Abstract—In the present paper, constructed wetland and ultraviolet (UV)/TiO\textsubscript{2} photocatalysis processes were employed to treat acid mine drainage. Acid mine drainage samples were collected from Mpumalanga (South Africa) and they were characterized for heavy metals and sulphate concentrations. Unvegetated up-flow constructed wetlands were employed as pre-treatment in order to remove maximum concentrations of heavy metals, and a slurry photocatalytic reactor was used to reduce Cr(VI) in the acid mine drainage effluents from the constructed wetlands under optimum conditions. The maximum removal of total chromium achieved by all constructed wetlands was 65% after the optimum hydraulic retention time (HRT) of 5 days; and was 68% for Cr(VI) photocatalytic reduction after the optimum HRT of 3 hrs in a slurry photocatalytic reactor. The experimental data obtained were tested by first order and second order kinetic models. It was clearly demonstrated that the experimental data of Fe and Cr fit quite well first order kinetic model equation.

Keywords—Acid mine drainage, constructed wetland, photocatalysis

I. INTRODUCTION

WASTEWATER containing high concentration of heavy metal and is acidic nature is known as acid mine drainage (AMD). It is generated when sulphide minerals such as pyrite are oxidized by atmospheric oxygen and ground/surface water [1]. The oxidation of pyrite releases dissolved ferrous ion and acidity into the water, which in turn releases high concentrations other heavy metals such as Fe, Mn, and Zn, and lower concentrations of Cu and Cd.

Frequently, the most important sites for the generation of AMD are the discharge from open pits, expulsion from underground mining shafts, as well as ore stockpiles [2]. The extreme pH and high ionic content are responsible for highly toxic wastewater, and its handling requires high cost of storage, remediation and disposal techniques. Neutralization of AMD with lime, calcium carbonate, caustic soda, and soda ash results in the production of voluminous sludge, and this sludge disposal represents further environmental problem and additional costs [3]. Constructed wetlands have attracted attention as an alternative low cost process to treat AMD [4].

Constructed wetlands are engineered systems that have been designed to employ natural processes including vegetation, soil, and microbial activity to treat contaminated water. Constructed wetlands possess the merits of low-cost and low-maintenance, and are capable of removing various pollutants including heavy metals, nutrients, organic matters, and micro-pollutants [5]. The performance of metals uptake by macrophytes in wetlands has been proven to be contradictory. Some authors have reported that macrophytes are effective for the removal of heavy metals by plant uptake [6], while other have reported conflicting results [7]. Since it has been proved that grazing animals can be harmed by high-shoot-concentration, it is important to have more on data on the plant-roots-and-shoot metal concentration [8]. The presence of toxic species such as hexavalent chromium in AMD however, poses a major threat to the environment even at low concentrations. The chromium removal treatment includes precipitation, ion exchange, photocatalysis, reverse osmosis, and adsorption process [9]. Most of these methods require high capital and recurring expenditure and consequently they are not suitable for small-scale industries [10].

Among all the aforementioned methods, photocatalysis is a highly effective and low cost process compared to the other methods. TiO\textsubscript{2} has received the most interest because of its photocatalytic activity, low cost, low toxicity, and high stability to light illumination [11]. Titania dioxide, TiO\textsubscript{2} illuminated with UV light has highly reductive electrons [12]. The reduction converts a variety of inorganic compounds, such as dichromate (Cr\textsubscript{2}O\textsubscript{7}\textsuperscript{2–}), to less hazardous substances (reduces Cr(VI) to Cr(III)), which is easier to dispose of or recycle [13]. Therefore in this study, unvegetated upflow constructed wetlands and UV/TiO\textsubscript{2} were employed to treat Cr (VI) – laden
AMD with a hypothesis that CW can reduce high concentration of heavy metals in AMD, and subsequently reduce toxic Cr (VI) in CW effluents photocatalytically.

