Hybrid Treatment of Acid Mine Drainage using a Combination of MgO-NPs and a Series of Constructed Wetland Planted with *Vetiveria Zizanioides*

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Abstract : An efficient, environmentally friendly and low cost hybrid approach was duly developed for the treatment of acid mine drainage (AMD). The hybrid approach combined a nano-and-biotic system operating in a step-wise modular. Specifically, the treatment chains were made up of different stages of which, stage 1 focused on activated MgO-NPs for the neutralization of AMD and stage 2 focused on the polishing of product water using a series of constructed wetland (CWs) planted with *Veteveria zizanioides*. In stage 1, raw AMD was treated with MgO-NPs at a ratio of 1:100 (1g/100 mL), at 500 rpm, and 1 h of hydraulic retention time (HRT) whilst in stage 2, the pre-treated water was explicitly fed into the series of CWs for polishing. The pH was observed to increase from 2.9 to 10.4 and the removal efficiency (RE) of chemicals species registered the following sequence, Fe (99.8%) ≥ Al (99.5%) ≥ Mn (99.24%) ≥ Zn (98.36%) ≥ Cu (97.38%) ≥ Ni (97.7%) ≥ SO_4^{2-} (80.59%). The Thenceforth, the XRD and FTIR analysis revealed that substrate and grass played a huge role in residual chemical species removal. The PH REdox EQuilibrium (in C language) (PHREEQC) geochemical model confirm that metals existed as di-and-trivalent complexes in solution. The product water conformed to prescribed standards, specifications, and guidelines.

Keys words: Acid mine drainage, hybrid approach, MgO-nanoparticles, series of constructed wetland.

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I. INTRODUCTION

Water resource is vital for the existence of life since it is at the core of sustainable and socio-economic development. However, anthropogenic activities have raised various concern due to the alarming volume of pollutants introduced to clean watercourse on daily basis thus rendering the water unsafe as required by regulatory bodies [1]. Out of the various causes of water pollution, acid mine drainage (AMD) is at the forefront, specifically in countries with advanced mining industry. This is due to magnitude of its environmental footprints. Acid mine drainage has been considered as a wastewater stream of grave concern due to its physicochemical composition and its ecological impacts [2]. Streams polluted by AMD have PH ≤ 2.5, high concentration of metals such as, Al,Fe, Mn, Ni, Cu, Zn, As, Cr, and Pb, radionuclides substance, rare earth metals and very high concentration of sulphate ions (SO_4^{2-}) thus degrading the receiving aquatic environment [3].

As such, decision-makers and scientific communities have taken a firm stance in finding long-term solutions to curtail the gigantic effects of AMD on environment and human health. This requires proper management practices to protect, reclaim, rehabilitate, and restore the ecosystem hence averting potential effects of AMD on the environment and this is mainly fulfilled using various treatment technologies such as active and passive [4]**.** However, Operating in stand-alone system, active and passive methods fail to treat AMD to required standards hence calling for advanced techniques and eco-friendly approaches to be designed and implement toward AMD treatment and management [5]. To the best of authors' knowledge, the combination of MgO-NPs and a series of constructed wetland (CWs) is new. This study was therefore aimed to design a hybrid approach combining magnesite nanoparticles (MgO-NPs) and a series of CWs planted with *Vetiveria zizanioides* for effective treatment of AMD.

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II. METHODS

A. Samples collection and characterization

Real AMD was collected from a discharge point at the Sibanye Gold mine in Krugersdorp, Gauteng, South Africa. Onsite characterization was conducted using multi-parameter meter (HANNA instruments, Johan//nesburg, RSA) to measure pH while initial concentration of metals was determined using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and the initial concentration of sulphate was analyzed using ion chromatography (IC).

B. Acquisition and characterization of magnesite, plants and compost soil

Cryptocrystalline magnesite with ≤ 32 µm particles size was procured from Sterkfontein carbonates (Pty) Ltd. Compost soil used for wetland substrate were purchased from Golden world Johannesburg while *Vetiveria zizanioides* were purchased from Nandadram Ecovillage farm in Kwa-Zulu Natal, South Africa. MgO-NPs and plant roots were characterized using different analytical techniques: X-ray diffraction analysis (XRD) for minerals composition while Fourier Transform Infrared Spectrometer (FTIR) was performed to determine the metals-functional groups.

C. Acquisition of reagents

Reagents used in this study were of analytical grade (AG) and were purchased from Merck South Africa.

