A continuous process for the biological treatment of heavy metal contaminated acid mine water

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Abstract

Alkaline precipitation of heavy metals from acidic water streams is a popular and long standing treatment process. While this process is efficient it requires the continuous addition of an alkaline material, such as lime. In the long term or when treating large volumes of effluent this process becomes expensive, with costs in the mining sector routinely exceeding millions of rands annually. The process described below utilises alkalinity generated by the alga *Spirulina* sp., in a continuous system to precipitate heavy metals. The design of the system separates the algal component from the metal containing stream to overcome metal toxicity. The primary treatment process consistently removed over 99% of the iron (98.9 mg/l) and between 80 and 95% of the zinc (7.16 mg/l) and lead (2.35 mg/l) over a 14-day period (20 l effluent treated). In addition the pH of the raw effluent was increased from 1.8 to over 7 in the post-treatment stream. Secondary treatment and polishing steps depend on the nature of the effluent treated. In the case of the high sulphate effluent the treated stream was passed into an anaerobic digester at a rate of 4 l/day. The combination of the primary and secondary treatments effected a removal of over 95% of all metals tested for as well as a 90% reduction in the sulphate load. The running cost of such a process would be low as the salinity and nutrient requirements for the algal culture could be provided by using tannery effluent or a combination of saline water and sewage. This would have the additional benefit of treating either a tannery or sewage effluent as part of an integrated process.

1. Introduction

South Africa has been and still is one of the world's leading producers of precious metals and minerals. The pollution of surface waters by acid mine drainage (AMD) and acidic effluents from refineries is a serious problem in the country. Pollution from these sources adversely affects the aesthetic appearance of surface waters and destroys living organisms that inhabit them, making the water systems more vulnerable to organic pollution. In addition the majority of mines are located in the most highly industrialised and hence heavily populated areas, where the demand for fresh water for domestic and industrial use is highest [1].

The principles governing the generation of AMD are relatively well understood. Upon exposure to oxygen and water and in the presence of oxidising bacteria, pyrite and other sulphide minerals are oxidised to produce dissolved metals, sulphate and acidity [2].

The conventional processes for the treatment of AMD or acidic, metal laden effluents from industry involve neutralisation by the addition of alkaline chemicals such as limestone, lime, sodium hydroxide, sodium carbonate or magnesia. The pH is increased as a result and leads to the precipitation of metals. These active systems generally require the construction of a plant with a variety of reactor systems, such as agitated reactors, precipitators, clarifiers and thickeners. Aside from the initial construction costs the continuous cost of reagents make these systems unattractive from a financial perspective [2 and 3]. A medium sized mining operation may spend well over a million rand annually on the cost of lime alone.

In recent years there has been a trend toward the implementation of passive treatment schemes. These take advantage of naturally occurring geochemical and biological processes to improve water quality with minimal operation and maintenance requirements [2]. Constructed wetlands and anoxic limestone drains (ALDs) are two of the most popular passive treatment methods [3 and 4].

The majority of active and passive treatment systems depend on precipitation as the primary method for metal removal from acidic effluents. The precipitation is effected by adding inorganic hydroxide or carbonate salts [5], by the action of microbially generated sulphide [6] or a combination of the two [7].

A considerable amount of research has been conducted on algae as a bioremediation agent, but this research has primarily focussed on the ability of some species to adsorb or accumulate metal ions from solution [8]. The production of extracellular components, such as chelatins and polysaccharides, which are capable of complexing metal ions has also been extensively studied [9]. While the ability of certain algal species to increase the alkalinity of the surrounding medium as a by-product of their inorganic carbon accumulating mechanism has been documented [10], the potential use of this alkalinity in the precipitation of metals has, to date, not been widely reported.

Research performed by our group has illustrated that direct treatment of AMD by an algal culture is effective over a short time period [11 and 12]. The sustainability of the direct treatment system was however poor. Payne et al. [13]. have demonstrated that copper, lead and zinc are toxic to *Spirulina* cells when accumulated to concentrations in excess of 7 µmol/g.