II. METHODOLOGY

A. Equipment

Three identical laboratory scale unvegetated up-flow vertical constructed wetlands were set up using cylindrical plastic pipes of internal diameter and the length of 14 cm and 50 cm respectively [14]-[15]. An impermeable film was placed at the bottom and sides of the columns. Each CW was divided into two compartments. Three CW were layered with sand (5-8 mm) in the first compartment and clinoptilolite (2-5 mm) in the second compartment as a main adsorbent. A laboratory scale slurry photocatalytic recycle reactor with an inner diameter of 40 mm and height of 340 mm was fabricated using a quartz material. The reactor contained an inlet on one end and outlet on the other end (both with inlet diameters of 25 mm), and it was operated as a recycle reactor. The reactor was placed inside a shading box with 12 UV lamps (8W x 4; 6W x 4; 4W x 4W) installed on the inside walls. The lamps were mounted 1 – 2 cm apart from each other, and the distance between the lamps and the reactor was 4 cm. Peristaltic pump was employed to circulate the wastewater inside the reactor.

B. Materials

Titanium butoxide, ethanol (99.99%), urea, ammonium sulphate, and chromium sulphate hydrate were all purchased from Sigma-Aldrich (South Africa). Acid mine drainage samples were collected from Mpumalanga, South Africa. Three 100L polypropylene drums were used to store the samples (collected from three locations), which is in accordance with the commonly accepted sampling procedures [16]. Filtration of the samples was carried out in the laboratory using a portable vacuum filter and a 0.45 µm Millipore filter. The performance of unvegetated upflow constructed wetlands samples was evaluated by treating three real AMD samples with varying heavy metals concentrations. The slurry photocatalytic reactor was employed to reduce Cr(VI) in constructed wetlands effluents. Atomic absorption spectrometer was used to analyze the concentration of total chromium and iron in constructed wetlands effluent, and UV-vis spectrophotometer was used to analyze concentration of Cr(VI) reduced photocatalytically.

III. RESULTS AND DISCUSSIONS

A. Heavy metals removal by batch experiments

Figure 1 shows the removal of Fe and Cr using both clinoptilolite and coarse silica sand. After 5 days, the high percentage removal was achieved for Fe on clinoptilolite (98%) and coarse silica sand (96%); and for Cr on clinoptilolite (80%) and coarse silica sand (67%). Referring to their main removal mechanisms, it was found that Fe is removed through hydrolysis and oxidation to form insoluble compounds; this results in different oxyhydroxides, hydroxides, and oxides formation which in turn can co-precipitate other metals [17]. Chromium present as Cr(VI), which is relatively mobile and after release into the pore, it migrates downward into the reducing zone and precipitates as Cr(OH)₃ [18]. The hydrolysed form of Cr(VI) is readily absorbed by hydrous Fe oxides [19]. Also, since oxiferric hydroxide surface charge is negative in acidic environment, and positive in basic conditions, the removal of the oxyanions such as chromate, iron co-precipitation must take place under the acidic environment. The experimental data was used to study the adsorption isotherms, thermodynamics, and reaction kinetics.

![Fig. 1 Fe and Cr removal on (a) clinoptilolite, (b) coarse silica sand](image_url)
B. Adsorption Isotherms

In this study, the adsorption isotherms were studied for Fe and Cr adsorption on clinoptilolite and coarse silica sand. The data obtained was fitted to the Langmuir adsorption isotherm which is the most popular and is a two-parameter equation described as:

\[ \frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \]  
(1)

Where constants \( b \) and \( q_m \) relate to the energy of adsorption and adsorption capacity and their values are obtained from the slope and intercept of the plot of \( C_e/q_e \) versus \( C_e \) (not shown) for temperature 288K. The linear nature of the plot shows that the adsorption follows the Langmuir isotherm. The value of \( b \), which is a measure of heat of adsorption, is utilized to calculate dimensionless separation parameter \( R_L \) [20]. The adsorption data obtained are also fitted to the Freundlich isotherm which is the earliest known relationship described by the following equation:

\[ \log q_e = \log K + \frac{1}{n} \log C_e \]  
(2)

Where \( K \) and \( n \) are Freundlich constants which correspond to adsorption capacity and adsorption intensity respectively. The slope (1/n) and intercept (K) of a log-log plot of \( q_e \) versus \( C_e \) are determined. The Freundlich exponent 1/n gives an indication of the favourability of adsorption conditions. The value of 1/n < 1 represents a favourable adsorption conditions.

