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Performance evaluation of eggshell waste material for remediation of acid mine drainage from coal dump leachate

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ABSTRACT

In this study, eggshell (ES) powder was evaluated as a cheap and biocompatible waste material for the pre-treatment of acid mine drainage (AMD) leachate from coal dump. First, the composition of the AMD and physiochemical properties of the ES powder were determined using various standard characterization techniques. Then the removal efficiency of the target metal contaminants and the acid-neutralisation effect were explored in batch and kinetic set-ups. Thereafter, the settling rate of sludge formed after separately reacting ES and limestone powders with AMD was explored. Results revealed that the AMD leachate was highly acidic and contaminated with both cations and anions. Thermogravimetric analysis (TGA) and X-ray fluorescence (XRF) analyses demonstrated that ES powder was thermally stable up to 700 °C and CaO was the main component, respectively. Scanning electron microscopy (SEM) and EDX spectra confirmed the removal of contaminants. Both the decrease in particle size and increase in mass of ES enhanced the treatment efficiency. Although complete Fe and Al removal was achieved, Mn and sulphates posed a challenge as they were partially removed. Meanwhile, ES demonstrated superior acid-neutralizing effect to limestone and the mine water clarity and pH were shifted to acceptable levels. Both Fe and Al removal proceeded through an exothermic process while it was opposite for Mn. Kinetics were rapid and the sludge from ES powder settled faster compared with that from limestone powder. Cost analysis indicated that significant financial savings can be realised by substituting limestone with ES material. The findings suggest that ES waste could be an efficient and cheap material in the pre-treatment of AMD effluents.

1. Introduction

Mining industry plays an integral part towards the growth and development of South Africa's economy. However, fragmentation of sulphide bearing minerals (FeS_2) during mining and mineral extraction exposes them to oxygenated environment leading to a series of complex geochemical reactions that generate acid mine drainage (AMD). Acid mine drainage is highly acidic (pH < 3), has a high concentration of dissolved iron, aluminium, manganese and sulphates; causing a devastating impact on water resources and consequent damage to the health of biota (Colvin and Burns, 2011; Ríos et al., 2008). Although certain rocks, especially those containing large amounts of dolomite or calcite can naturally neutralise AMD, this is not the situation in South Africa's coal and gold mine deposits as natural neutralisation effects are overwhelmed (McCarthy, 2011). Numerous cases of highly acidic water with elevated concentrations of metal ions and sulphates beyond acceptable standards have been reported (da Silveira et al., 2009; De Beer et al., 2010; Enslin et al., 2010; Tutu et al., 2008). Consequently, to ameliorate the AMD problem, pragmatic efforts have been constantly sought to offer innovative, efficient and less costly treatment methods that could serve as a supplement or as alternative to the existing AMD treatment technologies and to improve the level of compliance.

Numerous methods such as lime neutralisation and precipitation (Coulton et al., 2003), ion-exchange (Khan, 2014), adsorption (Hong et al., 2014; Masindi et al., 2015), electrochemical (Chartrand and Bunce, 2003) and bioremediation (Johnson and Hallberg, 2005; Rakotonimaro et al., 2017; Sierra-Alvarez et al., 2006) are used for AMD treatment. Amongst these, limestone/lime neutralisation and precipitation of metals in the form of hydroxides and gypsum, followed by a period of settling in sedimentation basins is by far the most widely used method for AMD pre-treatment (Gitari et al., 2008; Johnson and Hallberg, 2005; Maree et al., 2013). Although effective, chemical precipitation requires large quantity of treatment reagents, resulting in voluminous and highly hydrated sludge, which dries and compacts

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poorly, posing disposal and storage challenges. Moreover, limestone mining may have significant negative impact on the environment and the public health. Although limestone is cheap, it exhibits slow reaction time, and its properties are geologic dependant, meaning inconsistency in grade can affect the overall performance of a given treatment system (da Silveira et al., 2009; Skousen, 2014). Due to such limitations, it is an important challenge for industries and researchers to explore other natural materials for effective and economical pre-treatment/neutralising of AMD. Furthermore, such alternative solutions would be more viable if they can be used in an existing treatment facility with minimal changes.

Recently, adsorption technology, employing naturally-derived materials has received increasing attention (Bulut and Tez, 2007), as an effective, efficient and economical method for sequestration of heavy metals from aqueous solution (Bulut and Tez, 2007; Faur-Brasquet et al., 2002; Gupta and Nayak, 2012; Yu et al., 2001). This is because most of the reported synthetic adsorbents require long preparation recipe and are generally expensive. Thus, there has been a shift in focus towards low-cost agriculturally-derived materials with desirable adsorptive and acid neutralisation characteristics (Oke et al., 2008). Literature reports indicate that activated carbon (Goher et al., 2015), chitosan (Bassi et al., 2000), banana and orange peels (Annadural et al., 2003), sugar cane bagasse (Joseph et al., 2009), sawdust (Yu et al., 2001) and rice husks (Hegazi, 2013) among others, have the potential to sequestrate metal ions from polluted water.

