dan Proses Filtrasi Sederhana untuk Mengolah Air Bekas Galian Tambang Intan. Polusi air yang disebabkan aktivitas pertambangan dapat membunuh kehidupan akuatik. Penelitian ini bertujuan untuk mengolah air tercemar bekas galian tambang intan di Kalimantan Selatan, Indonesia menggunakan proses fitoremediasi dan filtrasi sederhana. Eichornia Crassipes (eceng gondok) digunakan sebagai biomassa selama proses fitoremediasi. Media penyaring seperti kerikil ( $10-15 \mathrm{~mm}$ ) dan pasir ( $0,1-1 \mathrm{~mm}$ ) ditambahkan ke dalam reaktor filtrasi sederhana yang memiliki aliran atas (dari bawah ke atas). 16 L air bekas galian tambang intan dituangkan ke dalam 5 reaktor (volume 60 L ) dan di uji selama 7 hari pada proses fitoremediasi menggunakan metode batch. Analisis pra-perlakuan air tercemar bekas galian tambang menunjukkan BOD sebesar $8,9 \mathrm{mg} . \mathrm{L}^{-1}$ dan COD sebesar $22 \mathrm{mg} . \mathrm{L}^{-1}$ melebihi maksimum nasional yaitu 2 dan $10 \mathrm{mg} . \mathrm{L}^{-1}$, berturut-turut. Berdasarkan eksperimen, fitoremediasi dan filtrasi memiliki kemampuan untuk meningkatkan DO ( $4.7 \mathrm{mg} . \mathrm{L}^{-1}$ ) dan mengurangi BOD ( $3.2 \mathrm{mg} . \mathrm{L}^{-1}$ ), COD ( $6.5 \mathrm{mg} . \mathrm{L}^{-1}$ ), $\mathrm{Fe}\left(0.6 \mathrm{mg} . \mathrm{L}^{-1}\right)$, Mn ( $0.16 \mathrm{mg} . \mathrm{L}^{-1}$ ) serta ammonia ( $0.63 \mathrm{mg} . \mathrm{L}^{-1}$ ) dari nilai awal air bekas galian tambang. Fitoremediasi menghasilkan performa lebih baik dalam penyisihan dibandingkan filtrasi. Nilai akhir COD memenuhi baku mutu, sedangkan parameter lain tidak memenuhi peraturan pemerintah mengenai kualitas air.


## 1. Introduction

Mine wastewater typically contains many pollutants, including heavy metals that have a significant and negative impact on the environment [1]. The Kalimantan island in Indonesia is well-known to be home to the oldest diamond mine in the world [2]. Mining activities reported by Indonesia's Environmental Agency reveal that the river flowing nearby the diamond mine has also become polluted. High chemical oxygen demand (COD) levels and iron (Fe) and manganese ( Mn ) concentrations have been measured in the river. These heavy metals and other metalloid pollutants can degrade human health as well as the natural ecosystem [3].

Numerous studies have been reported of the use of phytoremediation in a constructed wetland (CW) for the removal of contaminants in mine effluent [4]-[6]. CW is a promising technology that involves the use of natural processes that require low maintenance and operational costs [7]. Eichhornia crassipes i.e., the water hyacinth [8], grows widely in tropical regions and often damages local water ecology by covering the entire water surface, thereby preventing sunlight from penetrating into the water [9]. However, this plant shows great promise for application in the phytoremediation of water bodies, as it reduces the amount of pollutants in the water, including the total suspended solids, total dissolved solids, biochemical oxygen demand (BOD), COD, and heavy-metal compounds [10].

Another advance technology involves the application of a membrane that filters and captures particles from surface water and wastewater [11]-[13]. Although this membrane performs well, it is very expensive. Studies have shown that filtration can be made cost-effective by the use of gravel, granular material, and sand [14], [15]. Typically, the effective size of sand particles is $0.1-0.3$ mm [16], but coarser sand has also been used in filtration reactors [17]. The simple filtration approach has been reported to achieve good removal of Fe [18].

Many studies have focused only on the performance of filtration in treating groundwater [18] and water from coal mines [19]. In this work, we compare studies of phytoremediation and filtration in the treatment of water contaminated by diamond mine tailings. We used a phytoremediation process that employs water hyacinth as the biomass and adsorbent plant. In the filtration process, we used a continuous mode of up-flow (bottom to top) for the water flow and added gravel and sand as filter media.

## 2. Materials and Methods

Characterization of diamond-nine-tailings water. For this study, diamond-mine-tailings water samples were taken from the tailing pond located in the village of Pumpung, Sungai Tiung district, South Kalimantan, Indonesia (as shown in Figure 1). Measurements of the pH , COD, BOD, iron ( Fe ), manganese ( Mn ), ammonia $\left(\mathrm{NH}_{3}-\mathrm{N}\right)$, and dissolved oxygen (DO) were performed twice, in a preliminary characterization, and after treatment. Examinations of the samples were performed with reference to pH (SNI 06-6989.11-2004), COD (SNI 06-6989.2-2004), BOD (SNI 6989.72:2009), Fe (SNI 06-6854-2002), Mn (SNI 06-6855-2002), and ammonia (SNI 06-6876-2002)

Phytoremediation process. The phytoremediation process was conducted using a wetland setup concept, with water hyacinth as the biomass and adsorbent plant with variations in mass $(250 \mathrm{~g}, 500 \mathrm{~g}, 750 \mathrm{~g}$, and 1000 $\mathrm{g})$. The volume of the diamond-mine-tailings water samples was 16 L in a batch system with a 7-day retention time. The samples were analyzed after 3 days, 5 days, and 7 days. Figure 2(A) shows the setup of the phytoremediation process, for which there were five reactors constructed from 60-L plastic boxes for testing without any water hyacinth and with four different masses of water hyacinth. V1, V2 V3, and V4 contained biomasses of $250 \mathrm{~g}, 500 \mathrm{~g}, 750 \mathrm{~g}$, and 1000 g , respectively.


Figure 1. Locations from Which Diamond-mine-tailings Water Samples Were Collected


Figure 2. Setups of (A) Phytoremediation and (B) Filtration Processes

Phytoremediation process. The filtration process was conducted in a reactor containing gravel and sand. This system operated with water flowing in a continuous upflow (bottom to top) at a debit volume of $0.001 \mathrm{~m} 3 . \mathrm{s}^{-1}$. In this process, we used three different thicknesses of filter media, as shown in Figure 2(B), for each of the filtration reactors. The reactors labeled F1, F2, and F3 contained mass ratios of gravel to sand of 25:75, 50:50, and $75: 25$, respectively. Reactors F4, F5, and F6 contained mass ratios of sand to gravel of 25:75, 50:50, and 75:25, respectively

## 3. Results and Discussion

Characteristic of diamond-mine-tailings water taken from diamond mine pond. Diamond-mine-tailings water was collected from the pond at the diamond mine in Cempaka, South Kalimantan, Indonesia. The quality of this water was first investigated to establish the condition of the raw water, the results of which are shown in Table 1. In the table, we can see that the diamond-mine-tailings water does not meet requirements of Indonesian water quality standard $82 / 2001$ class I for

Tabel 1. Characteristics of Diamond-mine-tailings Water

| Parameters | Unit | Raw water | Quality standard <br> (Indonesian <br> Government <br> $\mathbf{8 2 / 2 0 0 1 )}$ |
| :---: | :---: | :---: | :---: |
| Ph | - | $6.98-7.04$ | $6.00-9.00$ |
| BOD | $\mathrm{mg} \mathrm{L}^{-1}$ | 8.90 | 2.00 |
| COD | $\mathrm{mg} \mathrm{L}^{-1}$ | 22.00 | 10.00 |
| DO | $\mathrm{mg} \mathrm{L}^{-1}$ | 3.10 | $6.00^{*}$ |
| Fe | $\mathrm{mg} \mathrm{L}^{-1}$ | 3.53 | 0.30 |
| Mn | $\mathrm{mg} \mathrm{L}^{-1}$ | 1.37 | 0.10 |
| Ammonia | $\mathrm{mg} \mathrm{L}^{-1}$ | 2.52 | 0.50 |

*Minimum standard

BOD, COD, Fe, Mn, and ammonia [20]. However, the pH value is under the permissible limit. This is because the pond was present prior to the diamond mining operation began and had already been polluted by organic and heavy-metal contaminants with low pH . To investigate the effectiveness of phytoremediation, we then grew water hyacinth using that water.