The results of both regressed isotherms are tabulated in Table II. The Correlation coefficient (R²) shows that the Langmuir model is better than the Freundlich model in simulation of the adsorption of the isotherm. The agreement of the Langmuir model with the experimental results suggests that a monolayer coverage of Fe and Cr on the outer surface of the adsorbents. Weber and Chakarborti [20] expressed the essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant separation factor \( R_L \), which is defined as:

\[ R_L = \frac{1}{1 + bC_o} \]  
(3)

Where \( b \) is the Langmuir constant and \( C_o \) is the initial concentrations of Fe and Cr. According to McKay et.al [21] \( R_L \) values between 0 and 1 indicate favourable adsorption. The data obtained represent favourable adsorption in the case of adsorption of Fe and Cr ions (\( R_L = 0.021 \) – 0.084). This may be attributed to the fact the zeolites in general are weakly acidic in nature and sodium-form exchangers are selective for hydrogen, which leads to high pH values when exchangers is equilibrated with relatively dilute electrolyte solutions [22], making metal hydroxide precipitation feasible.

The Freundlich adsorption capacity \( K \) followed the trend Fe > Cr for clinoptilolite, and Cr > Fe for coarse silica sand. The value of 1/n < 1 represents a favourable adsorption conditions, as new sites could be available and the adsorption capacity would be increased. In this study, 1/n > 1 for both Cr and Fe on both clinoptilolite and silica sand, which was an indication of weak adsorption bonds. This indicated that the capacity of the adsorbent decreased because of its saturation [23].

C. Thermodynamic Parameters

The thermodynamic equilibrium constant (Kc) was obtained by calculating the apparent equilibrium constant Kc at different initial concentrations of Fe and Cr, and extrapolating to Zero [24]. The experiments were carried out at the temperatures of 298.15 K, 301.15 K, and 303.15 K.

\[ K_c = \frac{C_a}{C_e} \]  
(5)

Where \( C_a \) is the concentration of Fe and Cr adsorbed on the of adsorbents at equilibrium in mg/L and \( C_e \) is the equilibrium concentration of Fe and Cr (II) in solution in mg/L. The thermodynamic constants, Gibb’s free energy (\( \Delta G^0 \)), enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)) are calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. The Gibb’s free energy change of the process is related to equilibrium constant (Kc) by:

\[ \Delta G^0 = -RT \ln K_c \]  
(6)

The Gibb’s free energy change is related to the enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)) as:

\[ \ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  
(7)

The thermodynamic parameters as calculated are reported in Table III. The negative value of \( \Delta H^0 \) indicates exothermic nature of adsorption. The enthalpy change due to chemisorption takes value between 40 – 120 kJ/mol, which is larger than that due to physisorption [25]. Therefore, the low value of heat obtained in this study indicated that adsorption is likely due to physisorption. The negative value of the free energy change (\( \Delta G^0 \)) is an indication of a spontaneous process whereby no energy input from outside system is required. The negative value of entropy (\( \Delta S^0 \)) shows a decreased disorder at the solid/liquid interface during Fe and Cr adsorption.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( K_m ) (mg/g)</td>
<td>( b ) (L/mg)</td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.96</td>
<td>812</td>
</tr>
<tr>
<td>Cr</td>
<td>0.90</td>
<td>387</td>
</tr>
<tr>
<td>Silica Sand: Fe</td>
<td>0.95</td>
<td>635</td>
</tr>
</tbody>
</table>

