Techno-economic Assessment of Potential for Zinc Removal from Lake Water using Maize Cornstover Activated Bio-charcoal

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This paper focuses on activating the carbon in maize corn stover so that the material can be used as an adsorbent for removal of excess zinc in lake water. The maize corn stover was converted to bio-charcoal then chemically activated using phosphoric acid at temperatures ranging from 450 ^oC to 600 ^oC in the absence of oxygen. A yield of 44% of activated carbon from the maize corn stover was obtained. The activated carbon produced had a zinc removal efficiency of around 25% for a retention time of 4 hours in the adsorber. A process was designed for the removal of zinc in lake water using activated carbon from maize corn stover bio-charcoal. A process control system was carried out for temperature, pressure, and flow for the adsorption column. An economic analysis for the process with a plant treating 4500 m^3 of water was conducted and it established that the process is viable. The rate of return on investment was found to be 32.5%, and the payback period of the project was found to be 3.08 years with the cost of water being $0.18 per kilolitre.

Keywords: Bio-charcoal; Maize cornstover; Process and equipment design; Water treatment; Zinc

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INTRODUCTION

Currently in Zimbabwe there is removal of heavy metals in water using activated carbon made from other sources, and this activated carbon is imported from other countries such as South Africa. Statistics show that Morton Jeffrey in Harare, Zimbabwe uses about 3.8 tonnes of activated carbon per day targeting the removal of zinc (Kativhu 2013). Current treatment processes for metal contaminated waste streams include chemical precipitation, membrane filtration, ion exchange, carbon adsorption, coagulation-flocculation, flotation, electrochemical treatment, electro-dialysis, solvent extraction, and freeze crystallization (Bailey *et al.* 1999). However, these methods often generate a toxic sludge, high initial cost, and high maintenance and operation cost; these problems have led to the search for alternative methods that are efficient for heavy metal removal. Hence this led to the development of a method known as bio-sorption that uses sorbents of biological origin for removal of heavy metals from aqueous solutions mainly biochar (Zvinowanda *et al.* 2009; Inyang *et al.* 2012; Adil *et al.* 2014; Zhao and Luo, 2014; Tau *et al.* 2015; www. chemengonline.com). Bio-sorption makes use of naturally occurring waste material to remove heavy materials from industrial wastewater

(Zvinowanda *et al.* 2009). Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metals ions from wastewater streams. Corncob waste has been investigated as adsorbent for heavy metals, activated carbons having surface area in the range of 538 to 943 m^2g^{-1} as prepared from corncob were used (Adogoke and Bello 2015).

The zinc in water can be removed by activated carbon from maize corn stover bio-charcoal, which is an agricultural waste locally available in large quantities. The adsorptive characteristic of activated carbon is manipulated in this process to remove the heavy metals. Maize is a versatile cereal crop that is grown widely throughout the world in a range of agro ecological environments and contains lignocellulose material, after every season corn stover left unutilized in the fields causing potential greenhouse effects. As a way to address issues related to sustainability, the lignocellulose material possesses several desirable characteristics to use an adsorbent *i.e.* a low-cost material which is mesoporous) and hence can be used as a good precursor of activated carbon (Adogoke and Bello 2015). The maize corn stover bio-charcoal contain cellulosic surface hydroxyl groups that can bind positively charged metal ions and this is achieved through the introduction of addition surface active groups (Adogoke and Bello 2015).

Based on the background given, this study looked at the potential of removing zinc irons from lake water using the process of adsorption, the adsorption column process control and hazard operability analysis as well as the techno-economic assessment for implementing this study at Lake Chivero.

EXPERIMENTAL

Several experiments were carried out in order to determine if activated carbon from maize corn stover remove heavy metals from water. Corn stover (Fig. 1) results from maize which is the major staple food in Zimbabwe.

Fig. 1. Maize corn stover used in this experiment to make bio-charcoal

These experiments included: activation of carbon in maize corn stover bio-charcoal using phosphoric acid, analysis of water before treatment with activated carbon from maize corn stover bio-charcoal, analysis of water after treatment with activated carbon from maize corn stover bio-charcoal and varying the amount of activated carbon in treating the water. Wastewater was obtained from Lake Chivero in Zimbabwe.

Activation of Carbon from Maize Corn Stover Bio-charcoal

The maize corn stover was prepared for carbonization by measuring a 50 0g sample. Five samples were used for analysis. The temperature of the furnace was set at 450 ^{o}C for conversion of the maize corn stover to bio-charcoal. After an hour the maize corn stover bio-charcoal were removed in the furnace and phosphoric acid was added. The maize corn stover bio-charcoal was then put back in furnace at 600^{o}C for 30 minutes to activate the carbon. The yield of the bio charcoal was determined by weighing the final mass after carbonization against the initial mass before carbonization. The activated carbon was then cooled to standard room temperature before application in lake water treatment. The characteristics of the biochar were determined by Fourier Transform Infrared Spectroscopy (FTIR) spectra with the methodology described by Zhang and Luo (2014).