The DO concentration of the raw diamond-mine-tailings water was measured to be $3.1 \mathrm{mg} \mathrm{L}^{-1}$. The minimum standard for the DO concentration as per the Indonesian Government Regulation No $82 / 2001$ is $6 \mathrm{mg} \mathrm{L}^{-1}$. This means that the DO concentration in this sample does not meet the standard due and must be increased. In fact, the low DO concentration is related to serious pollution from organic matter [21] in the water.

Comparison of performances of phytoremediation and filtration processes in organic degradation of diamond-mine-tailings water. Figure 3(A) shows the DO concentrations of water after treatment. After 7 days of treatment, the DO of the diamond mine-tailing pond water was about $4.7 \mathrm{mg} . \mathrm{L}^{-1}$, or $34 \%$ of the maximum DO value measured, which was still lower than the minimum DO standard shown in Table $1\left(6 \mathrm{mg} . \mathrm{L}^{-1}\right)$ The same value was obtained for the control sample (without water hyacinth). Although water hyacinth itself has little impact in treating diamond mine-tailing pond water, its roots act as microbial growth media that provide oxygen to the rhizosphere for the microbial degradation of organic contaminants. This was confirmed by the difference in the DO values between the control sample and those to which water hyacinth had been added. Increases in the DO values of domestic wastewater by the application of water hyacinth has also been reported by Rezania et al. [22]. However, water hyacinth has also been reported to be unable to release oxygen into water, as compared with another submerged plant, and instead cause decreases in DO concentration [23]. The outcome depends on the water hyacinth mat used [24], as large water hyacinth mats can limit the oxygen exchange and thereby decrease the DO concentration.

Furthermore, after 3 days, DO showed no significant increase, increasing by only $10 \%$ ( $3.42 \mathrm{mg} . \mathrm{L}^{-1}$ ) via the sand filtration method shown in Figure 3(B). This is due to the laminar water flow used in the filtration reactor [25]. The flow of the diamond-mine-tailings water was initially at a low rate of $0.001 \mathrm{~L} . \mathrm{s}^{-1}$ when introduced into the filtration reactor, which caused the water flow to become turbulent, thereby slightly increasing the DO level.

Water hyacinth plays a crucial role in maintaining the health of natural water ecosystems, specifically by increasing the oxygen content via photosynthesis [26]. Based on the results of this work, we can conclude that phytoremediation can better increase DO than filtration in the treatment of diamond-mine-tailings water.
The enhancement of DO after treatment contributed to the reduction in the organic pollution load (BOD and COD) by reducing its retention time. Increasing the DO level in diamond-mine-tailings water impacts the degree of $\mathrm{CO}_{2}$ depletion from photosynthesis, which can promote more aerobic conditions. Figure 5(A) shows that phytoremediation was effective in the removal of BOD at a maximum of $64 \%$ ( $3.2 \mathrm{mg} . \mathrm{L}^{-1}$ ) for 500 g (V2) of biomass. This suggests that the removal of BOD was greater as the root system of the water hyacinth acted as an effective media for microbial growth, thereby providing oxygen to the rhizosphere (rhizo-filtration). The schematic in Figure 4(A) illustrates the microbial degradation of organic pollutants by the water hyacinth [27].

As shown in Figure 5(B), the BOD removal by filtration achieved a maximum of $60 \%$, which is $13 \%$ lower than that reported by Alsaqqar et al. [28]. This disparity is because these authors had performed filtration after secondary treatment. The trends of BOD removal for phytoremediation and filtration were similar, whereby the BOD concentration gradually decreased over 5 days, then started to increase after 7 days. This increase may
possibly be due to the decay of plants or the organic decomposition process becoming sub-optimal due to weather factors [29], [30].

In addition, the COD concentration gradually decreased (by around three times the initial concentration) after 7 days of treatment using a CW, as shown in Figure 6. This indicates that a CW is very effective in the removal of COD by up to $70 \%$, which yields a concentration less than the maximum acceptable limit. The greatest reduction was obtained by the $500-\mathrm{g}$ biomass of water hyacinth (V2). In an earlier study, by Abdelhakeem et al. [31] reported a $75 \%$ COD removal by a vertical subsurface flow constructed wetland (VSSFCW). In addition, batch feeding has also been reported to facilitate organic removal by improving the oxidation condition to enable better removal of heavy-metal compounds [32]. The amount of oxygen supplied to the rhizosphere corresponds to the plant density, which affects the biodegradation process and biological adsorption [33].

Compared to the CW model, filtration was less effective. However, the highest efficiency of $66 \%$ (7.1 $\mathrm{mg} . \mathrm{L}^{-1}$ ) COD removal was achieved when using a combination of $25 \%$ gravel on top and $75 \%$ sand on the bottom layer (F6). This result is very achievable in practice and is well below the required standard value. A high organics content was observed in the filter that had a high composition of sand ( $75 \%$ ) as well, thereby increasing the microbial activity, which diminishes the DO concentration in the filter [34]. However, organic adsorption also occurred during filtration [35]. When mine-tailings water passed through the filters, biological activity occurred at the water-sand interface, which is known as the schmutzdecke layer [36], i.e., algae, bacteria, humus, and protozoa were growing on the sand layer. The organic compounds in the raw water was thus greatly reduced by these biological organisms, which enabled the improvement in water quality [36].


Figure 3. DO Values After Treatment by (A) Phytoremediation and (B) Simple Filtration
(A)

(B)


Figure 4. Schematic Diagrams of Pollutant Adsorption by Water Hyacinth in (A) Phytoremediation Process and (B) Simple Filtration Process using Up-flow System and Gravel and Sand as Materials


Figure 5. BOD Concentrations after Treatment by (A) Phytoremediation and (B) Filtration


Figure 6. COD Concentration Values After Treatment by (A) Phytoremediation and (B) Filtration

Comparison of phytoremediation and filtration processes in heavy-metal degradation in diamond-mine-tailings water. Figure 7 shows the performances of phytoremediation and filtration in the removal of heavy-metal Fe ions. This heavy-metal concentration was greatly decreased as much as $81 \%$ after 7 days of retention time, whereas the control sample was reduced by just $8.2 \%$. The V2 sample exhibited the highest removal rate of the various biomasses, which is consistent with that of the COD removal. The pH value can indicate the bio-sorption process, which may influence the metal chemistry and ions in the biomass. pH values ranging from $3.5-9$ are optimum for the adsorption of metals onto the roots of water hyacinth [37]. In this work, our pH was measured to be 6.9. The various bacteria present in the root, including Bacillus, Azotobacter, Enterobacter, Staphylococcus, and Pseudomonas, also play a role in the oxidation process [38].

