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Treatment of Acid Mine Drainage Using Un-Activated Bentonite and Limestone

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Abstract—The use of un-activated bentonite, and un-activated bentonite blended with limestone for the treatment of acid mine drainage (AMD) was investigated. Batch experiments were conducted in a 5 L PVC reactor. Un-activated bentonite on its own did not effectively neutralize and remove heavy metals from AMD. The final pH obtained was below 4 and the metal removal efficiency was below 50% for all the metals when bentonite solid loadings of 1, 5 and 10% were used. With un-activated bentonite (1%) blended with 1% limestone, the final pH obtained was approximately 7 and metal removal efficiencies were greater than 60% for most of the metals. The Langmuir isotherm gave the best fit for the experimental data giving correlation coefficient (R^2) very close to 1. Thus, it was concluded that un-activated bentonite blended with limestone is suitable for potential applications in removing heavy metals and neutralizing AMD.

Keywords—acid mine drainage, bentonite, limestone, heavy metal removal.

I. INTRODUCTION

ACID mine drainage (AMD) is a major source of water contamination in coal and metal mining industries worldwide. This environmental unfriendly phenomenon results from drainage of water from areas that have been mined for coal or other mineral ores. The water has a low pH because of its contact with sulphur-bearing material and is considered to be harmful to aquatic organisms. AMD contains high concentration of dissolved Fe and dissolved SO_4^{2-} produced by oxidation of pyrites (FeS_2) [1]. Certain areas in South Africa specifically Gauteng are identified as priority areas requiring immediate action because of lack of adequate measures to control the problem related to AMD [2]. Limestone is a common reagent used worldwide for neutralization of AMD as it is cost-effective, widely available and is often present in the local natural environment [3]. Dissolution of one mole of limestone consumes one to two moles of acidity and may release alkalinity (as HCO_3^-) into solution [3]. Treatment of AMD with limestone could increase the pH to about 6-7.5, allowing metals to be removed from the solution via precipitation and sorption.

Limestone is mostly used in both active and passive AMD treatment. Active systems use some form of mechanical procedure to continuously add an alkaline reagent to reach a designated pH, whilst passive treatment techniques rely on biological neutralisation without mechanical assistance [4].

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Thus, short term laboratory studies indicated that limestone alone can be as effective as this layered system for neutralisation of toxic mine water containing moderate concentrations of Fe^{3+} and Al^{3+} [4]. A major disadvantage of this method is the requirement of large doses of alkaline materials to increase and maintain pH values typically from 4.0 to above 6.5 for optimal metal removal [5]. Bentonite is a promising low-cost adsorbent which has been studied extensively for removal of toxic metal ions from wastewater [6]. It is an alumina silicate clay made up of sodium and calcium montmorillonites [7]. It has a high specific surface area, high plasticity, and can expand several times its original volume when placed in water [8]. The bentonite ability to swell is a result of the incorporation of water molecules between the (tetrahedral-octahedral-tetrahedral) sheets in association with the interlayer cations (Na^{2+} and Ca^{2+}), which are driven off when the bentonite is heated in air. The expulsion of water leads to the layers collapsing, causing the bentonite clay to have an unbalanced structure with an overall slightly negative charge. This is balanced by exchangeable cations that are adsorbed around the edges of the fine clay particles [8]. To improve the adsorptive properties of bentonite clay, it can be acid activated. This involves all the cations present in the bentonite (typically Ca^{2+} , Na^{2+} and Al^{3+}) being replaced by H^+ by the addition of either sulphuric or hydrochloric acid. Acid activation changes the clay's physical and chemical properties, but keeps its layered structure. It has been estimated that quality reserves of bentonite in South Africa will be sufficient for up to 67 years at the current production rate of 120 kt/a [8]. The newest bentonite mine and largest deposit ever to be found in South Africa, is the Yellow Star Quarries in the Kroonstad district. It has been estimated that this deposit, which contains approximately 750 000 m^3 bentonite, can be mined at 4 000 m^3/month [9]. The mine was commissioned in 2007 and has an expected lifetime of over 10 years during which the clay will be mined and the project will be economically feasible [9].

