DOI https://doi.org/10.5281/zenodo.10049652#145

TWIST, 2024, Vol. 19, Issue 2, pp. 175-179

TWIST

Journal homepage: www.twistjournal.net

Reductive Leaching of Manganese from Spent Zinc-Carbon Batteries Using Plant Biomass as Reducing Agent

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Abstract
The huge demand for manganese (Mn) based materials necessitates its extraction from various secondary sources, out of which the spent zinc-carbon battery is one of the most important source, due to its numerous applications in various appliances resulting into huge disposal after complete discharge. The hydrometallurgical routes using acids as leaching agents are commonly found more economical and efficient in extracting the metal values from the spent zinc-carbon batteries. The efficiency of Mn leaching depends upon the nature of the reducing agent used during leaching and most of the reducing agents are harmful chemicals. For large scale Mn metal value recovery from such batteries necessitates the development or use of cost effective and environmental friendly reducing agent. In this regard, the present study reports recovery of Mn metal values from spent zinc-carbon battery using cellulosic biomass as reducing agent and from the study it is found that maximum ~ 57% of Mn can be leached out when the leaching is carried out in 1M H_2SO_4 solution at a temperature of 80^0C using biomass as reducing agent.

Keywords
Reductive leaching, Manganese, Spent batteries, Zinc-carbon, Plant biomass

INTRODUCTION

The widespread industrial application of manganese in various sectors such as steel production to batteries, glass, non-ferrous alloys, catalysts, animal feed, fertilizers, colourant or pigment, medicine, food industry, matches/fireworks and chemical production, makes it a strategic element, after iron, aluminium and copper [1,2]. The use of manganese to substitute nickel in stainless steel production has widely gained popularity around the globe. Thus, the manganese market is projected to be driven by a steady production of stainless steel over the forecast period, the major factor driving the growth of the manganese market revenue.

Electrolyte manganese metal is the fastest-growing category due to the growing usage of electrolyte manganese metal in batteries both for lithium-ion rechargeable batteries and non-rechargeable alkaline cells. Overall, the growing demand for steel products in the construction & infrastructure industry and using it in batteries are the key market drivers enhancing market growth

The manganese industry is projected to grow from USD 23.21 billion in 2022 to USD 32.70 billion by 2030, exhibiting a compound annual growth rate (CAGR) of 5.02% during the forecast period (2022 - 2030) [3].

Manganese occurs principally as pyrolusite, braunite, psilomelane, and rhodochrosite. Only ores are not sufficient for this huge necessity of this metal and hence extracting the metal value from secondary source can be a suitable alternative.

Zinc–carbon dry cell batteries are the most used primary batteries in the world [4]. The demand of Zn-carbon batteries is steadily increasing due to the popularity of electronic products from home appliances to personal portable, since these batteries is easy to manufacture and safe to carry [5]. Zinc-Carbon dry cells run out rapidly and are thrown away. Such batteries after complete discharge usually dispose directly to the environment that may create environmental pollution. Disposal of spent batteries represents an increasing environmental problem in terms of heavy metals content when these devices are disposed of in inadequate way [6]. On a resource management level, batteries could be considered as an ore of secondary raw materials and valuable metals such as zinc and manganese can be recovered from spent zinc-carbon batteries. Moreover, the use of recycled metals in battery production instead of virgin metals has positive environmental impacts through reduced energy use and reduced pollution related to the mining of the virgin source [6,7]. Since Mn and MnO_2 are the precious material having numerous applications, a cost-effective and an environmental friendly method needs to be developed to extract the metal value from these spent batteries.

Among the existing methods of metal recycling from spent batteries, pyrometallurgical process though effective but highly energy consuming. The hydrometallurgical routes are commonly found more economical and efficient than pyrometallurgical methods. The metal separation routes based on hydrometallurgical operations are characterised by lower energy consumption, higher metal selectivity and no air pollution, as there are no particles produced. However, some pre-treatment steps are necessary to improve metal dissolution rates in the aqueous phase, like batteries sorting, dismantling, magnetic separation and leaching [8].