The authors of a previous study agree that CWs offer a promising technology for the removal of Fe ( $74.1 \%$ ) [39]. However, the authors of another study found the photoreduction of $\mathrm{Fe}^{2+}$ to $\mathrm{Fe}^{3+}$ to increase in the presence of organic matter, which could then recycle back into the water [40], [41]. Compared to filtration process, this process was found to be much more effective. Filtration achieved only $78 \%$ ( $0.7 \mathrm{mg} . \mathrm{L}^{-1}$ ) Fe removal, with the control achieving $9.8 \%$. Here, F6 was also found to be the best combination. The diffusion process of $\mathrm{O}_{2}$ into water creates $\mathrm{Fe}_{2} \mathrm{O}_{3}$, which then precipitates as $\mathrm{Fe}(\mathrm{OH})_{3}$ [42], resulting in the DO value increasing as compared to that of the control sample. However, the concentration was still higher than the permissible limit after both the CW and filtration treatments. Another study investigated the use of multilayers and kinetic degradation fluxion, which successfully removed chlorine, lead mercury, and iron [43]. Multilayers perform better than dual layers.

Figure 8 clearly shows that the trend of the Mn concentration is similar to that of the Fe concentration (Figure 7). The optimum result ( $87.7 \%$ of Mn reduction) by the phytoremediation process was also obtained by V2 (500 g of water hyacinth). The lowest reduction in the Mn concentration, as shown in Fig. 8(A), was that by 1000 g of water hyacinth. However, the Mn concentrations for V1 to V4 are lower than that of the control. These results show that the capacity of a biomass greatly influences the optimal adsorption of heavy-metal contaminants. The water hyacinth has a unique characteristic in that it can grow and proliferate despite extreme conditions. Moreover, the water hyacinth grows very fast in water with a pH in the range of 5.5-7.0 [44]. In addition to its extremely fast growth and proliferation rate, water hyacinth also readily covers the water surface, which means sunlight and oxygen cannot easily penetrate this covering to promote photosynthesis underwater [45]. As such, we strongly agree that 500 g of water hyacinth is the optimum mass given the capacity and volume of the reactor as a function of its growth time.

If we compare the results in Figures 7(A) and 8(A), we see that the efficiency Mn removal is lower than that of Fe removal. This is because the Fe ions are adsorbed before the Mn ions. The electronegativities and covalent indexes of Fe and Mn ions are very different. Also, the lower ion interactions are actively stronger and faster due to their ligand polarization abilities [44, 46]. In Table 2, we can compare the results obtained in this work with those reported elsewhere, from which we can clearly see that our work obtained excellent removal of heavy-metal ( Fe and Mn ) within only 7 days.

Similar trends are also evident when using filtration (Figure 8(B)) with phytoremediation, whereby all sample variations successfully reduced the Mn concentration. The optimum Mn removal of $78.7 \%$ was obtained by sample F6 (gravel 75\%, sand 25\%). The composition


Figure 7. Fe Concentrations After Treatment by (A) Phytoremediation and (B) Filtration


Figure 8. Mn Concentrations After Treatment by (A) Phytoremediation and (B) Filtration

Table 2. Comparison of Phytoremediation Results in Water and Wastewater Treatment

| No | System | Water/feed | Before (mg/L) | Time (d) | Efficiency | Ref |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | Constructed wetland using water hyacinth | Diamond tailings mine | BOD (8.9); COD (22); DO (3.1); Fe (3.53); Mn (1.37); Ammonia (2.52) | 7 days | DO (34\%); COD (70\%); BOD (64\%); Fe (80.6\%); Mn (87.7\%); Ammonia (74.8\%) | This work |
| 2 | Constructed Wetland ( $\mathrm{Q}=5 \mathrm{~m}^{3} / \mathrm{d}$ ) Water hyacinth (Eichornia dulcis) and Eleocharis dulcis | Acid Mine Drainage <br> (AMD) | $\begin{aligned} & 23.12 \\ & 25.50 \end{aligned}$ | 25 days | $\begin{aligned} & \mathrm{Fe}=87.11-95.28 \% \\ & \mathrm{Mn}=70.08-79.84 \% \end{aligned}$ | [44] |
| 3 | Constructed wetland using Water hyacinth | Industrial wastewater | $\begin{aligned} & 837.6 \\ & 52.55 \end{aligned}$ | 28 days <br> 21 days | $\begin{gathered} \text { COD (83.7\%) } \\ \text { Ammonia (71.6\%) } \end{gathered}$ | [57] |
| 4 | Constructed wetland using water hyacinth | Domestic wastewater | $\begin{gathered} 418.36 \\ 215.42 \\ 33.01 \end{gathered}$ | 2 month | $\begin{gathered} \text { COD (79\%) } \\ \text { BOD (86\%) } \\ \text { Ammonia (72\%) } \end{gathered}$ | [58] |
| 5 | Open pond using water hyacinth compared to water lettuce | Domestic sewage | 13.15 | 1 month | $\begin{gathered} \text { Ammonia (58.64\%) } \\ \text { COD= } \\ \text { WH (40.44\%) } \\ \text { WL (43.84\%) } \end{gathered}$ | [56] |
| 6 | Phytoremediation process using <br> Water hyacinth (E. crassipies) | Sukinda Chromite Mine wastewater | $\begin{aligned} & \text { BOD (352) } \\ & \text { COD (423) } \end{aligned}$ | 15 days | BOD ( $50 \%$ ) or $176 \mathrm{mg} / \mathrm{L}$ COD (34\%) or $279 \mathrm{mg} / \mathrm{L}$ | [59] |
| 7 | Phytoremediation process using Water hyacinth (E. crassipies) | Downstream of 18 river, China | COD (105.53) | 18 days | COD (70.12\%) | [60] |

Table 3. Comparison Results of Filtration Process in Water and Wastewater Treatment

| No | System | Water/feed | Before (mg/L) | Time | Efficiency | Ref |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | Constructed wetland using water hyacinth | Diamond tailings mine | $\begin{gathered} \text { BOD (8.9); COD (22); } \\ \text { DO (3.1); Fe (3.53); } \\ \text { Mn (1.37); } \\ \text { Ammonia (2.52) } \end{gathered}$ | 7 days | $\begin{gathered} \text { DO (10\%); COD (70\%); } \\ \text { BOD (64\%); Fe (78.7\%); } \\ \text { Mn (84.9\%); } \\ \text { Ammonia (58.9\%) } \end{gathered}$ | This work |
| 2 | Filtration using six layers (gravel, manganese sand, sea sand, quartz sand, activated carbon | Groundwater | $\begin{aligned} & \mathrm{Fe}(3.667) \\ & \mathrm{Mn}(1.692) \end{aligned}$ | - | $\begin{gathered} \mathrm{Fe}(97 \%) \\ \mathrm{Mn}(35.7 \%) \end{gathered}$ | [18] |

of the filtration media in this work had gravel in the first layer and sand as the last layer, which facilitated the easy passage of water through each layer from sand to gravel (up-flow system). As it requires just two layers of virgin materials, this filtration process is very simple, requiring no carbonization or activated carbon. This process is also referred to as the rapid sand filtration process. Its effectiveness was also reported by Chaudhry et al. [47], who found that virgin sand shows a good propensity for the removal of heavy metals.