TABLE II

ISOTHERMS PARAMETERS FOR Fe AND Cr ADSORPTION AT pH 3
D. Kinetic Modelling of Clinoptilolite and Coarse Silica Sand Treating Simulated AMD

The first order equation was applied in the analysis of kinetic data. The linear form of the first order equation [26] is given below:

\[-\ln \left( \frac{C_t}{C_0} \right) = K_1 t \]  

(8)

Where \(C_t\) (mg/l) is the concentration of Fe and Cr in solution at a given time \(t\), \(C_0\) (mg/l) is the initial Fe and Cr ion concentration in solution, \(K_1\) (min\(^{-1}\)) is the first order rate constant of adsorption. The applicability of this equation was tested by a linear plot of \(-\ln(C_t/C_0)\) against \(t\). The first order kinetic parameters are presented in Table IV.

The second order equation was also used to analyse kinetic parameters [26], this equation in its linear form is given below:

\[\left( \frac{1}{C_t} - \frac{1}{C_0} \right) = K_2 t \]  

(9)

Where \(K_2\) (Lmg\(^{-1}\)min\(^{-1}\)) is the second order rate constant for the adsorption process. This isotherm was tested by a linear plot of \((1/C_t-1/C_0)\) versus \(t\). The second order kinetic parameters are presented in Table IV.

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E. Acid Mine Drainage Treatment in Constructed Wetlands

Three real AMD samples were characterized (Table VI); and treated in three identical unvegetated upflow constructed wetlands, and the focus was on the removal of Fe and Cr only. Hydraulic Retention Time HRT, was varied between 3 – 5 days to determine the efficient, and the HRT of 5 days was found to be the efficient for maximum metal removal (Figure 2). At the end of experimental period of 20 days, the experimental data was fitted to the first kinetic dynamic order [29]-[30].

TABLE VI

| AMD MINING CHARACTERIZATION | Douglas North | Middelburg South | T&D Decant |  |
|----------------------------|---------------|-----------------|------------|
| PH                         | 3.7           | 2.65            | 2.55       |
| SO4 (mg/L)                 | 2690          | 3595            | 6055       |
| Fe (mg/L)                  | 280.815       | 148.483         | 20.776     |
| Al (mg/L)                  | 246           | 143.335         | 9.95       |
| Ca (mg/L)                  | 80.133        | 359.936         | 430.245    |
| Li (mg/L)                  | 0.413         | 4.157           | 3.99       |
| Mg (mg/L)                  | 0.065         | 0.082           | 0.03       |
| Zn (mg/L)                  | 44            | 216             | 211        |
| Cu (mg/L)                  | 5.7           | 8.6             | 5.55       |
| Co (mg/L)                  | 1.729         | 2.727           | 0.559      |
| Ni (mg/L)                  | 2.6           | 3.187           | 0.867      |
| Mn (mg/L)                  | 6.095         | 35.852          | 11.771     |
| Cr (mg/L)                  | <200          | 460             | 41000      |

*Concentration was below detection, therefore spiked into the wastewater.
In the present study, the first order model with two parameters was used to describe the removal mechanism of the different CWs. If steady and plug flow conditions are assumed, the pseudo first order dynamic model can be used to describe the reduction of pollutants. The equation can be written as:

\[
\ln \left( \frac{C}{C_0} \right) = - k_v t
\]  

(11)

Where \( C \) is the concentration of the quantity concerned (mg/L), \( t \) is the hydraulic resident time (h), and \( k_v \) is the volumetric rate constant (h\(^{-1}\)).