To overcome the problem of heavy metal toxicity we have developed a system which separates the growing culture from the untreated effluent. The system described below combines the principles of passive treatment with some simple, low cost reactors associated with active treatment methods. The result is a system that has the potential to be as effective as active treatment processes, but with the cost and sustainability advantages of passive treatment systems.

2. Process description

The proposed process is graphically illustrated in Fig. 1.
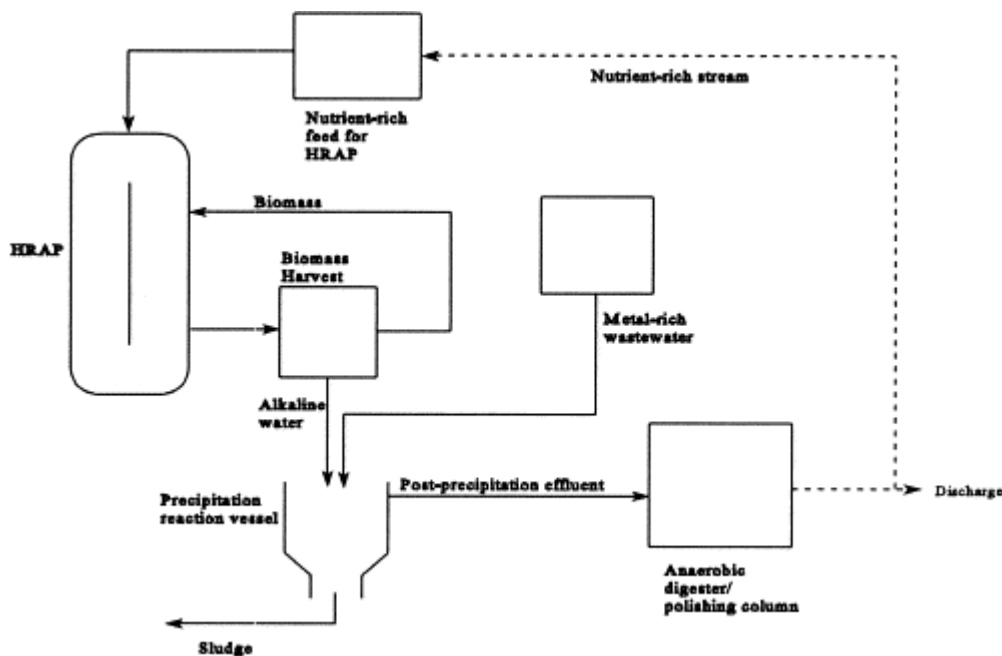

Fig. 1. A generalised description of the process for treating acidic, metal containing effluents.

2.1. Component description

The function of the various components of the process are discussed in the following section. The system has been designed to be as low-tech and cost effective as possible.

2.1.1. Algal feed tank

This vessel holds the feed solution for the algal culture. As *Spirulina* is a halophilic alga the feed solution will need to have salinity of approximately 1.5%. Ideally a cheap or waste source of salinity, such as sea water or tannery effluent would be used. In the absence of a suitable source of saline water the feed would need to be supplemented.

2.1.2. Effluent storage tank

This tank holds the raw effluent before it is pumped into the reaction vessel. The nature of the effluent will determine the rate of pumping. Factors such as the acidity and metal concentration of the effluent as well as the productivity of the algal culture need to assessed in order to determine the optimal feed rates. These rates are dynamic and can be adjusted should the conditions change.

2.1.3. Algal growth vessel

This vessel is used for the cultivation of the algal biomass and in large scale systems would most likely be a high rate pond. A feed solution, which will depend on the location of the plant, is fed in continuously from the feed tank. The alkalinity is generated in this vessel as a by-product of the algae's inorganic carbon assimilation process. Typically the pH in this vessel is in excess of 9. The vessel has an overflow port, covered by a course filter to prevent excessive loss of biomass. The rate of overflow is thus determined by the rate at which the feed is pumped in.