In other work, Thuy et al. [18] reported that filtration with six layers of gravel, activated carbon, manganese sand, and sea sand can remove Fe ions very rapidly (approximately $97 \%$ in groundwater treatment). Different materials and water samples achieve very specific results. However, the use of more layers of filter media tends to increase cost and require a reactor with a bigger volume. Error! Reference source not found. shows a comparison of our results with those obtained in previous work. The Mn removal from diamond-mine-tailings water by filtration also shows a higher removal percentage (compared to Figure 8) than that for Fe . This result is opposite to that reported by Thuy et al. [18], where the Mn removal was just $35.7 \%$ (lower than that obtained in this work), less than that for Fe. This findings is likely explained through the following equations (1-3):

$$
\begin{align*}
& \mathrm{Fe}\left(\mathrm{HCO}_{3}\right)_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{Fe}(\mathrm{OH})_{2} \downarrow+2 \mathrm{H}_{2} \mathrm{CO}  \tag{1}\\
& 4 \mathrm{Fe}(\mathrm{OH})_{2}+2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2} \rightarrow 4 \mathrm{Fe}(\mathrm{OH})_{3} \downarrow  \tag{2}\\
& 2 \mathrm{Mn}\left(\mathrm{HCO}_{3}\right)_{2}+\mathrm{O}_{2}+5 \mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{Mn}(\mathrm{OH})_{4} \downarrow+4 \mathrm{H}_{2} \mathrm{CO}_{3} \tag{3}
\end{align*}
$$

Equations 1 and 2 show the oxidation processes for Fe ions. Fe (II) hydrogen carbonate is a labile salt compound that is easily decomposed into Fe (II) hydroxide (Eq. 2). In the process of pumping tailings water into the filtration reactor, $\mathrm{Fe}^{2+}$ ions appear with oxygen in the air, which leads to their chemical reaction and the formation of Fe (III) hydroxide (Eq. 2) with a large particle size. This is the reason why the Fe ions easily precipitate. A similar oxidation process occurs with manganese ions (Eq. 3). The multiple reactions cause Fe and Mn to transform into more stable ions that precipitate more easily. Through these chemical reactions, the Fe removal rate is effectively higher than that of Mn removal, which differs from the results
obtained in this work. This is due to the lower initial concentration of Mn than Fe ions in the sample. Hence, the Mn ions were easy to remove by precipitation and then became trapped at the surface of the first layer of filtration material. The water hyacinth is most powerful in its adsorption of heavy metals such as Fe and Mn , which accumulate on the root surface, a process referred to as rhizo-filtration by the authors of [37, 48]. Figure 4 shows a schematic of the adsorption process during phytoremediation by water hyacinth.

Figure 9(A) shows the removal of ammonia via phytoremediation, the result of which are similar to those for Fe and Mn removal, with the optimum value obtained by V2 ( 500 g of mass water hyacinth) with a $75 \%$ ammonia removal efficiency ( $0.6 \mathrm{mg} . \mathrm{L}^{-1}$ ). This could be explained by the fact that the heavy-metal accumulation increases with increasing pH , as reported in previous research [44]. The water hyacinth is extremely efficient in adsorbing ammonia in water because ammonia is very much needed for its nutrition. Deng and Ni [49] and Wu et al. [50] reported that the adsorption process of ammonia occurs specifically at the roots, as illustrated in Figure 4.

The water hyacinth is reported to preferentially adsorb ammonia before nitrates [51], [52]. This is also consistent with previous research by Aoi and Hayashi [53], who found water hyacinth to consume the ammonia present in water molecules, and only consume nitrates once the ammonia content has been almost entirely consumed. This explains the low removal percentage of nitrates, approximately $28 \%$. The ammonia removal efficiency observed in this work was quite high compared to that reported by Mayo and Hanai [54] of $81 \%$ and Rezania et al. [55] of $85 \%$, with retention times of 44 days and 21 days, respectively. Qin et al. [56] also found water hyacinth to have a better removal efficiency of nitrogen (ammonia, nitrate, nitrite) of $58.64 \%$, due to its high accumulation capacity as compared to water lettuce.

In contrast, ammonia removal by filtration is not effective due to the fact that the materials used in this work were virgin. As reported Chaudhry et al. [47], virgin materials are those without carbonization (natural materials). As noted above, filtration systems using virgin


Figure 9. Ammonia Concentrations after Treatment by (A) Phytoremediation and (B) Filtration
materials have a good propensity for reducing heavymetal contents. This is linked to the fact that the chemical reactions of Fe and Mn occur during the feed pumping into the reactor, as illustrated in Figure 4(B). The pumping process starts at different depths and the appearance of bubbles indicates the occurrence of oxidation. In contrast, ammonia requires biotic media for its adsorption and reduction of its content. Phytoremediation uses the water hyacinth as a bio-filter to adsorb the contaminant.

## 4. Conclusion

Both phytoremediation and filtration processes can be used to treat diamond-mine-tailings water, and each effectively enables treatment of this water via the application of the wetland setup concept using Einchhornia crassipes (water hyacinth) as the biomass and adsorbent plant for phytoremediation and gravel and sand as the filter media for simple filtration. The best results were obtained using a mass of 500 g of water hyacinth and a gravel to sand ratio of 25:75. Phytoremediation achieved better results than filtration for all parameters. In the experiment, the phytoremediation and filtration processes demonstrated an ability to increase DO ( $4.7 \mathrm{mg} . \mathrm{L}^{-1}$ ) and reduce BOD ( $3.2 \mathrm{mg} . \mathrm{L}^{-1}$ ), COD ( $6.5 \mathrm{mg} . \mathrm{L}^{-1}$ ), $\mathrm{Fe}\left(0.6 \mathrm{mg} . \mathrm{L}^{-1}\right)$, Mn ( $0.16 \mathrm{mg} . \mathrm{L}^{-1}$ ), and ammonia ( $0.63 \mathrm{mg} . \mathrm{L}^{-1}$ ) concentrations from those measured in raw diamond-mine-tailings water. The COD concentrations had been reduced to the permissible limit, whereas those of the other parameters still failed to meet government regulations for water quality. To improve these results, another type of plant or multilayer material could be applied.

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# Comparison of Phytoremediation and Filtration for Diamond-mine-tailings Water Treatment 

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#### Abstract

The water pollution caused by diamond mine activities can kill aquatic life. In this work, we used phytoremediation and filtration to treat pond water polluted by the tailings of a diamond mine located in South Kalimantan, Indonesia. Einchhornia crassipes (water hyacinth) was utilized as the biomass for the phytoremediation process. Gravel ( $10-15$ mm ) and sand ( $0.1-1 \mathrm{~mm}$ ) were used as filter media in the simple filtration setup, using an up-flow system (bottom to top). In the experiment, 16 L of diamond tailing water was poured into five phytoremediation reactors (each 60 L in 20 ume), which were then tested over seven days. A pretreatment analysis of the tailings water showed that its biochemical oxygen demand ( BO 31 of $8.9 \mathrm{mg} \mathrm{L}^{-1}$ and chemical oxygen demand (COD) of $22 \mathrm{mg} \mathrm{L}^{-1}$ exceeded the national maximum standards of $2 \mathrm{mg} \mathrm{L}^{-1}$ and $10 \mathrm{~m} 63 \mathrm{~m}^{-1}$, respectively. The experimental results demonstrate that 2 oth phytoremediation and filtration could increase the dissolved oxygen concentration ( $4.7 \mathrm{mg} . \mathrm{L}^{-1}$ ) and reduce the BOD $\left(3.2 \mathrm{mg} . \mathrm{L}^{-1}\right), \mathrm{COD}\left(6.5 \mathrm{mg} . \mathrm{L}^{-1}\right), \mathrm{Fe}\left(0.6 \mathrm{mg} . \mathrm{L}^{-1}\right), \mathrm{Mn}\left(0.16 \mathrm{mg} . \mathrm{L}^{-1}\right)$, and ammonia $\left(0.63 \mathrm{mg} . \mathrm{L}^{-1}\right)$ concentrations from those measured in the raw diamond-mine-tailings water. The phytoremediation performance was better than that of filtration. The COD values were successfully reduced to the permissible limit, although the other parameters still failed to meet the government water quality regulation requirements.