The rate constant always has two expression ways \( k_v \) and \( k \). Literature is available on \( k_v \) with subsurface flow constructed wetland and \( k \) with surface flow constructed wetland [31]. Removal rate constant represents the removal ability of the CWs. In theory, the removal rate constant relates to temperature, medium and pollutants. Therefore, in this study the temperature was kept at room temperature and the removal efficiencies Fe and Cr were analysed. In order to compare the removal ability of up-flow constructed wetlands, the volumetric rate constant, \( k_v \), was determined.

The heavy metal removal was investigated as a function of hydraulic retention time and data were fitted to a pseudo first-order reaction model as reported by various authors who have worked on heavy metals removal using constructed wetland [29]-[30]. The \( k_v \) values and the correlation coefficients were calculated and the results are listed on Table VII.

The removal efficiencies for Fe are higher than the efficiencies for Cr in all constructed wetlands. These results well agree with the results reported in the literature [31]. The constructed wetlands had different rate constants because of the different heavy metals concentration in AMD. The results showed that the constructed wetlands treating DND and TDB AMD samples did not have significant differences in the volumetric rate constant in respect to Fe and Cr. However, the volumetric rate constants (with respect to Fe and Cr) of the constructed wetland treating SSC AMD sample were significantly different. It is indicated that the CWs had better purification effect on Fe than that on Cr in all AMD samples. Also, all three constructed wetlands proved to have the relative same satisfactory removal efficiencies for chromium despite the varying initial concentrations of chromium in all AMD samples.

F. Photocatalytic Reduction of Constructed Wetlands Effluent

Table VIII shows the characterization of the constructed wetland effluents. The constructed wetland effluents were treated photocatalytically using a slurry photocatalytic recycle reactor for Cr(VI) reduction. The synthesized TiO\(_2\) core-void-shell was employed as a photocatalyst and HRT of experiment was 3 hrs and the recycle rate was kept constant at 400 ml/min. After 3 hrs, the samples were analyzed for Cr(VI) and Fe(III) reduction using a UV-vis spectrophotometer. The spent catalyst was rinsed with deionized water and dried overnight at 120 ºC, then re-used.

Photocatalytic reduction of Cr(VI) was achieved only for the DND sample (68%), and the Fe(III) reduction was found to be 83% (figure 3). The reason why photocatalytic reduction for the SSC and TDB samples was not achieved may be attributed to the high concentration of Cr(VI) accumulating on the active sides of the catalyst, resulting in the light-screening-effect and no production of the photogenerated pair hole/electron. Furthermore, the presence of Aluminium,
Calcium, Magnesium, and Silicon might have impacted negatively on the overall photocatalytic reduction of Cr(VI) by also accumulating on the active side of the catalyst. Photocatalytic reduction (54%) of Cr(VI) in the DND sample was also achieved using a spent catalyst. The achievement of Cr(VI) in the DND is attributed to the low concentration of Cr(VI); the presence of Fe(III); and the structural morphology of the catalyst [33]-[34].

<table>
<thead>
<tr>
<th>TABLE VIII</th>
<th>CONSTRUCTED WETLAND EFFLUENTS CHARACTERIZATION</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(DND)</td>
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<tr>
<td>pH</td>
<td>2.4</td>
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<tr>
<td>SO₄ (mg/l)</td>
<td>2710</td>
</tr>
<tr>
<td>Fe (mg/l)</td>
<td>28</td>
</tr>
<tr>
<td>Al (mg/l)</td>
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<tr>
<td>Ca (mg/l)</td>
<td>&lt;2</td>
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<tr>
<td>Mg (mg/l)</td>
<td>79</td>
</tr>
<tr>
<td>Si (mg/l)</td>
<td>83</td>
</tr>
<tr>
<td>Cr (mg/l)</td>
<td>72</td>
</tr>
</tbody>
</table>

IV. CONCLUSIONS

Unvegetated upflow constructed wetland and slurry photocatalytic reactor were designed and commissioned. It was found that the main mechanism for metal removal was precipitation/co-precipitation. The HRT was investigated and found that the main mechanism for metal removal was the co-precipitation of the catalyst [33]-[34].

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