II. EXPERIMENTAL

A. Materials

Acid mine drainage was collected from a local gold mine site and analysed to find the concentration of heavy and other elements present. Un-activated bentonite and limestone supplied by the G&W Base Company were analysed using X-Ray Diffraction (XRD) and X-Ray fluorescence (XRF).

B. Apparatus

A 5 l PVC batch reactor fitted with three baffles and an overhead stirrer with a 4-blade pitch blade impeller was used to conduct the experiments. pH/conductivity meter (model Mettler Toledo, InLab 74X Series) was used to measure the pH and conductivity of the solution.

A pipette and 50ml plastic vials were used for sampling the solution. Inductively coupled plasma - optical emission spectroscopy (ICP-OES; model spectro Arcos FSH12) was used to determine the concentration of metals before and after treatment. X- Ray Fluorescence (XRF; model Magix Pro Phillips) and XRD were used to determine the composition of bentonite and limestone.

C. Experimental Procedure

3 L of freshly collected AMD was added to the batch reactor, thereafter a pre-determined amount of bentonite with/without limestone (Table I) was then added. Agitation was commenced and a residence time of 3 h was used for each experimental run.

TABLE I
EXPERIMENTAL DOSAGE

| Run no. | AMD effluent (L) | Un-activated Bentonite (g) | Limestone (g) |
|---------|------------------|----------------------------|---------------|
| 1 | 3 | 30 | |
| 2 | 3 | 150 | |
| 3 | 3 | 300 | |
| 4 | 3 | 30 | 30 |

The pH and conductivity were measured and 50 ml sample was collected every 15 min for 3 h. The collected samples were filtered to avoid further reactions occurring and stored for ICP analysis. At the end of the experiment the used bentonite with/without limestone was recovered by filtering the solution, and dried. The elemental composition of the solid samples was then determined by XRF.

III. RESULTS AND DISCUSSION

A. Characterization of bentonite and limestone

The mineralogical composition of the bentonite and limestone was determined using XRD and the results are shown in Table II. XRF was used to determine the elemental composition of the bentonite and limestone and the results are shown in Table III.

TABLE II
CHEMICAL ANALYSIS OF BENTONITE AND LIMESTONE

| Constituent | Concentration (%) | |
|--------------------------------|-------------------|-----------|
| | Bentonite | Limestone |
| N ₂ O | 1.2 | 0.077 |
| MgO | | 1.7 |
| A ₂ O ₃ | | 2 |
| SiO ₂ | 83 | 6.9 |
| P ₂ O ₅ | 0.31 | 0.017 |
| SO ₃ | 0.03 | 0.035 |
| K ₂ O | 4 | 0.095 |
| Ca | 1.8 | 88 |
| Ti ₂ | 1.1 | 0.11 |
| MnO | 0.067 | 0.19 |
| Fe ₂ O ₃ | 8.5 | 1 |

TABLE III
ELEMENTAL ANALYSIS OF MAJOR AND TRACE ELEMENTS

| Element | Concentration (%) | |
|---------|-------------------|-----------|
| | Bentonite | Limestone |
| N | 0.87 | 0.057 |
| O | 49 | 31 |
| Mg | 0 | 1.1 |
| A | | 1.1 |
| Si | 39 | 3.2 |
| P | 0.13 | 0.0076 |
| S | 0.012 | 0.014 |
| K | 3.3 | 0.079 |
| C | 1.3 | 63 |
| T | 0.67 | 0.065 |
| Mn | 0.052 | 0.15 |
| Fe | 6 | 0.71 |
| Cu | | |
| Zn | 0.018 | |
| A | 0 | |
| Rb | 0.026 | |
| Sr | 0.028 | |
| Zr | 0.034 | |
| B | 0.11 | 0.096 |
| Pb | 0 | |

The results showed that bentonite contained montmorillonite (SiO₂) as a major constituent. On the other hand, limestone contained calcium oxide as a major constituent.