D. Experimental procedure

The experiment was dictated by the study aim and objectives. The experiment consisted of two categories of which phase 1 focuses on the neutralisation of AMD using MgO-NPs and phase 2 focuses on the use of a series of CWs in the bioremediation step **(Fig 1).** In the **neutralisation step,** the experiments were optimized using the one-factor-at-a-time (OFAAT) and the solid: liquid of 1:100 (w/v or 1 g/100 ml), 500 rpm of mixing, and 1 hr of hydraulic retention time (HRT) was the optimum as reported by the study of Masindi et al [6]. In the bioremediation step, two series of staged CWs (treatment and control) were constructed using circular basins of 100 litres capacity each measuring 62 cm of diameter (d) and 45 cm high (h) and a drum of 1000 litres capacity as reservoir tank to contain AMD water and fresh water for control **(Fig 1).** The wetlands were continuous flow system where water was flowing in continuous drop into the system for the duration of the experiment. The hydraulic retention time (HRT) of the system was determined using the Darcy's law formula as illustrated in (1) taking into consideration the number of the wetland cell and their parameters (size and porosity of the substrate), the HRT was calculated as follow:

$$\text{HRT} = \frac{3\pi r^2 \text{yd}}{\text{Qav}} \quad (1)$$

Where:

π is the constant (3.14),

r is the radius of each wetland cell (m),

y is the depth of water in the wetland cell (m),

d is the porosity of the wetland substrate (%), and

Q_{av} is the average flow of water within the system (m^3/d).

$$\text{HRT} = \frac{3(3.14\times (0.31)^2 \times 0.2)\times 0.59}{0.0035} = 30.52 \text{ days}$$

$$HRT = 30.52 \text{ days}$$

The calculated HRT was ≈ 30 days. The flow rate was maintained low (3.5 litres/day) and the HRT long (30.52 days) in order to allow the water to spend more time in wetland cell and thereby improve the system [7].

Fig 1: illustration of the constructed hybrid pilot treatment plan

E. Leachates and substrate sampling and plants harvest

Leachate (500 mL) from the outlet of each wetland and substrate (soil samples) from the bottom of each wetland were daily collected for a period of 30 days retention time and analyzed for metals content.

F. Analytical methods

Leachates, from both wetlands (control and treatment cell) were analyzed following standard methods as mentioned in the previous section [8].

G. Contaminants removal efficacy

The treatment efficiency of hybrid system (neutralization and bioremediation) in AMD water treatment was determined gradually. All parameters of concern were analyzed daily and the removal efficiency (RE) was calculated gradually every 5 days interval for the duration of the experiment (30 days). RE was calculated for all pollutants as illustrated in (2) [9] and the increment was calculated for pH [9] as illustrated in (2).

$$RE = \frac{Ci - Cf}{Ci} \times 100 \quad (2)$$

Where:

C_i is the initial concentration of each parameter in the AMD water,

C_f is the final concentration of each parameter after hybrid treatment, and

RE (in percentage) is the removal efficiency of each parameter after hybrid treatment

$$I = pHf - pHi \quad (3)$$

Where: pH_f is the final value of pH of the treated AMD, pHi is the initial pH value of AMD water, and I is the increment of pH.

H. Geochemical modelling

Speciation and potential precipitation of metals during the interaction of AMD, substrate and plants roots [10]. The water-Q4 database was utilized. The plants-substrate was modelled using PH REdox EQuilibrium (in C language) (PHREEQC). The water potential precipitation of metals was determined using saturation indexes (SI) of which, SI ≤1 denotes under-saturation, SI ≈ 1 denotes saturation, and SI ≥ 1 denotes super-saturation.

III. RESULTS AND DISCUSSION

A. Remediation studies

This section reports the result of the interaction of raw AMD with the hybrid system (Neutralization and bioremediation).