In the leaching of tetravalent manganese, a reducing agent is usually used to reduce Mn(IV) to soluble Mn(II). Use of SO_2 and other chemical like oxalic acid are not found to be environmental friendly [9].

There are various other non-harmful reducing agents such as citric acid and carbohydrates in the form of glucose can be used in this regard [10].

Carbohydrates are low cost and nonhazardous reducing agents that may be used either in pure form or as an extracted material from various biobased wastes, i.e. waste biomass which are good sources of carbohydrate. When cellulosic biomass is subjected to acid hydrolysis, the cellulose is converted into sugar (carbohydrate), which can be used as a reducing agent during manganese (Mn) leaching.

It is a fact that when cellulosic biomass is treated with dilute acid, there is a disruption of its complex structure and the cellulosic part is converted into simple sugar as per the following reaction [11] (Fig. 1):

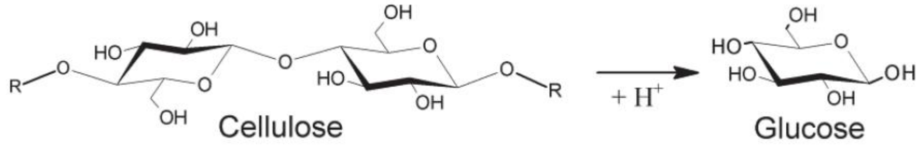

Fig. 1 Conversion of cellulose into sugar [12]

Hence, such cellulosic biomass can be used as a cheap, environmental friendly reductant in manganese leaching. Based on this concept, the current research work is based on comparative reductive leaching of Mn metal value from spent zinc-carbon battery through dilute H_2SO_4 leaching with and without the use of biomass derived sugar as reducing agent.

EXPERIMENTAL

The zinc-carbon battery consists of a zinc can (serves as the battery container and anode), a manganese dioxide cathode and an electrolyte of ammonium chloride and/or zinc chloride dissolved in water. Carbon (acetylene black) is mixed with manganese dioxide to improve conductivity and retain moisture and is also called black mix, depolarizer or cathode. A carbon rod, serving as the current collector for the positive electrode is inserted into the black mix. The battery is inserted into a steal can with plastic separator. As the battery is discharged, the zinc is oxidized and the manganese dioxide is reduced. A simplified overall battery reaction can be written as [8]:

$$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3$$

Battery dismantling and processing of battery materials

Spent zinc carbon batteries of AA type of different manufacturers were collected from local areas of Bhubaneswar, India. All batteries were dismantled manually to remove iron scrap, plastic and paper. After removing them the remaining part of battery was cut and the residual zinc part and manganese part (black powdery mass) were separated manually without disturbing or crushing the carbon rod (current collector). The black battery powdery mass (except the graphite rod cathode material) i.e. the MnO_2 powder mixed with acetylene black mix, as discussed above was ground to fine particle using mortar pestle followed by water leaching to remove impurities. For water leaching, certain quantity of the black grounded powdery mass was taken in 250ml beaker to which required quantity of distilled water was added and subjected to mixing in a magnetic stirrer. After water leaching the total content in the beaker was filtered and the residue of filtration was collected and dried.

Leaching with dilute H_2SO_4

For leaching of Mn, among various acids, sulfuric acid (H_2SO_4) is attractive due to its accessibility and low price. For that reason leaching experiments were carried out using sulfuric acid solutions. Though various factors such as H_2SO_4 concentration, reaction time, temperature as well as solid to liquid ratio affect the efficiency of Mn leaching, but in the present study only the effect of time period of leaching on Mn recovery was studied, because the main objective of the study is to know the effect of biomass as natural reductant during acid leaching of Mn from spent zinc-carbon batteries. The acid leaching was carried out with 1M H_2SO_4. 2 gm of the dried black powdery mass was taken in a 100 ml beaker to which 30 ml. of 1M H_2SO_4 solution was added. Leaching was carried out using a magnetic stirrer at a stirring speed of 400 rpm, at a temperature of 85^0C. At different time intervals (30, 60, 90, 120 minutes) the leached solution was analysed for Mn content. The Mn content in the leached solution at different time intervals was determined by standard titration method using EDTA.