It was noted from the results in Table III that the bentonite had high concentration of calcium compared to Na, however, the difference was small to make reach a conclusion that this bentonite was a calcium bentonite.

B. Effects of bentonite and limestone solid loading

AMD is characterized by low pH, high specific conductivity, high concentrations of iron, aluminum, and manganese, and low concentrations of toxic heavy metals. The variation of pH with time at different bentonite solid loading is shown in Figure 1. The pH of the AMD effluent changed from 2.3 to approximately 4 when AMD was treated with bentonite at a solid to liquid ratio of 1:100 (30 g), 5:100 (150 g) and 10:100 (300g) respectively (Figure 1). There was no significant change observed in pH when bentonite was added at 1% solid loading.

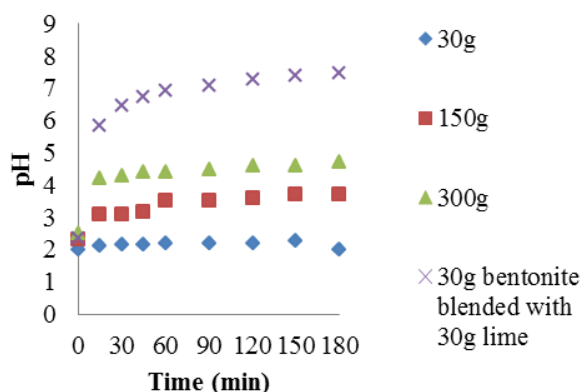


Fig. 1 Variation of pH with bentonite and limestone loading

Figure 1 showed that the pH of AMD effluent increased rapidly from 2.3 to 7.5 when the un-activated bentonite (30g) was blended with limestone (30g) at a ratio of 1:1.

C. Effect of bentonite and bentonite blended with limestone on the conductivity of AMD.

Conductivity is a measure of the amount of ions present in a solution. Fig. 2 indicates the change in conductivity of AMD with time.

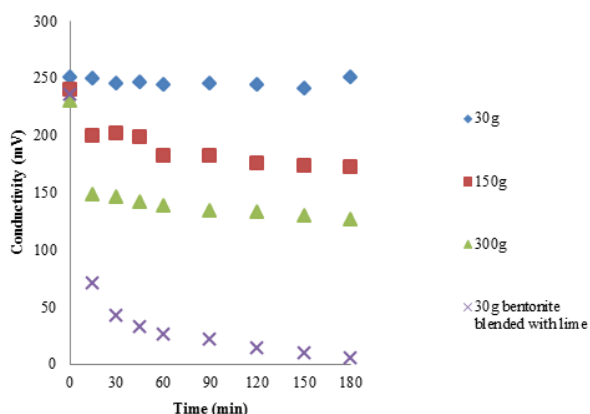


Fig. 2 Variation of AMD conductivity with bentonite and limestone loading

The results showed that at a dosage of 30g (1%) un-activated bentonite did not have an impact on the conductivity of the AMD effluent. However, it was observed that the conductivity of AMD decreased with an increase in bentonite dosage. Effective decrease in the conductivity of AMD effluent was observed when bentonite (30g) was blended with limestone (30g), as the conductivity decreased from 240mV to approximately zero mV. This indicated that the amount of heavy metals and other anions mainly SO_4^{2-} decreased rapidly when limestone was added together with the bentonite.

D. Heavy metal removal from AMD

It was observed that the removal of heavy metals from the effluent increased with increasing adsorbent dosage and

residence time when the effluent was treated with un-activated bentonite only.

Figure 3, 4 and 5 illustrate the removal efficiency of heavy metals at different solid to liquid ratio of un-activated bentonite to AMD. It was further observed that the removal efficiency of elements such as Cd, Co, Cr, Fe, Mn increased with an increase in bentonite dosage.