B. Effect of a hybrid system on pH

The effect of neutralization with MgO-NPs and bio-remediation with CWs on pH was evaluated over a period of 30 days and the obtained results are reported in **Fig 2.**

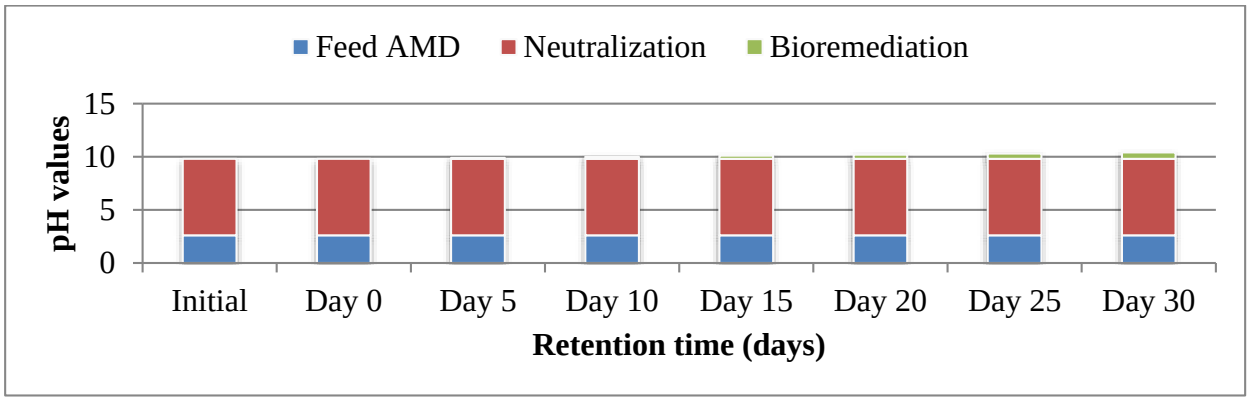

Fig 2: Variation in pH as a function of neutralisation with MgO-NPs and bio-remediation using a series of CWs planted with *Vetiveria zizanioides*

Explicitly, as shown in **Fig 2** the results revealed that the hybrid system was able to increase the pH of AMD from 2.6 to 10.4 corresponding to a total increment of 7.8. The neutralization step of the hybrid system raised the pH from 2.6 to 9.8 while the bioremediation step further raised the pH from 9.8 to 10.4. In light of the findings, it can be noted that MgO-NPs contributed to 92.30% of total pH increment while CWs contributed to 07.70% (**Fig 2**).

Effect of hybrid system on the concentration of sulphate

The effect of neutralization and bioremediation on SO_4^{2-} level was evaluated over a period of 30 days retention time and the results are reported in **Fig 3.**

Fig 3 clearly portrayed that the hybrid system (neutralization with MgO-NPs and a bioremediation with series of CWs) was able to reduce SO_4^{2-} concentration in AMD water from the initial concentration of 3137 mg/L to 608.7 mg/L corresponding to an overall RE of 80.59%. In the control experiment, MgO-NPs reduced SO_4^{2-} in tap water from 250 mg/L to 50.4 mg/L and the bioremediation step further reduced it from 50.4 mg/L to 0.002 mg/L. The reduction of SO_4^{2-} in AMD water after treatment with MgO-NPs may be attributed to the formation of sulphate bearing minerals such as gypsum and oxy-hydrosulphates. Thenceforth, the reduction of SO_4^{2-} in a series of CWs may be attributed to plant accumulation since SO_4^{2-} plays a huge role in plant metabolism.

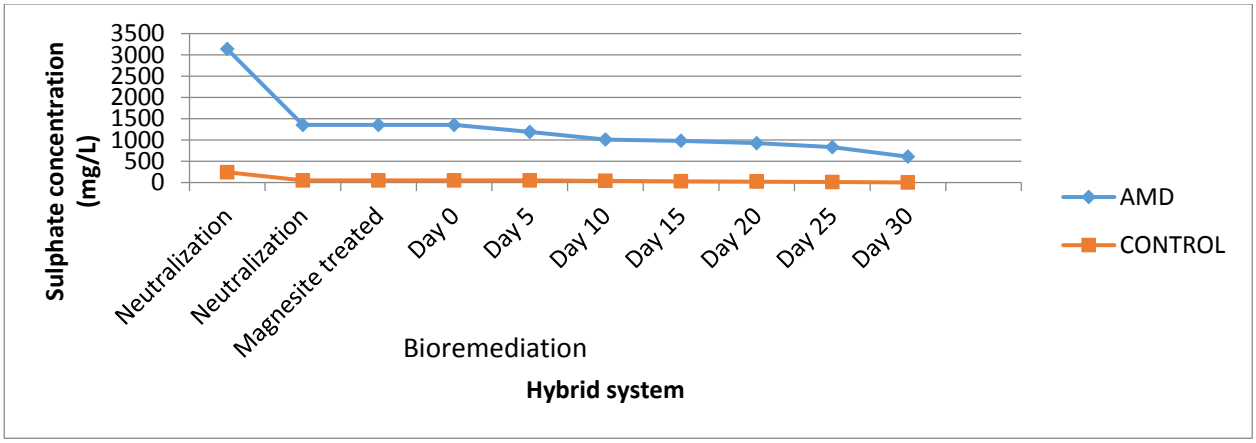

Fig 3: Variation in sulphate concentration as a function of neutralisation and bio-remediation.

