Physics and Chemistry of the Earth xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Physics and Chemistry of the Earth

journal homepage: www.elsevier.com/locate/pce

Investigating waste rock, tailings, slag and coal ash clinker as adsorbents for heavy metals: Batch and column studies

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ARTICLE INFO

Keywords:
Adsorption
Kinetics
Coal ash clinker
Heavy metal
Mining wastewater

ABSTRACT

Wastewater from the mining industry is a concern because most of the time it contains heavy metals with concentrations above permissible levels, posing a threat to terrestrial and aquatic life. The study was conducted to evaluate the effectiveness of locally available waste materials (waste rock, tailings, coal ash clinker, and slag) generated by BCL (Ltd) mine, a copper and nickel mining and smelting company in Botswana, for removal of nickel and copper from the real mining wastewater. Batch adsorption studies were conducted to establish the adsorptive efficiency and kinetics of each media with respect to nickel and copper ions. The best media was further evaluated through fixed bed column studies at 24 and 48 h empty bed contact time. The results indicate that the percentage removal for coal ash clinker, waste rock, smelter slag and tailings was 98%, 15%, 3% and −3% with respect to copper ions, and 46%, 9%, 7% and 2% with respect to nickel ions for each media respectively. Coal ash clinker followed pseudo first order kinetic model and Langmuir isotherm model with respect to nickel ions indicating the dominance of physisorption and mono layer coverage respectively. The Langmuir separation factor (R_L) was 0.37 suggesting favourable adsorption onto the media. Fixed bed column studies revealed that copper was completely retained in the bed at both 24 and 48 h contact times. In the case of nickel, removal efficiency ranged between 83% and 99% when contact time was 48 h and between 68% and 99% when the contact time was reduced to 24 h. Breakthrough was not reached after 19 bed volumes. It can be concluded that coal ash clinker is a better candidate for the removal of copper and nickel ions from mining wastewater.

1. Introduction

Technological advancement in the mining industry has led to a significant growth in mineral production and to the economic growth of different nations. This growth has considerably increased the amount of liquid waste (wastewater) and solid waste generated by the industry. Of particular concern to this study is the mining wastewater which is quite distinctive. In most cases the mining wastewater contains heavy metals with concentrations above statutory levels (Odle, 2004). Most heavy metals are toxic and their toxicity can persist for a long period of time after introduction to the environment because they do not undergo microbial degradation compared to organic contaminants (Gupta and Babu, 2009). The problems associated with heavy metals in wastewater have stimulated regulatory bodies to come up with stringent regulations governing the emission of such metals into the environment. Table 1 below outlines the permissible limits for some heavy metals from different authorities as well as the health hazards related to such metals (BOBS, 2012; The gazette of India, 1991; WHO, 1997).

Copper and nickel are amongst the heavy metals that are found in wastewater. These metals have been reported to have toxic and carcinogenic effect to aquatic organisms (Malkoc and Nuhoglu, 2006). It has been reported by Shabalala et al. (2017) that the effluent from acid mine drainage are acidic and contain high concentrations of iron and other trace metals which can have severe impact to the aquatic life and stunt terrestrial plant growth. Though copper is an essential nutrient required in small amounts, it can cause gastroin-intestinal disturbance that include nausea and vomiting and long term use of water above the limit can cause liver or kidney damage (Mohan and Streelakshmi, 2008). Industrial wastewater that contains copper and nickel is common since these two elements are used in industries such as manufacture of electrical wires, battery manufacturing, electroplating and they are also present in mining wastes.

It has been reported from various literature sources that most of the conventional technologies (chemical precipitation, reverse osmosis, electrodialysis) for heavy metal removal are relatively expensive in terms of capital and operational costs, and the methods do not necessarily have the capacity to remove all the pollutants to statutory levels (Chiban et al., 2012). Conventional methods such as

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https://doi.org/10.1016/j.pce.2018.02.013
Received 10 April 2017; Received in revised form 12 October 2017; Accepted 27 February 2018
1474-7065/

Table 1
Trade effluents limits for copper and nickel from different authorities.

Metals	Permissible limits for industrial effluent discharge (mg L^{-1})						Health hazards
	Botswana Standard		Indian Standard			WHO	
	Inland surface water	Public sewers	Inland surface water	Public sewers	Marine coastal area	Inland surface water	
Nickel	0.3	20	3.0	3.0	5.0	–	Causes chronic bronchitis, reduced lung function, cancer of lungs.
Copper	1	5	3.0	3.0	3.0	0.05–1.5	Long term exposure causes stomach-ache, irritation of nose, mouth, eyes, headache.

precipitation, have been reported to be cost prohibitive, and are ineffective at low metal concentrations. These methods also generate toxic sludge which also brings about the burden of disposal (Malkoc and Nuhoglu, 2006). The same has been echoed by Meunier et al. (2003) who reported that removal methods such as electrodeposition, electrocoagulation, membrane separation and many more are expensive and or too inefficient in reducing metal ions to recommended standards. Because of the above reasons, researches are now very intensive into finding some alternative methods for the removal of metals from water, wastewater and industrial effluents.