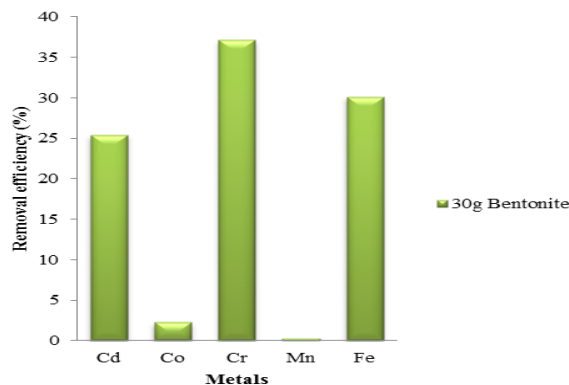


Fig. 3 Metal removal efficiency using 1% un-activated bentonite

As the percentage of un-activated bentonite was increased from 30g (1%) to 150g (5%) the removal efficiency of Zn, Cu, Fe, Pb and Mn increased (Fig. 3 and 4).

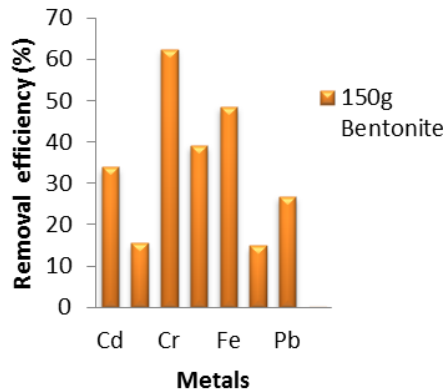


Fig. 4 Metal removal efficiency using 5% un-activated bentonite

As the solid dosage of un-activated bentonite was further increased to 300g (10%), there was an increase in the removal efficiency of Fe, Cd, Co, Fe, Mn, Pb and Zn.

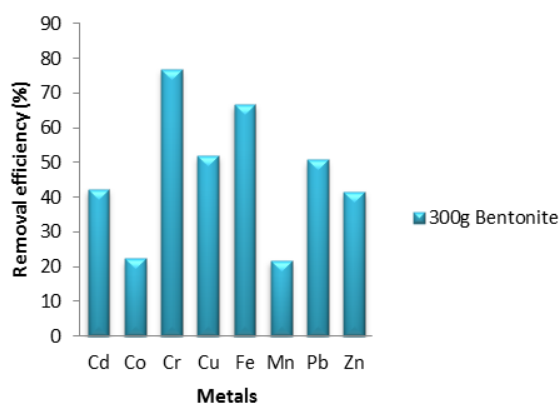


Fig. 5 Metal removal efficiency using 10% un-activated bentonite

The amount of heavy metal ions removed from AMD when treated with un-activated bentonite blended with limestone increased significantly compared to that obtained with bentonite alone. The removal efficiencies were above 60% for most of the metals as shown in Figure 6. Un-activated bentonite adsorbed or precipitated heavy metals from solution, whereas limestone neutralized the AMD to the required pH. An increase in pH from an average of 2.3 to 7.5 resulted in an increase in removal efficiency of many heavy metals such as Fe, Cu, Mn, Si, Al, Cd, Co, Pd and Zn. These results corresponded well with theory that states that adsorption is mostly affected by pH changes.

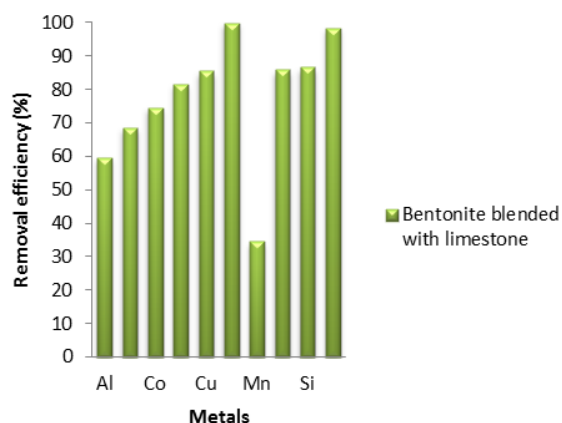


Fig. 6 Metal removal efficiency using un-activated bentonite (1%) blended with limestone (1%)

E. XRF analysis results of used bentonite and bentonite blended with limestones

The residual used solids were also analysed to evaluate the mechanisms of metal removal (i.e. adsorption or precipitation). The results are shown in Table IV.