C. Effect of hybrid system on the levels of metals

The effect of the hybrid system (neutralization and bioremediation) on the levels of metals was evaluated over a period of 30 days retention time and the results are reported in **Fig 4 (a-f).**

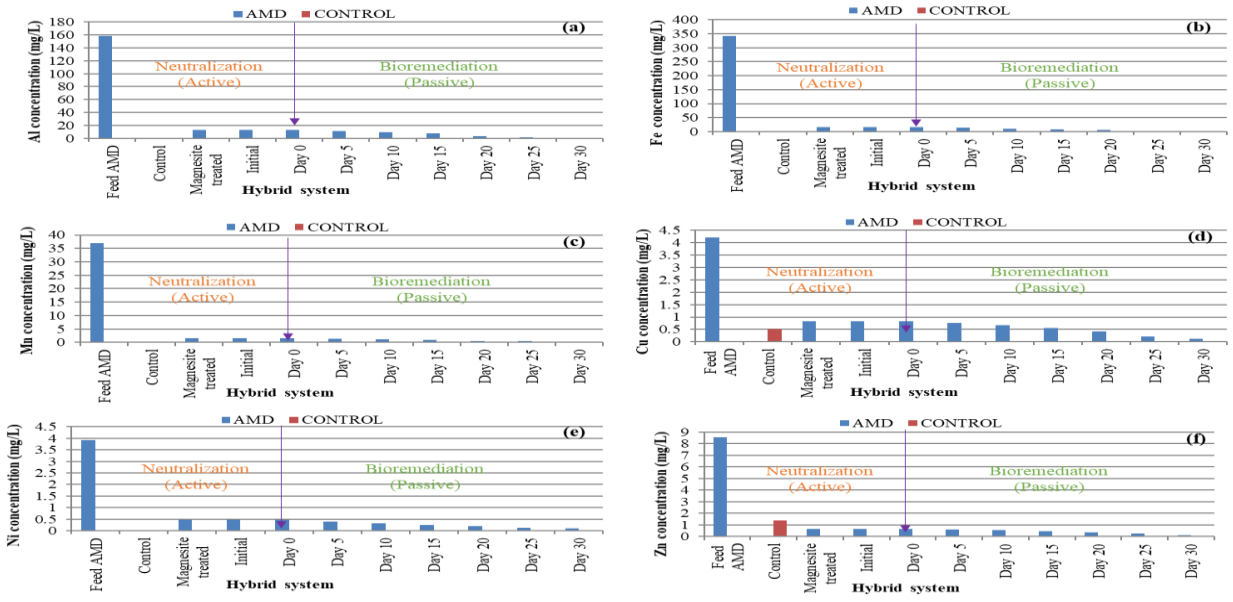

Fig 4 (a-f): Variation in metals level as a function of neutralisation and bio-remediation.

From **Fig 4**, It followed that the treatment of raw AMD with MgO-NPs and a series of CWs planted with *Vetiveria zizanioides* led to a significant reduction of metals with RE as fellow: Al (99.8%) > Al (99.5%) > Mn (99.24%) > Zn

(98.36%) > Ni (97.7%) > Cu (97.38%). In the control experiment, all metals were completely removed after the treatment of tap freshwater with MgO-NPs. The findings revealed that the neutralization step contributed more to metals removal in AMD water. Specifically, after the treatment of AMD water with MgO-NPs for one hour retention time, the pH increased significantly leading to the precipitation, adsorption and co-precipitation of metals with Al precipitated at pH > 4 [11], Cu precipitated at PH > 6 [11], Fe precipitated at PH> 3 [12], Mn precipitated at PH > 5 [11], Ni precipitated at PH > 4.5 [12] and Zn precipitated at PH > 8.7 [11]. The metals removal in the bioremediation step (series of CWs) may be attributed mainly to different types of biological processes such as precipitation, co-precipitation, filtration, rhizo-filtration, ion-exchange, sedimentation with substrate, the interaction between microorganism and plant uptake controlling pollutant removal in CWs [5].