#### Abstract

Abstrak Metode Perbandingan antara Proses Fitoremediasi dan Proses Filtrasi Sederhana untuk Mengolah Air Bekas Galian Tambang Intan. Polusi air yang disebabkan aktivitas pertambangan dapat membunuh kehidupan akuatik. Penelitian ini bertujuan untuk mengolah air tercemar bekas galian tambang intan di Kalimantan Selatan, Indonesia menggunakan proses fitoremediasi dan filtrasi sederhana. Eichornia Crassipes (eceng gondok) digunakan sebagai biomassa selama proses fitoremediasi. Media penyaring seperti kerikil ( $10-15 \mathrm{~mm}$ ) dan pasir ( $0,1-1 \mathrm{~mm}$ ) ditambahkan ke dalam reaktor filtrasi sederhana yang memiliki aliran atas (dari bawah ke atas). 16 L air bekas galian tambang intan dituangkan ke dalam 5 reaktor (volume 60 L ) dan di uji selama 7 hari pada proses fitoremediasi menggunakan metode batch. Analisis pra-perlakuan air tercemar bekas galian tambang menunjukkan BOD sebesar $8,9 \mathrm{mg} . \mathrm{L}^{-1}$ dan COD sebesar $22 \mathrm{mg} . \mathrm{L}^{-1}$ melebihi maksimum nasional yaitu 2 dan $10 \mathrm{mg} . \mathrm{L}^{-1} \cdot 2$ erturut-turut. Berdasarkan eksperimen, fitoremediasi dan filtrasi memiliki kemampuan untuk meningkatkan DO ( $4.7 \mathrm{mg} . \mathrm{L}^{-1}$ ) dan mengurangi $\mathrm{BOD}\left(3.2 \mathrm{mg} . \mathrm{L}^{-1}\right)$, COD ( $6.5 \mathrm{mg} . \mathrm{L}^{-1}$ ), $\mathrm{Fe}\left(0.6 \mathrm{mg} . \mathrm{L}^{-1}\right)$, $\mathrm{Mn}\left(0.16 \mathrm{mg} . \mathrm{L}^{-1}\right)$ serta ammonia ( $0.63 \mathrm{mg} . \mathrm{L}^{-1}$ ) dari nilai awal air bekas galian tambang. Fitoremediasi menghasilkan performa lebih baik dalam penyisihan dibandingkan filtrasi. Nilai akhir COD memenuhi baku mutu, sedangkan parameter lain tidak memenuhi peraturan pemerintah mengenai kualitas air.


Keywords: phytoremediation process, simple filtration process, diamond mine tailings water

## 1. Introduction

Mine wastewater typically contains many pollutants, including heavy metals that have a significant and negative impact on the environment [1]. The Kalimantan island in Indonesia is well-known to be home to the oldest diamond mine in the world [2]. Mining activities reported by Indonesia's Environmental Agency reveal that the river flowing nearby the diamond mine has also become polluted. High chemical oxygen demand (COD) levels and iron ( Fe ) and manganese ( Mn ) concentrations have been measured in the river. These heavy metals and other metalloid pollutants can degrade human health as well as the natural ecosystem [3].

Numerous studies have been reported of the use of phytoremediation in a constructed wetland (CW) for the removal of contaminants in mine effluent [4]-[6]. CW is a promising technology that involves the use of natural processes that require low maintenance and operational costs [7]. Eichhornia crassipes i.e., the water hyacinth [8], grows widely in tropical regions and often damages local water ecology by covering the entire water surface, thereby preventing sunlight from penetrating into the water [9]. However, this plant shows great promise for application in the phytoremediation of water bodies, as it reduce 27e amount of pollutants in the water, including the total suspended solids, total dissolved solids, biochemical oxygen demand (BOD), COD, and heavy-metal compounds [10].

Another advance technology involves the application of a membrane that filters and captures particles from surface water and wastewater [11]-[13]. Although this membrane performs well, it is very expensive. Studies have shown that filtration can be made cost-effective by the use of gravel, granular material, and sand [14], [15]. Typically, the effective size of sand particles is $0.1-0.3$ mm [16], but coarser sand has also been used in filtration reactors [17]. The simple filtration approach has been reported to achieve good removal of Fe [18].

Many studies have focused only on the performance of filtration in treating groundwater [18] and water from coal mines [19]. In this work, we compare studies of phytoremediation and filtration in the treatment of water contaminated by diamond mine tailings. We used a phytoremediation process that employs water hyacinth as the biomass and adsorbent plant. In the filtration process, we used a continuous mode of up-flow (bottom to top) for the water flow and added gravel and sand as filter media.

## 2. Materials and Methods

Characterization of diamond-nin 10 ilings water. For this study, diamond-mine-tailings water samples were taken from the tailing pond located in the village of Pumpung, Sungai Tiung district, South Kalimantan, Indonesia (as shown in Figure 1). Measurements of the $\mathrm{pH}, \mathrm{COD}, \mathrm{BOD}$, iron ( Fe ), manganese ( Mn ), ammonia $\left(\mathrm{NH}_{3}-\mathrm{N}\right)$, and dissolved oxygen (DO) were performed twice, in a preliminary characterization, and after treatment. Examinat 28 s of the samples were performed with reference to pH (SNI 06-6989.11-2004), COD (SNI 06-6989.2-2004), BOD (SNI 6989.72:2009), Fe (SNI 06-6854-2002), Mn (SNI 06-6855-2002), and ammonia (SNI 06-6876-2002).

Phytoremediation process. The phytoremediation process was conducted using a wetland setup concept, with water hyacinth as the biomass and adsorbent plant with variations in mass $(250 \mathrm{~g}, 500 \mathrm{~g}, 750 \mathrm{~g}$, and 1000 g ). The volume of the diamond-mine-tailings water samples was 16 L in a batch system with a 7-day retention time. The samples were analyzed after 3 days, 5 days, and 7 days. Figure 2(A) shows the setup of the phytoremediation process, for which there were five reactors constructed from $60-\mathrm{L}$ plastic boxes for testing without any water hyacinth and with four different masses of water hyacinth. V1, V2 V3, and V4 contained biomasses of $250 \mathrm{~g}, 500 \mathrm{~g}, 750 \mathrm{~g}$, and 1000 g , respectively.