2.1.4. Biomass harvesting and filtration

The overflow from the algal growth vessel passes through a filtration step. *Spirulina* and many other algal species are excellent sources of protein. If the feed solution does not contain components, such as chrome if tannery waste is used, that make the biomass unfit for animal consumption the algae in the overflow can be harvested at this point. If the algae is unfit for consumption a sand filter is used to prevent algae entering the reaction vessel.

2.1.5. Reaction vessel

The reaction vessel is the site where the raw effluent is mixed with the high pH overflow from the algal tank. It is the site of the metal precipitation. The vessel is cone shaped at the bottom to facilitate sludge settling and removal. The vessel has an overflow port so that the treated effluent can again be passively collected.

2.1.6. Further treatment and polishing

Depending on the nature of the effluent it may require further treatment and polishing. The majority of acid mine drainage contains high sulphate loads and the primary treatment does not reduce these. In this case the overflow from the reaction vessel passes into an anaerobic digester where sulphate reducing bacteria convert the sulphate to sulphide, which precipitates out any remaining metal. Polishing may also be achieved by using a biosorbent such as *Azolla*. As the sludge generated is essentially inorganic and many of the metals found in AMD precipitate at different pHs it is possible to selectively recover metals such as copper and zinc by a sequential reduction in the pH of the sludge.

3. Materials and methods

3.1. Algal culture

The algae used in this experiment were cultivated in a 50-l raceway pond on Zarouk's defined media. The amount of EDTA in the media was reduced to prevent the downstream complexation of metals. Five litres of the algal culture was maintained in a cylindrical perspex vessel under normal day/night and temperature conditions. Tap water was used as the feed and was pumped in continuously at a rate of 1 ml/min. Daily samples were taken from the algal growth vessel to determine chlorophyll content, pH and salinity.

3.2. Effluent

An untreated effluent was obtained from a storage dam at a copper, lead and zinc mine in the North West Province, South Africa. The characteristics of the effluent are shown in Table 1.

Table 1. Composition of raw effluent and discharge specifications

Component	Units	Result	Specifications
pH		1.88	min 5.5, max 9.5
Sulphate	mg/l SO_4	4415.51	
Chloride	mg/l	984	
Bicarbonate	mg/l $CaCO_3$	0	
Copper	mg/l	3.49	max 1.0
Zinc	mg/l	7.16	max 5.0
Lead	mg/l	2.35	max 0.1
Iron	mg/l	98.95	max 0.3

The effluent was pumped into the reaction vessel at a rate of 1 ml/min. Daily samples were taken from the reaction vessel to measure pH, sulphate and Cu, Zn, Pb and Fe concentrations.

3.3. Control experiment

The growth medium used to culture the *Spirulina* has a high pH and salt content and will effect metal precipitation when mixed with the effluent. To determine the contribution of the media on the overall experiment a control was set up where the 5 l of algal culture was replaced with 5 l of media. The experiments were sampled in an identical fashion.

3.4. Anaerobic digester

The overflow from the reaction vessel was collected and supplemented with yeast extract (1 g/l), sodium lactate (0.4 g/l), ammonium chloride (0.05 g/l) and potassium sulphate (0.1 g/l). This mixture was pumped into a 20-l anaerobic digester at a rate of 4 l/day. The overflow from the digester was sampled daily to determine pH, sulphate, sulphide and metal concentrations.

3.5. pH profile

To determine the expected levels of precipitation a pH profile was performed on the raw effluent. Twelve 100-ml samples of the effluent were removed and the pH of the samples increased by the addition of 1 M NaOH. A pH range of 2–13 was used. All samples were allowed to react for 60 min after which a 10-ml sample was removed and centrifuged at 5000 rpm for 5 min. The percentage of Cu, Zn, Pb and Fe remaining in solution was determined. The experiment was performed in triplicate.

3.6. Analyses

Metal concentrations were determined using a GBC 909 Atomic Absorption Spectrophotometer attached to a GBC integrator. Salinity values were obtained using an Atago S/Mill-E hand held refractometer. Sulphates and sulphides were determined according to Standard Methods and chlorophyll determined according to the method of Lichtenthaler [14].