Leaching with dilute H_2SO_4 using biomass as reducing agent

For preparing dilute acid (H_2SO_4) treated biomass solution, 5g of biomass was mixed with 30 ml. of 1M H_2SO_4 solution in a 100 ml beaker. The resulting mixture was mixed through a magnetic stirrer for 30 minutes at a temperature of 80^0C. The produced acid treated biomass mixture solution was filtered using a normal filter paper and the filtrate of filtration was used for leaching of Mn and Mn content was determined in a similar procedure as adopted in dilute H_2SO_4 leaching.

RESULTS AND DISCUSSION

Leaching with dilute H_2SO_4

Manganese can be detected as various oxides form apart from MnO_2 depending on a discharge level of the battery. During acid leaching of the cathode material the following reactions are expected [8]:

$$MnO + H_2\,SO_4 \rightarrow MnSO_4 + H_2O$$
$$Mn_2O_3 + H_2SO_4 \rightarrow MnSO_4 + MnO_2 + H_2O$$
$$Mn_3O_4 + 2H_2SO_4 \rightarrow 2MnSO_4 + MnO_2 + 2H_2O$$

The presence of MnO_2 (insoluble in acid solution) both in the original cathode material as well as due to formation as a product of the above reactions, reduces the leaching efficiency in dilute acid leaching without reductant and in this regard the increased temperature and concentration of H_2SO_4 can enhance the leaching efficiency of Mn during acid leaching. It is found that increased in temperature from 20^0C to 60^0C can enhance the leaching efficiency of Mn from 20% (1M H_2SO_4) to 50% (2M H_2SO_4) during H_2SO_4 leaching [8]. However, in this present study, the temperature is maintained at 80^0C and acid concentration is 1M.

Fig. 2 represents the effect of time period of leaching of Mn in 1M H_2SO_4 leaching. It is found that with increase in time period the percentage of leaching of Mn increases and the maximum Mn leached out in the present experimental condition is found to be 49.43%.