D. Overall water quality

Chemical composition of AMD before and after treatment using a hybrid technology were compared to the DEA guidelines standard for effluent discharge and DWS guidelines standard for drinking water and the results are shown in **Table 1.**

TABLE I: Concentrations of chemical species for untreated and treated AMD against the DEA effluents discharge limits and DWS drinking water quality standard (all units in mg/L except pH and EC**)**

Parameters	Feed AMD	Treated AMD	Removal efficiency	DEA guidelines for effluent discharge	DWS guidelines for drinking water
pH	2.6	10.4	8.8 (increment	6-12	5.5-9.7
Al	158	0.71	99.5	20	0-0.9
Cu	4.2	0.11	97.59	20	0.1
Fe	341	0.66	99.80	50	0-0.1
Mn	37	0.28	99.24	20	0-0.05
Ni	3.92	0.09	97.3	10	0-0.07
Zn	8.55	0.14	98.36	20	0-0.5
Sulphate	3137	608.7	80.59	250-500	0-500

As shown in **Table 1**, the parameters of concern in raw AMD were pH, major ions (Al, Fe, Mn and ions sulphate) and trace ions (Cu, Ni and Zn). After the treatment of AMD with hybrid technology (A combination of neutralization with MgO-NPs and a bioremediation with a series of CWs, the product water had an increased pH, and reduced metals species and SO_4^{2-} concentration to acceptable standard as set by the DEA.

E. Characterization of the solids samples

The mineralogical compositions of feed and product materials after the treatment of AMD are shown in **Fig 5 (a-f)**.

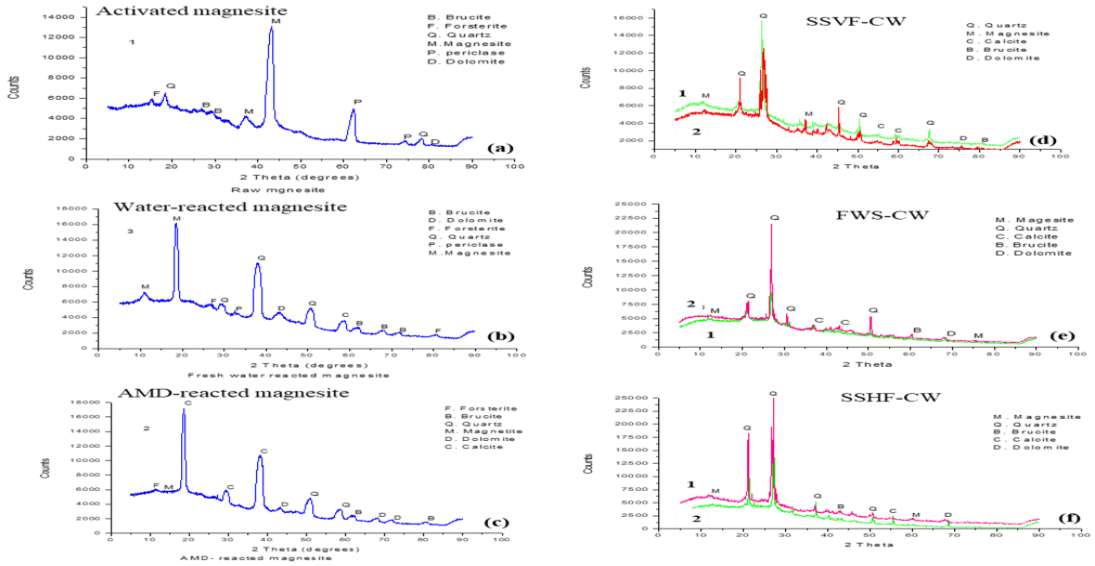

Fig 5 (a-f): XRD patterns of feed and product materials.