Figure 1. Locations from Which Diamond-mine-tailings Water Samples Were Collected


Figure 2. Setups of (A) Phytoremediation and (B) Filtration Processes

Phytoremediation process. The filtration process was conducted in a reactor containing gravel and sand. This system operated with water flowing in a continuous upflow (bottom to top) at a debit volume of $0.001 \mathrm{~m} 3 . \mathrm{s}^{-1}$. In this process, we used three different thicknesses of filter media, as shown in Figure 2(B), for each of the filtration reactors. The reactors labeled F1, F2, and F3 contained mass ratios of gravel to sand of $25: 75,50: 50$, and $75: 25$, respectively. Reactors F4, F5, and F6 contained mass ratios of sand to gravel of $25: 75,50: 50$, and $75: 25$, respectively

## 3. Results and Discussion

Characteristic of diamond-mine-tailings water taken from diamond mine pond. Diamond-mine-tailings water was collected from the pond at the diamond mine in Cempaka, South Kalimantan, Indonesia. The quality of this water was first investigated to establish the condition of the raw water, the results of which are shown in Table 1. In the table, we can see that the diamond-mine-tailings water does not meet requirements of Indonesian water quality standard $82 / 2001$ class I for

Tabel 1. Characteristics of Diamond-mine-tailings Water

| Parameters | Unit | Raw water | Quality standard <br> (Indonesian <br> Government <br> $\mathbf{8 2 / 2 0 0 1})$ |
| :---: | :---: | :---: | :---: |
| 12 |  |  | $6.00-9.00$ |
| Ph | - | $6.98-7.04$ | 2.00 |
| BOD | $\mathrm{mg} \mathrm{L}^{-1}$ | 8.90 | 10.00 |
| COD | $\mathrm{mg} \mathrm{L}^{-1}$ | 22.00 | $6.00^{*}$ |
| DO | $\mathrm{mg} \mathrm{L}^{-1}$ | 3.10 | 0.30 |
| Fe | $\mathrm{mg} \mathrm{L}^{-1}$ | 3.53 | 0.10 |
| Mn | $\mathrm{mg} \mathrm{L}^{-1}$ | 1.37 | 0.50 |
| Ammonia | $\mathrm{mg} \mathrm{L}^{-1}$ | 2.52 |  |
| *Minimum standard |  |  |  |

BOD, COD, Fe, Mn, and ammonia [20]. However, the pH value is under the permissible limit. This is because the pond was present prior to the diamond mining operation began and had already been polluted by organic and heavy-metal contaminants with low pH . To investigate the effectiveness of phytoremediation, we then grew water hyacinth using that water.

The D 56 oncentration of the raw diamond-mine-tailings water was measured to be $3.1 \mathrm{mg} \mathrm{L}{ }^{-1}$. The minimum standard for the DO concentration as per the Indonesian Government Regulation No $82 / 2001$ is $6 \mathrm{mg} \mathrm{L}^{-1}$. This means that the DO concentration in this sample does not meet the standard due and must be increased. In fact, the low DO concentration is related to serious pollution from organic matter [21] in the water.

Comparison of performances of phytoremediation and filtration processes in organic degradation of diamond-mine-tailings water. Figure 3(A) shows the DO concentrations of water after treatment. After 7 days of treatment, the DO of the diamond mine-tailing pond water was about $4.7 \mathrm{mg} . \mathrm{L}^{-1}$, or $34 \%$ of the maximum DO value measured, which was still lower than the minimum DO standard shown in Table $1\left(6 \mathrm{mg} . \mathrm{L}^{-1}\right)$ The same value was obtained for the control sample (without water hyacinth). Although water hyacinth itself has little impact in treating diamond mine-tailing pond water, its roots act as microbial growth media that provide oxygen to the rhizosphere for the microbial degradation of organic contaminants. This was confirmed by the difference in the DO values between the control sample and those to which water hyacinth had been added. Increases in the DO values of domestic wastewater by the application of water hyacinth has also been reported by Rezania et al. [22]. However, water hyacinth has also been reported to be unable to release oxygen into water, as compared with another submerged plant, and instead cause decreases in DO concentration [23]. The outcome depends on the water hyacinth mat used [24], as large water hyacinth mats can limit the oxygen exchange and thereby decrease the DO concentration.

Furthermore, after 3 days, DO showed no significant increase, increasing by only $10 \%$ ( $3.42 \mathrm{mg} . \mathrm{L}^{-1}$ ) via the sand filtration method shown in Figure 3(B). This is due to the laminar water flow used in the filtration reactor [25]. The flow of the diamond-mine-tailings water was initially at a low rate of $0.001 \mathrm{~L}_{\mathrm{s}}{ }^{-1}$ when introduced into the filtration reactor, which caused the water flow to become turbulent, thereby slightly increasing the DO level.

Water hyacinth plays a crucial role in maintaining the health of natural water ecosystems, specifically by increasing the oxygen content via photosynthesis [26]. Based on the results of this work, we can conclude that phytoremediation can better increase DO than filtration in the treatment of diamond-mine-tailings water.
The enhancement of DO after treatment contributed to the reduction in the organic pollution load (BOD and COD) by reducing its retention time. Increasing the DO level in diamond-mine-tailings water impacts the degree of $\mathrm{CO}_{2}$ depletion from photosynthesis, which can promote more aerobic conditions. Figure 5(A) shows that phytoremediation was effective in the removal of BOD at a maximum of $64 \%$ ( $3.2 \mathrm{mg} . \mathrm{L}^{-1}$ ) for 500 g (V2) of biomass. This suggests that the removal of BOD was greater as the root system of the water hyacinth acted as an effective media for microbial growth, thereby providing oxygen to the rhizosphere (rhizo-filtration). The schematic in Figure 4(A) illustrates the microbial degradation of organic pollutants by the water hyacinth [27].

As shown in Figure 5(B), the B 55 p removal by filtration achieved a maximum of $60 \%$, which is $13 \%$ lower than that reported by Alsaqqar et al. [28]. This disparity is because these authors had performed filtration after secondary treatment. The trends of BOD removal for phytoremediation and filtration were similar, whereby the BOD concentration gradually decreased over 5 days, then started to increase after 7 days. This increase may
possibly be due to the decay of plants or the organic decomposition process becoming sub-optimal due to weather factors [29], [30].

In addition, the COD concentration gradually decreased (by around three times the initial concentration) after 7 days of treatment using a CW, as shown in Figure 6. This indicates that a CW is very effective in the removal of COD by up to $70 \%$, which yields a concentration less than the maximum acceptable limit. The greatest reduction was obtained by the $500-\mathrm{g}$ biomass of water hyacinth (V2). In an earlier study, by Abdelhakeem et al. [31] reported a $75 \%$ COD removal by a vertical subsurface flow constructed wetland (VSSFCW). In addition, batch feeding has also been reported to facilitate organic removal by improving the oxidation condition to enable better removal of heavy-metal compounds [32]. The amount of oxygen supplied to the rhizosphere corresponds to the plant density, which affects the biodegradation process and biological adsorption [33].

Compared to the CW model, filtration was less effective. However, the highest efficiency of $66 \%$ (7.1 $\mathrm{mg} . \mathrm{L}^{-1}$ ) COD removal was achieved when using a combination of $25 \%$ gravel on top and $75 \%$ sand on the bottom layer (F6). This result is very achievable in practice and is well below the required standard value. A high organics content was observed in the filter that had a high composition of sand ( $75 \%$ ) as well, thereby increasing the microbial activity, which diminishes the DO concentration in the filter [34]. However, organic adsorption also occurred during filtration [35]. When mine-tailings water passed through the filters, biological activity occurred at the water-sand interface, which is known as the schmutzdecke layer [36], i.e., algae, bacteria, humus, and protozoa were growing on the sand layer. The organic compounds in the raw water was thus greatly reduced by these biological organisms, which enabled the improvement in water quality [36].