Tests for the Presence of Zinc in Water

A 200 mL sample of the untreated water was put in a test tube; two drops of sodium hydroxide were added to the water. The tube was observed for a formation of a precipitate. Then calcium carbonate was added afterwards and observations were made. The amount of precipitate formed was measured to equate the amount of zinc in water.

During the experiment for the removal of the heavy metals in water there were different variables that were considered. Five samples were used per run. Firstly the amount of activated carbon was varied between 0.5 and 4.0 g/m^3 and constant volume of water was used for the experiments to see the effect of the amount of activated carbon in the process. Synthetic water with different concentrations of zinc was made. Zinc concentrations were ranged between 0.2 and 0.6 g/cm^3. The amount of carbon was kept constant whilst the concentration of zinc in water was varied. The effect of the concentration of water and the amount of activated carbon used were noted.

Industrial Process Design

Feed preparation

The term feed preparation denotes the preparation of the maize corn stover. This is separation of the maize corn stover from other waste material.

Carbonization

This is the thermochemical decomposition of the maize corn stover at temperatures of 450 ^{o}C in the absence of oxygen. The maize corn stover was carbonized for an hour at 450 ^{o}C. After that they are removed and phosphoric acid was added and the maize corn stover was put back in the furnace for 30 minutes at 600 ^{o}C for the carbonization. After carbonization, cooling was then done with a fan to cool the activated carbon.

Economic assessment

The economic analysis gives the economic feasibility of the project. It gives detail of the amount of money that will be required to implement this process. There is further calculation of the major equipment cost using the cost indexes and scaling. The payback period, the rate of return on investment and breakeven point will be calculated, and appropriate conclusions are deduced (Perry and Green 1984; Peters and Timmerhaus 1993).

RESULTS AND ANALYSIS

Bio-charcoal Properties

The bio-charcoal had particle sizes of 1.4 µm through sieve analysis using a sieve shaker, and 0.5 to 4.0 g/cm^3 was added during zinc removal. This is the standard procedure for determining the size of the biochar in accordance to Behazin *et al.* (2016). The bio-charcoal is black in colour and is indicated in Fig. 2.

Fig. 2. Bio-charcoal from maize corn stover used for zinc ions removal

Activation of Carbon in Maize Corn Stover

The activated carbon produced had a dark grey colour and was a course powder with different particle sizes. The mass difference shows that for the raw materials (corn stover) resulted in a 44% yield of the activated carbon. The activated carbon was mixed with distilled water. The activated carbon settled at the bottom after about an hour and pH was tested using pH meter. The pH was slightly acidic, which is characteristic of activated carbon. The NaOH was then added to neutralise the activated carbon which should function at neutral.

Test for the Presence of Zinc in Water

A white precipitate that dissolved with time was observed in the water after adding sodium hydroxide. A white precipitate that is insoluble in water was formed after adding a calcium carbonate. The white precipitate showed the presence of the zinc metal in the water.

The results show that an increase in the amount of activated carbon for the same volume of water will also increase the amount of zinc that is removed from the water. As the amount of activated carbon was increased from 0.5 g/cm^3 to 4.0 g/cm^3, the amount of zinc precipitate increased, thus showing that the zinc remaining in the water had been reduced from 25 mg/L to 14 mg/L (Fig. 3). In addition, the results also showed that for a constant amount of activated carbon there were differences in the amount of volume the zinc adsorbed. For the same amount of activated carbon but different volumes the activated carbon will be more efficient in the lesser amount of water. Thus the amount of precipitate formed in the test tube with lesser volume will be greater. The results show that as the amount of activated carbon increased the concentration of zinc in water decreased with a removal efficiency of around 25%. Experiments were done up to the concentration of acceptable daily intake of men, which is 15 mg/day.

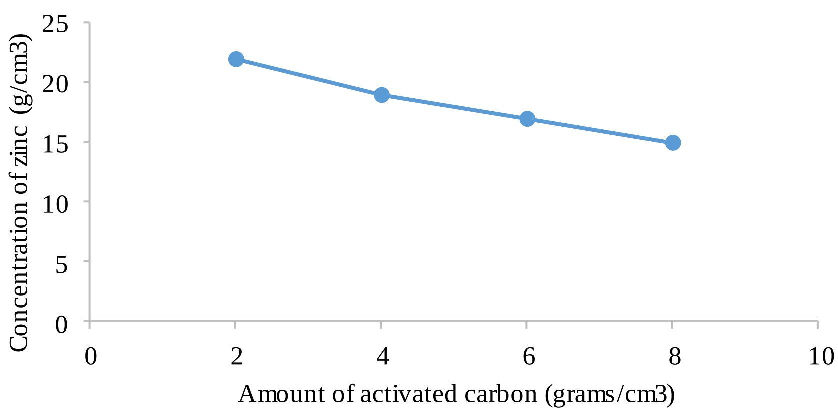

Fig. 3. Amount of zinc ions removed for varying activated carbon content

INDUSTRIAL PROCESS DESIGN

Adsorption of Zinc Particles

The activated carbon is then packed in the adsorption column at a loading of 0.5 to 4 g/m^3 .The water is then put in the column where adsorption will take place. The activated carbon would have become negatively charged after adding phosphoric acid so the negatively charged activated carbon will attract the positively charged zinc metal ions from its surface. That’s how the zinc metals are removed from the water by the activated carbon.