As shown in **Fig 5 (a-c),** the XRD analysis revealed that raw MgO-NPs contains magnesite, periclase, brucite, dolomite, forsterite and quartz. MgO-NPs reacted with AMD water contains calcite, brucite. In the AMD-reacted MgO-NPs, periclase was absent and this may be attributed to the dissolution of magnesium oxide (MgO). In the fresh water reacted with MgO-NPs, the XRD analysis revealed the presence of periclase, brucite, dolomite, forsterite, quartz and dolomite which are found in activated MgO-NPs (**Fig 5c**). As shown in **Fig 5 (d - f)**, the X-ray diffraction of substrate from the staged wetland (treatment and control) showed several peaks spread over the range 2Θ from 10° to 68° however, at different intensity. The peaks at 2Θ= 20.6°, 28°, 45° and 50° may correspond to Quartz (SiO_2) which is the major elemental composition of compost [13]. The peak at 2Θ = 43° may correspond to calcite [13] while the peak at 2Θ = 68° may correspond to dolomite [13] thereby revealing that substrate played a huge role in metals removal in the bioremediation step.

F. Metals functional groups of activated magnesite and the plants roots

To understand the interaction between MgO-NPs and the roots before and after contacting AMD, the metals functional groups were determined using FTIR analysis and the results are shown in **Fig 6 (a-d).**

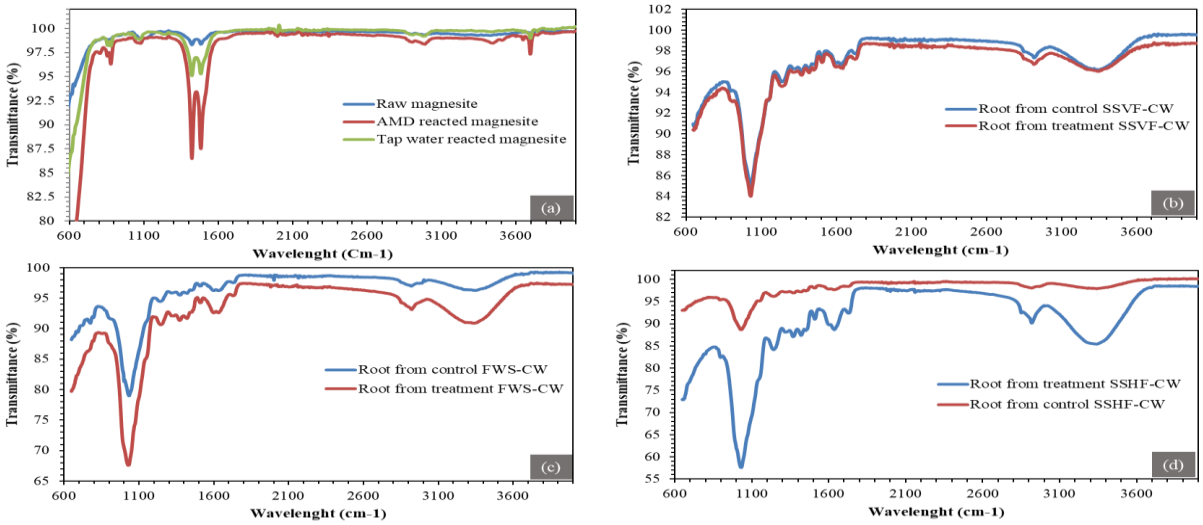

Fig 6 (a-d): Metal functional groups for raw and reacted magnesite and roots.

As shown **Fig 6a,** the results showed a system of bands which in raw MgO-NPs may be characteristic of brucite since it is a mineral form of magnesium hydroxide and it correspond to band 902 cm^{-1}. In tap water reacted MgO-NPs, the system of band at 900, 1038 and 1192 cm^{-1} is characteristic of brucite and may be associated with OH group adsorbed water after reaction with tap water. In the AMD-reacted MgO-NPs, the bands at 878 and 1072 cm^{-1} is characterized of brucite while band at 1432 and 1492 cm^{-1} may be associated with OH group adsorbed water [14]. In **Fig 6 (b-d),** the results indicated complex accumulation of pollutants by plants roots from both treatment and control wetland. The spectrum of the root grown in control wetland shows a band with peak at 856 cm^{-1} which shitted to a peak at 890 of the root grown in treatment wetland and this may be attributed to OH group [13].

IV. CONCLUSIONS

This study successfully confirmed that the combination of MgO-NPs and a series of CWs planted with *Vetiveria zizanioides* was efficient to treat AMD. Contact of MgO-NPs with AMD for 1 hr duration led to an increase of pH from 2.6 to 9.8 and significant reduction of $SO4^{2-}$ and metals (Al, Cu, Fe, Mn, Ni and Zn). The application of a series of CWs planted with *Vetiveria zizanioides* further increased the pH from 9.8 to 10.4 leading to more pollutants removal.

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