4. Results

4.1. pH profile

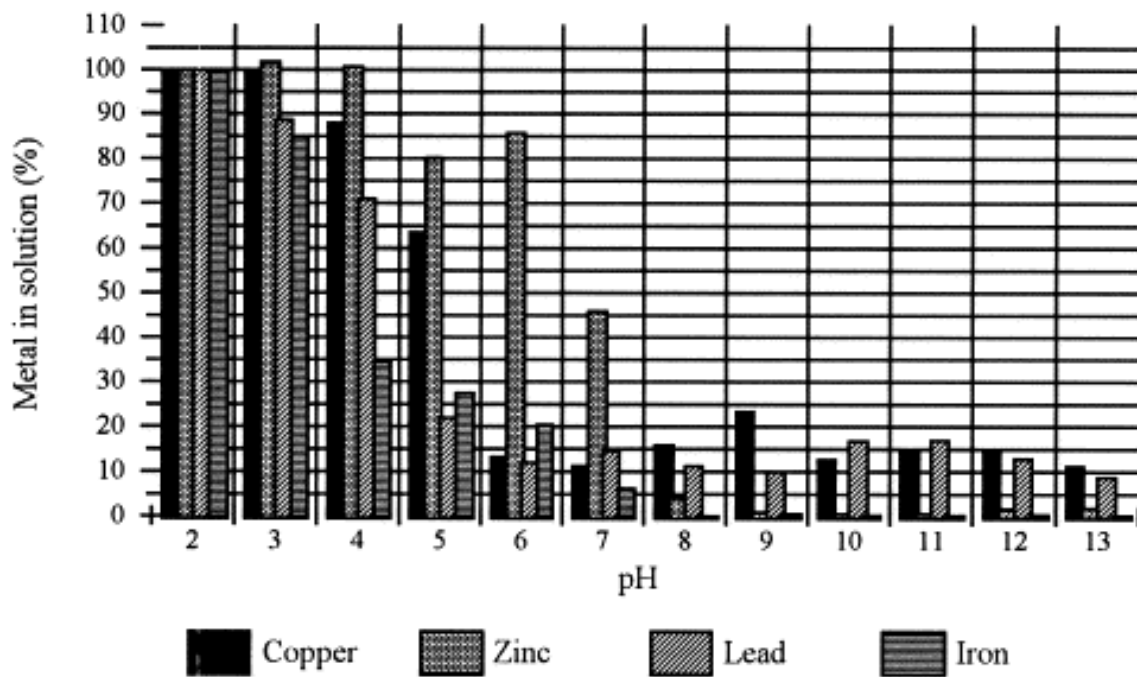The results of the pH profile are graphically illustrated in Fig. 2.

Fig. 2. pH profile on raw effluent illustrating the amount of metal remaining in solution following the increase of the pH from 1.8 by NaOH addition.

The results indicate that for effective precipitation of the majority of the metals as metal hydroxides the pH in the reaction vessel needed to be maintained above pH 8. The profile suggests that should the pH decrease below 8 the efficiency of zinc removal would be affected first, followed by copper, lead and eventually iron.

4.2. Bench scale reactor

In order to accurately compare the performance of the algal mediated precipitation process to that of the control the algal culture was fed on tap water with no additional nutrients or source of salinity. As expected the algal culture began to decline after a period of 6 days, as a result of nutrient and salinity stress. Although there is little change in the pH in the algal tank, due to the buffering capacity of the media, what decrease does occur is directly related to the strength of the algal culture, this is illustrated in Fig. 3.
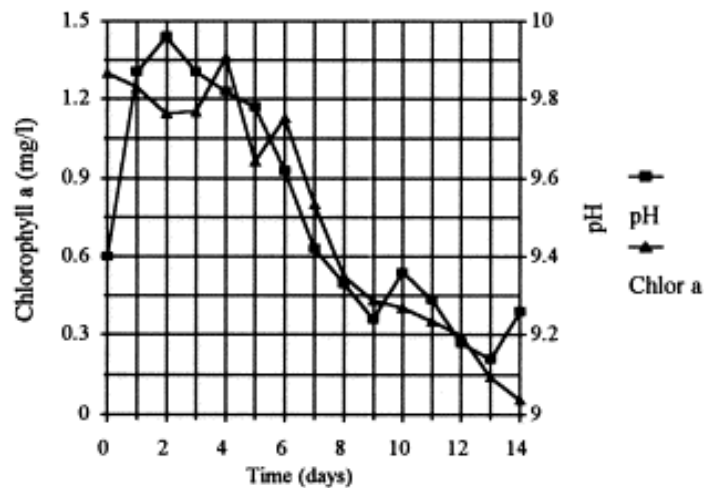
Fig. 3. Relationship between algal concentration, represented a mg chlorophyll *a*/l, and pH in the algal growth vessel.