Figure 3. DO Values After Treatment by (A) Phytoremediation and (B) Simple Filtration
(A)

(B)


Figure 4. Schematic Diagrams of Pollutant Adsorption by Water Hyacinth in (A) Phytoremediation Process and (B) Simple Filtration Process using Up-flow System and Gravel and Sand as Materials


Figure 5. BOD Concentrations after Treatment by (A) Phytoremediation and (B) Filtration


Figure 6. COD Concentration Values After Treatment by (A) Phytoremediation and (B) Filtration

Comparison of phytoremediation and filtration processes in heavy-metal degradation in diamond-mine-tailings water. Figure 7 shows the performances of phytoremediation and filtration in the removal of heavy-metal Fe ions. This heavy-metal concentration was greatly decreased as much as $81 \%$ after 7 days of retention time, whereas the control sample was reduced by just $8.2 \%$. The V2 sample exhibited the highest removal rate of the various biomasses, which is consistent with that of the COD removal. The pH value can indicate the bio-sorption process, which may influence the metal chemistry and ions in the biomass. pH values ranging from $3.5-9$ are optimum for the adsorption of metals onto the roots of water hyacinth [37]. In this work, our pH was measured to be 6.9 . The various bacteria present in the root, including Bacillus, Azotobacter, Enterobacter, Staphylococcus, and Pseudomonas, also play a role in the oxidation process [38].

The authors of a previous study agree that CWs offer a promising technology for the removal of Fe (74.1\%) [39]. However, the authors of another study found the photoreduction of $\mathrm{Fe}^{2+}$ to $\mathrm{Fe}^{3+}$ to increase in the presence of organic matter, which could then recycle back into the water [40], [41]. Compared to filtration process, this process was found to be much more effective. Filtration achieved only $78 \%\left(0.7 \mathrm{mg} . \mathrm{L}^{-1}\right) \mathrm{Fe}$ removal, with the control achieving $9.8 \%$. Here, F6 was also found to be the best combination. The diffusion process of $\mathrm{O}_{2}$ into water creates $\mathrm{Fe}_{2} \mathrm{O}_{3}$, which then precipitates $52 \mathrm{Fe}(\mathrm{OH})_{3}$ [42], resulting in the DO value increasing as compared to that of the control sample. However, the concentration was still higher than the permissible limit after both the CW and filtration treatments. Another study investigated the use of multilayers and kinetic degradation fluxion, which successfully removed chlorine, lead mercury, and iron [43]. Multilayers perform better than dual layers.

Figure 8 clearly shows that the trend of the Mn concentration is similar to that of the Fe concentration (Figure 7). The optimum result (87.7\% of Mn reduction) by the phytoremediation process was also obtained by V2 ( 500 g of water hyacinth). The lowest reduction in the Mn concentration, as shown in Fig. 8(A), was that by 1000 g of water hyacinth. However, the Mn concentrations for V1 to V4 are lower than that of the control. These results show that the capacity of a biomass greatly influences the optimal adsorption of heavy-metal contaminants. The water hyacinth has a unique characteristic in that it can grow and proliferate despite extreme conditions. Moreover, the water hyacinth grows very fast in water with a pH in the range of 5.5-7.0 [44]. In addition to its extremely fast growth and proliferation rate, water hyacinth also readily covers the water surface, which means sunlight and oxygen cannot easily penetrate this covering to promote photosynthesis underwater [45]. As such, we strongly agree that 500 g of water hyacinth is the optimum mass given the capacity and volume of the reactor as a function of its growth time.

If we compare the results in Figures 7(A) and 8(A), we see that the efficiency Mn removal is lower than that of Fe removal. This is because the Fe ions are adsorbed before the Mn ions. The electronegativities and covalent indexes of Fe and Mn ions are very different. Also, the lower ion interactions are actively stronger and faster due to their ligand polarization abilities [44, 46]. In Table 2, we can compare the results obtained in this work with those reported elsewhere, from which we can clearly see that our work obtained excellent removal of heavy-metal ( Fe and Mn ) within only 7 days.

Similar trends are also evident when using filtration (Figure 8(B)) with phytoremediation, whereby all sample variations successfully reduced the Mn concentration. The optimum Mn removal of $78.7 \%$ was obtained by sample F6 (gravel 75\%, sand 25\%). The composition


Figure 7. Fe Concentrations After Treatment by (A) Phytoremediation and (B) Filtration



Figure 8. Mn Concentrations After Treatment by (A) Phytoremediation and (B) Filtration

Table 2. Comparison of Phytoremediation Results in Water and Wastewater Treatment

| No | System | Water/feed | Before (mg/L) | Time (d) | Efficiency | Ref |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | Constructed wetland using water hyacinth | Diamond tailings mine | BOD (8.9); COD (22); <br> DO (3.1); <br> Fe (3.53); <br> Mn (1.37); <br> Ammonia (2.52) | 7 days | DO (34\%); COD $(70 \%) ;$ BOD (64\%); Fe (80.6\%); Mn (87.7\%); Ammonia $(74.8 \%)$ | This work |
| 2 | Constructed Wetland ( $\mathrm{Q}=5 \mathrm{~m}^{3} / \mathrm{d}$ ) Water hyacinth (Eichornia dulcis) and Eleocharis dulcis | Acid Mine Drainage (AMD) | $\begin{aligned} & 23.12 \\ & 25.50 \end{aligned}$ | 25 days | $\begin{aligned} & \mathrm{Fe}=87.11-95.28 \% \\ & \mathrm{Mn}=70.08-79.84 \% \end{aligned}$ | [44] |
| 3 | Constructed wetland using Water hyacinth | Industrial wastewater | $\begin{aligned} & 837.6 \\ & 52.55 \end{aligned}$ | 28 days <br> 21 days | $\begin{gathered} \text { COD (83.7\%) } \\ \text { Ammonia (71.6\%) } \end{gathered}$ | [57] |
| 4 | Constructed wetland using water hyacinth | Domestic wastewater | $\begin{gathered} 418.36 \\ 215.42 \\ 33.01 \end{gathered}$ | $\begin{gathered} 2 \\ \text { month } \end{gathered}$ | $\begin{gathered} \text { COD (79\%) } \\ \text { BOD (86\%) } \\ \text { Ammonia (72\%) } \end{gathered}$ | [58] |
| 5 | Open pond using water hyacinth compared to water lettuce | Domestic sewage | 13.15 | 1 month | $\begin{gathered} \text { Ammonia (58.64\%) } \\ \text { COD }= \\ \text { WH }(40.44 \%) \\ \text { WL }(43.84 \%) \end{gathered}$ | [56] |
| 6 | Phytoremediation process using Water hyacinth (E.crassipies) | Sukinda Chromite Mine wastewater | $\begin{aligned} & \text { BOD (352) } \\ & \text { COD (423) } \end{aligned}$ | 15 days | BOD (50\%) or $176 \mathrm{mg} / \mathrm{L}$ COD (34\%) or $279 \mathrm{mg} / \mathrm{L}$ | [59] |
| 7 | Phytoremediation process using Water hyacinth (E.crassipies) | Downstream of 18 river, China | COD (105.53) | 18 days | COD (70.12\%) | [60] |