TABLE IV
CHEMICAL ANALYSIS OF USED BENTONITE AND LIMESTONE

| Element | Concentration (%) | | |
|---------|-------------------|----------------------------------|---|
| | Used bentonite | Used bentonite blended limestone | Bentonite blended with limestone (leached in acidified water) |
| Na | 0.5 | 0.33 | 0.3 |
| O | 4 | 4 | 4 |
| M | | 1.4 | |
| Al | 1 | 6.8 | 7.2 |
| S | 3 | 1 | 1 |
| P | 0.08 | 0.04 | 0.05 |
| S | | 0.3 | 0.01 |
| K | 2.3 | 1.3 | 1.4 |
| Ca | 0.8 | 2 | 2 |
| T | 0.4 | 0.31 | 0.3 |
| M | 0.05 | 0.15 | 0.06 |
| F | 4.3 | 5.5 | 3.1 |
| C | | 0.07 | |
| Z | 0.01 | 0.01 | 0.01 |
| A | | | 0.001 |
| R | 0.01 | 0.01 | 0.01 |
| Sr | 0.01 | 0.008 | 0.01 |
| Z | 0.02 | 0.01 | 0.01 |
| B | 0.0 | 0.07 | 0.06 |
| Pb | | | 0.02 |

The results in Table IV were compared to the residual concentration in Table III, it was observed that the concentration of used bentonite for elements Na, Al, Si, Ca, Fe, Zn, and Sr decreased when compared to the initial concentration, this indicated that mainly precipitation process took place rather than adsorption. However, the opposite was realized on Mn as the final concentration increased when compared to the initial, indicating adsorption took place. Comparison of the results of bentonite blended with limestone and leached in AMD and acidic water (pH≈2) showed a decrease in the concentration of Mg, S, Mn and Fe (Table IV). This shows that some of the elements were adsorbed on the bentonite possible by ion exchange with exchangeable ions like Na.

F. Adsorption Isotherm at ambient temperature

To study the thermodynamic behaviour of the adsorption process, adsorption isotherms were used. In order to find the adsorption capacities of the metals adsorbed by bentonite, the experimental results were analyzed using the Langmuir (1) and Freundlich (2) isotherms. The following linearized equations were used for this purpose.

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{MAX}} + \frac{1}{k_L Q_{MAX}} \quad (1)$$

$$\log q_e = \log K_n + \frac{1}{n} \log C_e \quad (2)$$

Where C_e is the measured metal concentration in solution at equilibrium, q_e is the amount of metals adsorbed per unit weight of adsorbent, Q_{MAX} is the amount of metals adsorbed per unit weight of adsorbent in forming complete monolayer

coverage on the adsorbent surface, and k_L is the constant related to the net enthalpy of adsorption, K_n and $1/n$ are empirical constants..

Results of the adsorption isotherms for different metals are presented in Table V and plots of the isotherms are shown in Fig. 7-9. Metals were selected for the study of adsorption isotherms based on the high removal efficiency realized.

TABLE V
LANGMUIR ISOTHERM PARAMETERS

| Elements | Q_{max} (mg/g) | R^2 |
|----------|------------------------|-------|
| Mn | 0.02496 | 0.998 |
| Fe | 1.631 | 0.989 |
| Cd | 4.624×10^{-5} | 0.989 |
| Cr | 6.19×10^{-4} | 0.999 |
| Cu | 2.94×10^{-4} | 0.986 |