Fig. 4 illustrates the daily metal removal in the reactor vessel. On day 0 no effluent addition or overflow from the algal vessel had occurred, accounting for the lack of data points. As expected the percentage removal is directly dependent on the pH in the reaction vessel. The levels of iron and lead removal remained relatively constant over the duration of the experiment as the pH did not drop below 6. The percentage zinc removal decreased significantly as the pH in the reaction vessel dropped below 7. The copper removal followed an unexpected trend, with the removal increasing despite the decrease in the pH. Reasons for this will be suggested later.
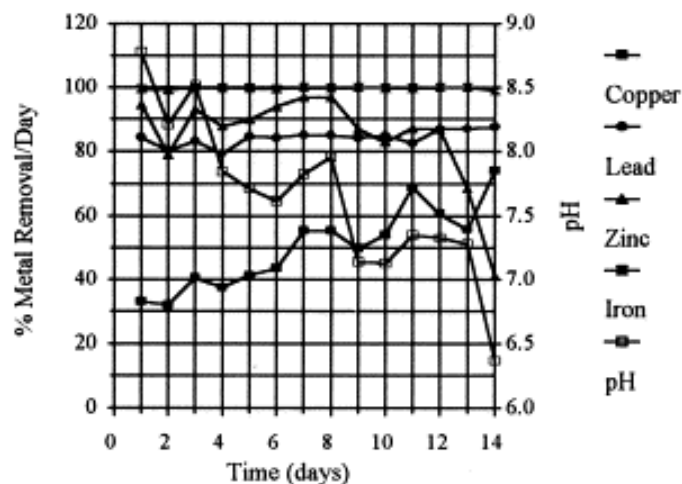
Fig. 4. Relationship between metal removal on each of the 14 days of the experiment and pH in the reaction vessel. Metal removal calculated from the reactor overflow.

4.3. Control reactor

The control reactor was run in an identical fashion to the experimental reactor, except that the initial algal culture was replaced by 5 l of Zarouk's Media, with reduced EDTA. The experiment was run over a period of 10 days, during which there was little change in the pH of the vessel containing the media. This could be accounted for by the buffering capacity of the media and the fact that water was being fed in. There was no increase in pH within the first 24 h as was observed in the experimental reactor. The data for the reaction vessel (Fig. 5), however differ markedly from the corresponding data in the previous experiment.
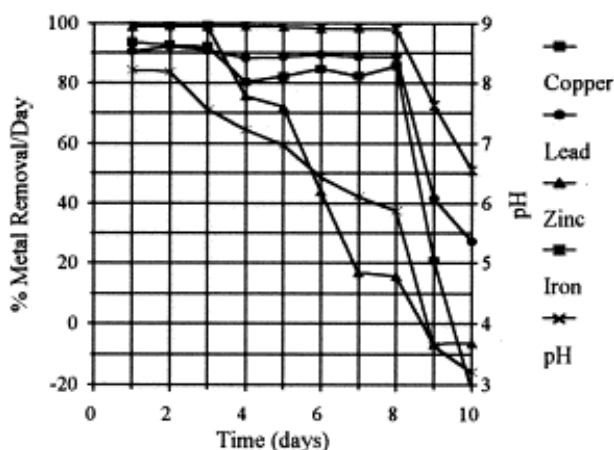

Fig. 5. Relationship between daily metal removal and pH in the control reactor over a 10-day period.