Table 3. Comparison Results of Filtration Process in Water and Wastewater Treatment

| No | System | Water/feed | Before (mg/L) | Time | Efficiency | Ref |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | Constructed wetland using water hyacinth | Diamond tailings mine | $\begin{gathered} \text { BOD (8.9); COD (22); } \\ \text { DO (3.1); Fe (3.53); } \\ \text { Mn (1.37); } \\ \text { Ammonia (2.52) } \end{gathered}$ | 7 days | $\begin{gathered} \mathrm{DO}(10 \%) ; \mathrm{COD}(70 \%) ; \\ \text { BOD (64\%); } \mathrm{Fe}(78.7 \%) ; \\ \text { Mn }(84.9 \%) ; \\ \text { Ammonia }(58.9 \%) \end{gathered}$ | This work |
| 2 | Filtration using six layers (gravel, manganese sand, sea sand, quartz sand, activated carbon | Groundwater | $\begin{gathered} \mathrm{Fe}(3.667) \\ \mathrm{Mn}(1.692) \end{gathered}$ | - | $\begin{gathered} \mathrm{Fe}(97 \%) \\ \mathrm{Mn}(35.7 \%) \end{gathered}$ | [18] |

of the filtration media in this work had gravel in the first layer and sand as the last layer, which facilitated the easy passage of water through each layer from sand to gravel (up-flow system). As it requires just two layers of virgin materials, this filtration process is very simple, requiring no carbonization or activated carbon. This process is also referred to as the rapid sand filtration process. Its effectiveness was also reported by Chaudhry et al. [47], who found that virgin sand shows a good propensity for the removal of heavy metals.

In other work, Thuy et al. [18] reported that filtration with six layers of gravel, activated carbon, manganese sand, and sea sand can remove Fe ions very rapidly (approximately $97 \%$ in groundwater treatment). Different materials and water samples achieve very specific results. However, the use of more layers of filter media tends to increase cost and require a reactor with a bigger volume. Error! Reference source not found. shows a comparison of our results with those obtained in previous work. The Mn removal from diamond-mine-tailings water by filtration also shows a higher removal percentage (compared to Figure 8) than that for Fe . This result is opposite to that reported by Thuy et al. [18], where the Mn removal was just $35.7 \%$ (lower than that obtained in this work), less than that for Fe. This findings is likely explained through the following equations (1-3):

37 $\left.\mathrm{HCO}_{3}\right)_{2}+\mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{Fe}(\mathrm{OH})_{2} \downarrow+2 \mathrm{H}_{2} \mathrm{CO}$
$4 \mathrm{Fe}(\mathrm{OH})_{2}+2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2} \rightarrow 4 \mathrm{Fe}(\mathrm{OH})_{3} \downarrow$
$2 \mathrm{Mn}\left(\mathrm{HCO}_{3}\right)_{2}+\mathrm{O}_{2}+5 \mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{Mn}(\mathrm{OH})_{4} \downarrow+4 \mathrm{H}_{2} \mathrm{CO}_{3}$ (3)
Equations 1 and 2 show the oxidation processes for Fe ions. Fe (II) hydrogen carbonate is a labile salt compound that is easily decomposed into Fe (II) hydroxide (Eq. 2). In the process of pumping tailings water into the filtration reactor, $\mathrm{Fe}^{2+}$ ions appear with oxygen in the air, which leads to their chemical reaction and the formation of Fe (III) hydroxide (Eq. 2) with a large particle size. This is the reason why the Fe ions easily precipitate. A similar oxidation process occurs with manganese ions (Eq. 3). The multiple reactions cause Fe and Mn to transform into more stable ions that precipitate more easily. Through these chemical reactions, the Fe removal rate is effectively higher than that of Mn removal, which differs from the results
obtained in this work. This is due to the lower initial concentration of Mn than Fe ions in the sample. Hence, the Mn ions were easy to remove by precipitation and then became trapped at the surface of the first layer of filtration material. The wate 50 yacinth is most powerful in its adsorption of heavy metals such as Fe and Mn , which accumulate on the root surface, a process referred to as rhizo-filtration by the authors of [37, 48]. Figure 4 shows a schematic of the adsorption process during phytoremediation by water hyacinth.

Figure 9(A) shows the removal of ammonia via phytoremediation, the result of which are similar to those for Fe and Mn removal, with the optimum value obtained by V2 ( 500 g of mass water hyacin 45 with a $75 \%$ ammonia removal efficiency $\left(0.6 \mathrm{mg} . \mathrm{L}^{-1}\right)$. This could be explained by the fact that the heavy-metal accumulation increases with increasing pH , as reported in previous research [44]. The water hyacinth is extremely efficient in adsorbing ammonia in water because ammonia is very much needed for its nutrition. Deng and Ni [49] and Wu et al . [50] reported that the adsorption process of ammonia occurs specifically at the roots, as illustrated in Figure 4.

The water hyacinth is reported to preferentially adsorb ammonia before nitrates [51], [52]. This is also consistent with previous research by Aoi and Hayashi [53], who found water hyacinth to consume the ammonia present in water molecules, and only consume nitrates once the ammonia content has been almost entirely consumed. This explains the low removal percentage of nitrates, approximately $28 \%$. The ammonia removal efficiency observed in this work was quite high compared to that reported by Mayo a1d Hanai [54] of $81 \%$ and Rezania et al. [55] of $85 \%$, with retention times of 44 days and 21 days, respectively. Qin et al. [56] also found water hyacinth to have a better removal efficiency of nitrogen (ammonia, nitrate, nitrite) of $58.64 \%$, due to its high accumulation capacity as compared to water lettuce.

In contrast, ammonia removal by filtration is not effective due to the fact that the materials used in this work were virgin. As reported Chaudhry et al. [47], virgin materials are those without carbonization (natural materials). As noted above, filtration systems using virgin


Figure 9. Ammonia Concentrations after Treatment by (A) Phytoremediation and (B) Filtration
materials have a good propensity for reducing heavymetal contents. This is linked to the fact that the chemical reactions of Fe and Mn occur during the feed pumping into the reactor, as illustrated in Figure 4(B). The pumping process starts at different depths and the appearance of bubbles indicates the occurrence of oxidation. In contrast, ammonia requires biotic media for its adsorption and reduction of its content. Phytoremediation uses the water hyacinth as a bio-filter to adsorb the contaminant.

## 4. Conclusion

Both phytoremediation and filtration processes can be used to treat diamond-mine-tailings water, and each effectively enables treatment of this water via the application of the wetland setup concept using Einchhornia crassipes (water hyacinth) as the biomass and adsorbent plant for phytoremediation and gravel and sand as the filter media for simple filtration. The best results were obtained using a mass of 500 g of water hyacinth and a gravel to sand ratio of 25:75. Phytoremediation achieved better results than filtration for all parameters. In the experiment, the phytoremediation and filtratio 2 processes demonstrated an ability to increase $\mathrm{DO}\left(4.7 \mathrm{mg} . \mathrm{L}^{-1}\right)$ and reduce BOD $\left(3.2 \mathrm{mg} . \mathrm{L}^{-1}\right)$, COD ( $6.5 \mathrm{mg} . \mathrm{L}^{-1}$ ), Fe ( $0.6 \mathrm{mg} . \mathrm{L}^{-1}$ ), Mn ( $0.16 \mathrm{mg} . \mathrm{L}^{-1}$ ), and ammonia ( $0.63 \mathrm{mg} . \mathrm{L}^{-1}$ ) concentrations from those measured in raw diamond-mine-tailings water. The COD concentrations had been reduced to the permissible limit, whereas those of the other parameters still failed to meet government regulations for water quality. To improve these results, another type of plant or multilayer material could be applied.

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