Recently, increased egg production and processing has resulted in increased eggshell (ES) waste; a non-edible product with very limited use and value. The disposal of ES waste is an environmental burden worldwide, and especially in countries where the egg product industry is well developed (Hassan and Aigbodion, 2015). According to Windhorst et al. (2013), approximately 124,800 tons of ES waste was produced globally in the year 2010 as a result of industrial egg processing. Furthermore, statistics by the Food and Agricultural Organization (FAO) indicates that the global egg production is likely to hit 86.8 million tons by 2030 (FAO, 2014). The projected increase in egg production therefore, means large quantities of ES will be produced and disposed of as waste. As a result, high disposal cost will continue to increase due to increase in landfill taxes and environmental concerns (Hassan and Aigbodion, 2015). Therefore, it is necessary to find alternative ways to transform ES into a valuable item for overcoming environmental challenges.

The main component of the ES is calcium carbonate ($CaCO_3$), which can be used as a complexing, binding or ions exchange agent for metal ions in liquid solution. Moreover, $CaCO_3$ is a significant alkalizing agent and when equilibrated with acidic water, it neutralises it; meaning heavy metals can precipitate and adsorb on ES particles' surface. Such characteristic make eggshell waste a potential material for removing contaminants, especially cations from the liquid phase. Few studies have explored ES as a promising scavenger for metal ions in aqueous solution (Ahmad et al., 2012; Elabbas et al., 2016; Ipeaiyeda and Tesi, 2014; Jai et al., 2007; Rubcumintara, 2014; Suheila, 2013; Zheng et al., 2007). Nonetheless, there is still a lack of practical applicability because previous studies focused mainly on removing dilute concentrations of metal ions from synthetic solutions, instead of using environmental water samples. Besides, adsorption alone is mainly suitable as a polishing step, and for it to be effective in highly contaminated waters, it may be considered important to supplement it with neutralisation. In view of the aforementioned, it can be a considerable task to examine the ability of ES waste for use as an effective precipitation and adsorption surface for both cations and anions present in highly acidic and contaminated environmental samples.

Thus the aim of this study was to examine ES waste as a cheap and biocompatible material for the pre-treatment and attenuation of AMD from toe seep coal dump leachate. To the best of our knowledge, there is hardly any literature report available regarding the application of ES waste for remediation of highly polluted AMD. Eggshell waste was collected, prepared, characterised and evaluated for the removal of main cations (Al, Fe, Mn) and anions (SO_4^{2-}) present in the AMD. Batch equilibrium and kinetic experiments were conducted to explore the influence of different process variables on the overall treatment efficiency. In addition, the performance of eggshell in terms of neutralisation efficiency, sludge settling rate and volume was compared with raw limestone of similar properties. Results obtained from this study provides important insights into the possible application of the ES waste as a cheap and effective substitute material for the pre-treatment of AMD.

2. Materials and methods

2.1. Materials

Eggshell waste was collected from the Tshwane University of Technology restaurant. Multi-ions standards solutions and analytical reagent grade (AR) chemicals were purchased from Merck (Pty) Ltd-South Africa. Limestone powder was obtained from G&W Mineral Resources (South Africa). Before use in adsorption experiments, all the glassware and polyethylene bottles were firstly soaked with 10% nitric acid for 24 h and thereafter were rinsed with deionised water and dried in a clean oven.

2.2. Acid mine water

Acid mine drainage (AMD) samples were obtained as Toe Seep Leachate from a waste coal dump in Anglo American Thermal Coal, Witbank (South Africa). Standard sampling procedures (EPA, 2007) were followed after which the samples were filtered using 45 µm cellulose acetate filters and were stored in polyethylene bottles at 4 °C. The concentration of metal ions in the samples was determined using inductively coupled plasma atomic emission spectrometer (ICP-AES, 9000, Shimadzu-Japan). Anions were quantified using the Metrohm 861 compact ion chromatograph (Switzerland) with a Metrosep A Supp 5 (6.1006.520) 150 × 4.0 mm analytical column. Before any analysis, both instruments were calibrated using standard solutions. The pH was measured with Orion Star A211 pH meter (Thermo Scientific). The meter was calibrated with 4.0, 7.0 and 10.0 buffer solutions before each set of trials.

The main chemical composition of AMD was determined and are displayed in Table 1. As it can be seen, the AMD is highly acidic pH = 2.43; which was way far below the recommended values (6.5–8.5) by the World Health Organization (WHO, 2011). Also, the

Table 1
Main chemical composition of raw AMD (toe seep leachate from coal discard dump) sample from Anglo American thermal coal, Witbank (South Africa).

Parameter	Value	Drinking guideline value
pH (at 25 °C)	2.43	6.5–8.5[a]
K (mg/L)	10.2	10[a]
Na (mg/L)	149.7	250[a]
Ca (mg/L)	606	200[a]
Mg (mg/L)	648	100[a]
Fe (mg/L)	6120	0.3[b]
Al (mg/L)	506	0.2[b]
Mn (mg/L)	155	0.1[b]
SO_4^{2-} (g/L)	28.98	0.25[b]
PO_4^{3-} (mg/L)	75	10[b]
NO_3^- (g/L)	137	50[b]
EC (mS/cm)	12.41	1.4[a]
Turbidity (NTU)	65.32	5[a]
TDS (g/L)	10.27	1.0[a]

TDS = (0.8 * EC) + (2.2 * 10ˆ − 6 * ECˆ2).
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