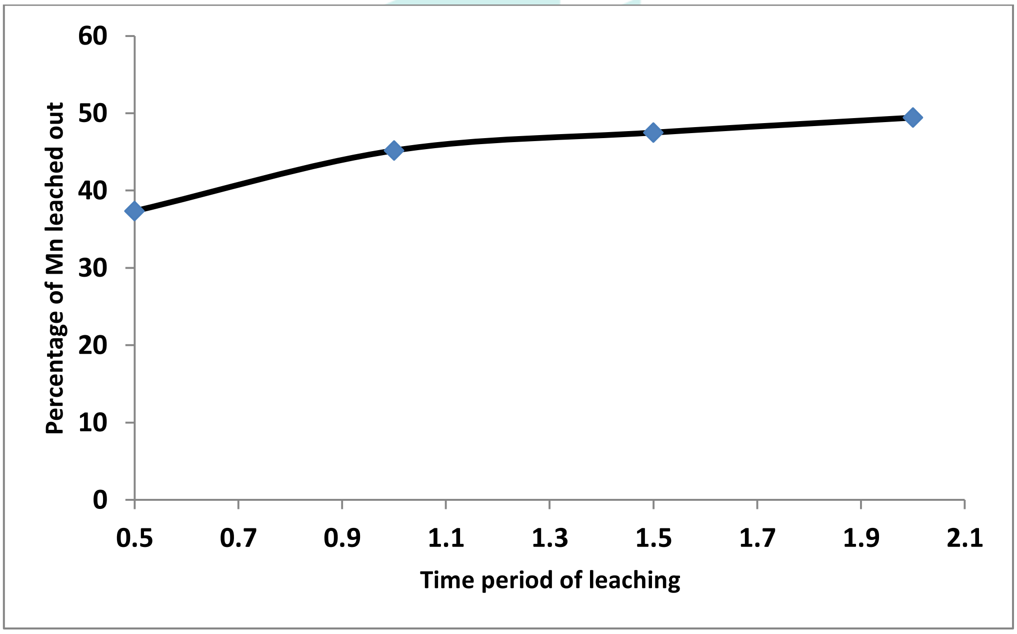

Fig. 2 Effect of time period on leaching of manganese in H_2SO_4 leaching

Leaching with dilute H_2SO_4 using biomass as reducing agent

Fig. 3 represents the effect of time period on Mn leaching in 1M H_2SO_4 treated biomass solution. The similar trend in increase in Mn leaching with increase in time period of leaching is observed as that 1M H_2SO_4 leaching (Fig. 3). However on comparison, it is found that a comparatively greater Mn is leached out at each time period of leaching when biomass is used as a reducing agent than that of the 1M H_2SO_4 leaching and a maximum Mn leached out is 57.06%, which is due to the reduction of insoluble Mn(IV) present in MnO_2 to soluble Mn(II). However, further studies needs to be performed to get the optimized conditions for Mn leaching with respect to pulp density, concentration of H_2SO_4, temperature and biomass reductant quantity during leaching for its practical application in recovery of Mn metal values from spent zinc-carbon batteries in a cost effective and environmental friendly way.

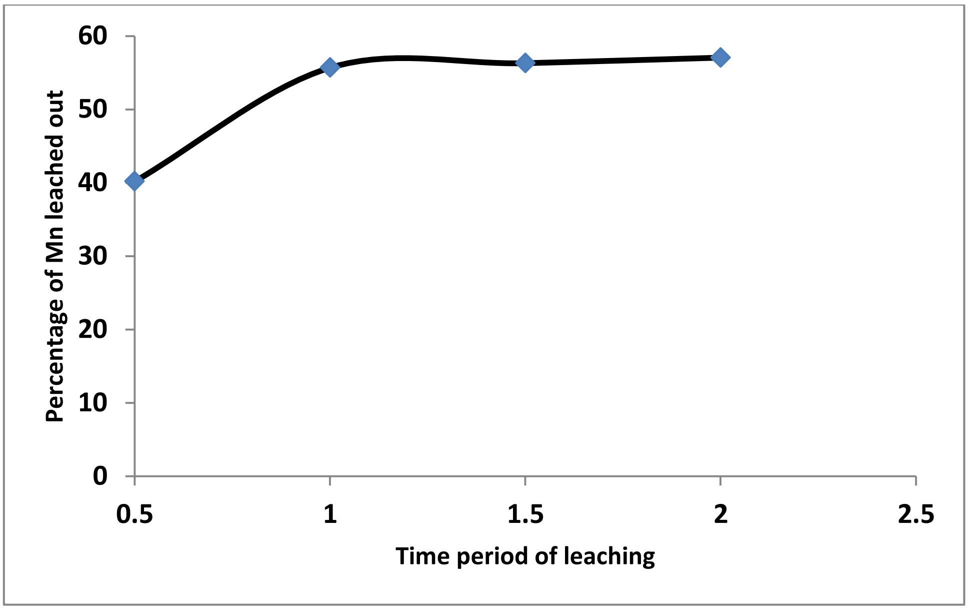

Fig. 3 Effect of time period on leaching of manganese in biomass treated H_2SO_4 solution

CONCLUSION

A new environmental friendly, cheap reductant i.e. biomass derived reductant has been used to leach out Mn from the cathode material of spent zinc-carbon battery. A maximum of ~ 57% of Mn can be leached out by using such biobased reductant for a time period of leaching 2h. For the same experimental conditions a maximum ~49% of Mn can be leached out when the leaching is carried out without using the biomass reductant. The higher leaching percentage of Mn in biomass reductant leaching suggests the successful reduction of Mn(IV) to soluble Mn(II) in presence of biomass reductant. Therefore, the study explores the potential application of a biomass waste as a reductant in Mn leaching from spent zinc-carbon battery and hence develops one cost effective and environmental friendly way of metal value extraction from spent zinc-carbon battery. Further studies needs to be made to develop the optimized condition for metal value extraction from spent zinc-carbon battery using such biomass as reducing agent.

CONFLICT OF INTERESTS

The authors declare no conflicts of interest within the article.

ACKNOWLEDGEMENT

The authors acknowledge C.V. Raman Global University to carry out the work.

FUNDING INFORMATION

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

DECLARATION OF CONFLICT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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