The results show that over the first 8 days the pH in the reactor declines steadily followed by a sharp decline, indicating that after 8 days the ability of the media to buffer the acidity of the effluent is exhausted. Over the first 6 days of the experiment, during which the algal culture in the previous experiment was still healthy, the pH dropped by almost two units compared to just over one unit. This coupled with the fact that the pH in the reaction vessel fed by the algal overflow only began to decline significantly after 13 days is clearly indicative of the role played by the algae in maintaining the alkalinity. The metal removal in the control experiment again conforms to the results predicted in the pH profile. The negative values observed for zinc from day 9 and copper on day 10 are due to the pH decreasing to such an extent that some metal which had previously been precipitated has returned into solution.

4.4. Anaerobic digester

Due to the high sulphate load of the effluent and the fact that negligible sulphate removal was achieved in the precipitation step the overflow from the reaction vessel was treated in an anaerobic digester. The composition of the overflow from the anaerobic reactor, after settling, is given in Table 2.

Table 2. Composition of anaerobic digester overflow and discharge specifications

Component	Units	Result	% Reduction	Specifications
pH		8.18		min 5.5, max 9.5
Sulphate	mg/l SO$_4$	295.83	89.07	
Copper	mg/l	0.100	94.30	1.0
Zinc	mg/l	0.221	93.82	5.0
Lead	mg/l	0.057	95.14	0.1
Iron	mg/l	0.263	99.47	0.3

Table 2 indicates that the process has successfully reduced the levels of all components which were analysed to within the discharge specifications.

5. Discussion

The data presented clearly indicates that the generation of alkalinity, associated with the growth of the alga *Spirulina* sp., in the described system is an efficient method for the treatment of heavy metal polluted acid waters. The system has the potential to run continuously, provided a suitable feed is supplied. The continuous cultivation of large volumes of *Spirulina* using saline wastes has previously been demonstrated [15 and 16].

The alkalisation of the medium by unicellular green algae is dependent on light, dissolved inorganic carbon (DIC) as HCO_3^- and air adapted cells with a DIC pump [10]. The equations explaining the conversion of CO_2 to HCO_3^-, photosynthetic CO_2 fixation and carbonate fixation have been elucidated [17].

The unusual trend for copper removal and the fact that the metal removal efficiency was slightly higher during the first 5 days in the control system can be explained in terms of the release of extracellular components by the algae. Under stress conditions the algae release extracellular polysaccharides, which are capable of chelating metal ions. The polysaccharides, produced as a result of nutrient stress in this study, would pass into the reaction vessel and chelate metal ions, particularly copper for which they have the highest affinity [18]. At low polysaccharide concentrations the complex remains soluble and hence the copper remains detectable in the reaction vessel overflow. As the experiment progressed the stress on the algae increased, and would result in a greater release of extracellular material. At higher concentrations, the polysaccharide–metal complex coagulates and would settle in the reaction vessel, resulting in a steady increase in copper removal by this mechanism as the experiment progressed.

The efficiency of the system exceeds that of the majority of reported passive treatment systems [2], both in terms of metal removal and volume treated relative to reactor surface area. A typical passive treatment system consisting of several ALDs and anaerobic cells may cover between 2800 and 4900 m^2 and treat between 124 and 300 m^3/day with an iron removal efficiency of approximately 60%. The alkalisation effect of these systems is not significant [2]. The algal treatment system for saline waste at the Mossop Western Leathers Tannery in Wellington, South Africa, functions in an identical manner to the algal growth vessel in this system. A 2500-m^2 high rate algal pond is capable of treating 125 m^3 of saline waste daily [15] which would relate to the generation of 125 m^3 of alkaline water in this system. Using an alkaline water to raw effluent ratio of 1:1, as in this study, that would allow the efficient treatment of 125 m^3 of raw effluent daily.

This increased efficiency, coupled with the reduced operating costs involved and the potential to simultaneously treat a second effluent suggests that the system described in this paper has considerable potential for the treatment of metal polluted acid waste waters.

Acknowledgements

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