Pan et al. (2010) developed a polymer based hybrid sorbent (HFO-001) for the removal of heavy metals such as lead, cadmium and copper from simulated electroplating and natural water solutions at batch and column modes. The resulting effluent met drinking water standards. The use of phosphate treated rice husk for the removal of heavy metals through fixed bed columns has been reported by Mohan and Streelakshmi (2008). The experiment was conducted using synthetic solutions. It was observed that metal uptake increased with media depth as a result of increased contact time. Inglezakis and Grigoropoulus (2004) conducted experiment on the effects of operating conditions on the removal of heavy metals by zeolite in fixed bed reactors and reported that removal efficiency was favoured by low volumetric flow rate. It was also reported that dilute solutions result in longer bed runs. Yan et al. (2015) conducted an experiment on the removal of As (III) and cadmium from copper smelting wastewater through granular TiO_2 columns. It was reported that As (III) and Cd at concentrations of 2590 ± 295 and 12 ± 2 mg L^{-1} respectively were reduced to 0.16 ± 0.11 *and* 0.0133 ± 0.0134 mg L^{-1} well below discharge limit.

The conventional adsorption method for heavy metal removal using synthetic adsorbents such as activated carbon yields good results but the cost of such engineered adsorbents is high (Bhatnagar and Minocha, 2006). In order to increase the profitability of mining entities and at the same time protecting the environment, the question of coming up with alternative methods is paramount.

This study focuses on the following objectives:

1) To investigate the potential of solids wastes generated by BCL mine for the removal of copper and nickel ions from effluent generated by BCL mine.
2) To investigate the environmental impact of the media
3) To select the best media for further investigation at a pilot scale.

The research is justified by the fact that there has been an extensive research carried out on various materials and most of the published work involve the use of synthetic (laboratory prepared) wastewater as opposed to the actual wastewater. Nothing much has been published on the use of mining waste as adsorbents. Given the paucity of information on that area, this research is important in the augmentation of existing literature on the use of waste materials in wastewater treatment through the sorption process. The study could provide an alternative environmental solution to the local mines and also reduce the costs associated with conventional methods.

2. Materials and methods

2.1. The study area

The research was conducted at BCL (Ltd) mine, a copper and nickel mining and smelting company in the north central part of Botswana in Selibe Phikwe town. The mine has been in operation since August 1956. By August 2016 BCL (Ltd) mine generated a monthly quantity of 81 000 tonnes of smelter slag, 145 140 tonnes of tailings, 24 000 tonnes of waste rock and 1650 tonnes of coal ash with clinkers. The monthly quantity of effluent generated by then ranged between 70 and 80 m^3 per hour (BCL, 2016).

2.2. Sampling and sample preparation

Materials investigated were copper and nickel smelter slag, tailings, coal ash clinker and waste rock, all from the respective waste dumps. Sampling was conducted in accordance with South African National Standards SANS 195: 2006 (2012–04 – 26). Seven vertical test holes were dug on each waste heap using peaks and shovels and the samples were collected from each hole, thoroughly mixed by quartering and stored in plastic bags before use. Large sample particles were crushed using a laboratory jaw crusher to achieve a desired particle size range. Particle size passing through 50 μm for each media was selected for pelletizing in preparation for the determination of the media chemical composition. The 50 μm size was selected because it enabled ease of pelletizing of the powder samples without any additives, before feeding the sample into the X-Ray Fluorescence spectrometer (XRF). The media size of at least 5 mm was selected for column tests in line with the recommendation by Chazarenc et al. (2007). In preparation for batch adsorption tests, the remaining media were further segregated into finer particles of sizes ranging from 0.425 mm to 1.18 mm using BS 3310-1 standard sieves. All samples were washed using de-ionized (DI) water, oven dried at a temperature of 105 °C and stored in separate containers before use.

As for the real wastewater, sampling and sampling preparation were carried out in accordance with Botswana Standard BOS ISO 5667–3:2003. Grab samples of mine wastewater were collected from the V- notch located between the cooling ponds and the nickel removal plant. The pH of the samples was recorded immediately after sampling using Sension pH + 5 benchtop pH kit. The samples were thoroughly mixed, stored in 5 L polyethylene bottles and kept in a temperature controlled room before use.

2.3. Physical and chemical characterization of materials

The chemical composition of each media ($<$ 50 μm) was determined through X-Ray Fluorescence Spectrometry – Tiger Bruker S8 (XRF)