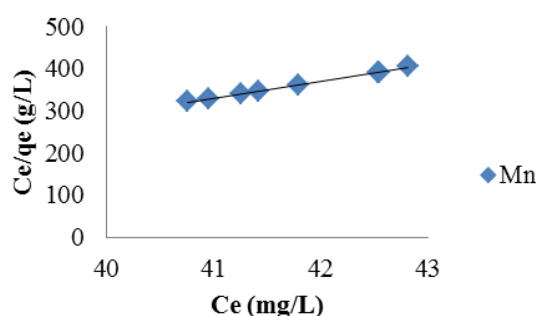


Fig. 7 Langmuir plot for Mn

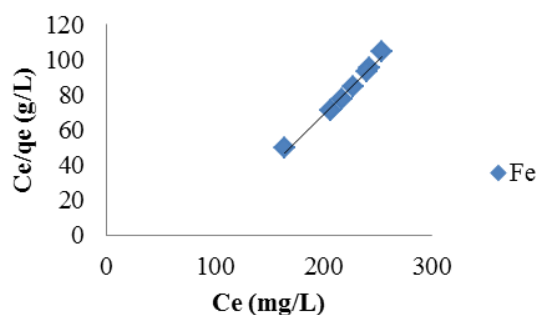


Fig. 8 Langmuir plot for Fe

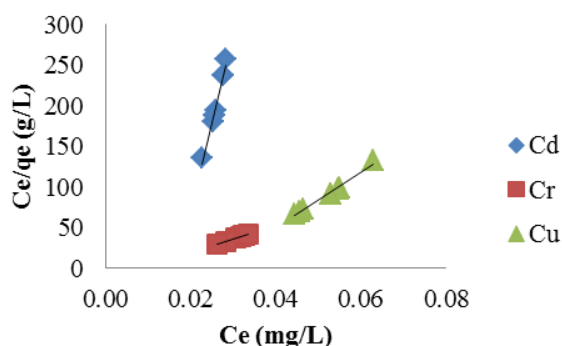


Fig. 9 Langmuir plots for Cd, Cr and Cu

For the metals shown in Fig. 7-9, the data fitted well on Langmuir plot. However, the data did not fit on Freundlich isotherm, therefore only a sample calculation is shown in Table VI and Fig 10.

TABLE VI
FREUNDLICH ISOTHERM PARAMETERS FOR Fe

| Elements | K_n | n | R^2 |
|----------|--------|-------|-------|
| Fe | 25.527 | 31.25 | 0.88 |

The correlation coefficient for this isotherm was low indicating that it did not fit the experimental data (Fig. 10). Thus, the rest of the plots for the Freundlich isotherm are not shown.

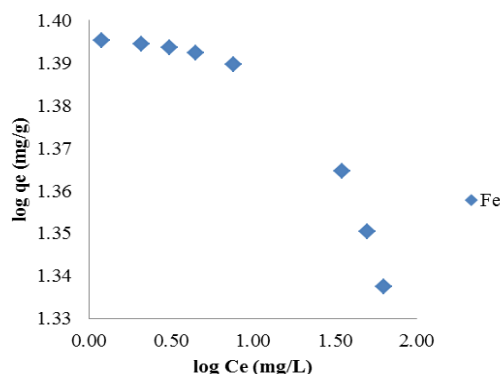


Fig. 10 Freundlich plots for Fe sorption on un-activated bentonite

IV. CONCLUSION

The study showed that un-activated bentonite blended with limestone was suitable for potential applications in removing heavy metals from AMD. The extent of removal was found to be highly dependent on pH.

When neutralizing AMD effluent with un-activated bentonite only, it was observed that this required a high percentage of solid adsorbent to be present in the solution. However, when treated with a mixture of limestone and bentonite (ratio 1:1) the heavy metal percentage removal increased rapidly, since limestone acted as a neutralizing agent and the bentonite as an adsorbent.

It was also observed that some heavy metals when using bentonite only were leached out of the solution (metals such as Al and Sr). It was also concluded that the main process that took place in the experiment was precipitation as it was observed from the sludge analysis results that the initial concentration of heavy metals in bentonite was higher than the final concentration for all the metals, except for Mn. It was also concluded that Langmuir isotherm was most suitable for the data obtained, as it fitted very well to various metals analysed.

It was recommended that further test works should be conducted to prove the possibility of some heavy metals (Al and Sr) being leached out of bentonite. It was also recommended that test works should be done to treat AMD samples with bentonite that has been acid treated (leaching out the absorbed metals) to determine the efficiency of the reused treated bentonite.

Further studies should also be conducted to determine under which conditions the bentonite is no longer reusable and the expected lifetime of the bentonite.

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