Filtration

The water will then be separated from the activated carbon after adsorption process by the filtration process. Then the desorption process will be carried out to remove the zinc metal from the activated carbon such that the activated carbon can then be recycled after that for re-use in the adsorption column.

Water Storage

The purified water will then be stored and will be ready for distribution. The overall process description is shown in Fig. 6.

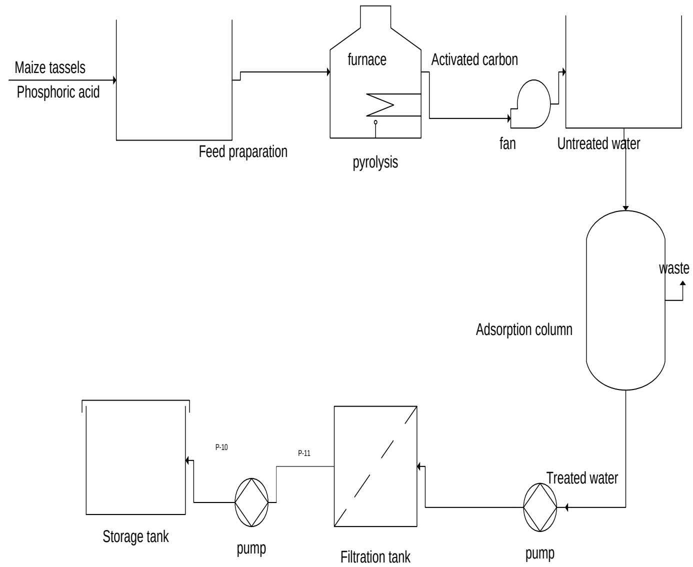

Fig. 4. Industrial process design for zinc ions removal using activated carbon from maize corn stover bio-charcoal

PACKED BED ADSORPTION COLUMN DESIGN

The following design considerations were made for the packed bed adsorption column: materials of construction, volume of the column, diameter of the column, height of the column, mass transfer properties, particle characteristics i.e. pore size, surface area and densities, operating conditions *i.e.* flow rate, feed and product concentration, pressure and time. A summary of the design parameters is shown in Table 1.

Table 1. Summary of the Adsorption Column

Parameter	Description
Function	Lake water treatment
Operation	Continuous
Type	Packed bed
Volume	47.46 m^3
Height	5.145 m
Diameter	3.43 m
Temperature	25^{o}C
Pressure	1atm
Type of packing	Activated carbon from maize corn stover bio-charcoal
Height to diameter ratio	1.5
Material of construction	Carbon steel
Shape	Cylindrical

The material selected for constructing the bio-sorption reactor is carbon steel due to its high strength. It is a material that is capable of withstanding high design stress; it is highly corrosion resistant under humidity and other extreme weather conditions. In addition, it has excellent fire resistance with no toxic fume emissivity. It is generally an appealing material that is both durable and also affordable. A schematic representation of the adsorption column is given in Fig. 5.

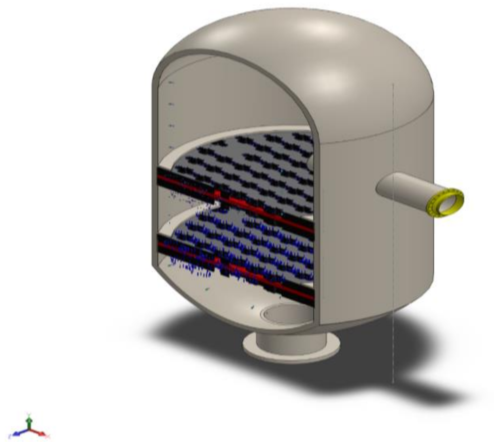

Fig. 5. Cross-sectional view of the adsorption column

ADSORPTION COLUMN PROCESS CONTROL AND HAZOP ANALYSIS

Process Control

Process control enables the engineers to keep their operations running within the optimum and acceptable limits in an economic way whilst ensuring maximum profits. In addition it also ensures the safekeeping of the environment. There ought to be full utilisation of the raw material so as to ensure maximum profits. The energy used has to be low as well; that's why in this project the carbon in maize corn stover will be activated chemically and not physically since the chemical activation uses temperatures that are much lower than the physical activation. Process control is basically done to increase efficiency whilst simultaneously upholding the need to be economic and environmentally friendly. The main control variables that need to be measured and controlled in a packed bed column are:

Air temperature – the temperature should be maintained at room temperature in the adsorption column thus they should be kept at around 25°C. This is to avoid over pumping as well as under pumping of water.

Pressure – pressure should be maintained at 1 atmosphere which is the atmospheric pressure and it is controlled by relief valves.

Flow – the flow of water in the adsorption column. The flow control is usually associated with inventory control in a storage tank or in the adsorption column. Peristaltic pump may be used to control flow rate and this controls by squeezing and releasing pulse flow. The process control diagram is indicated in Fig. 8.

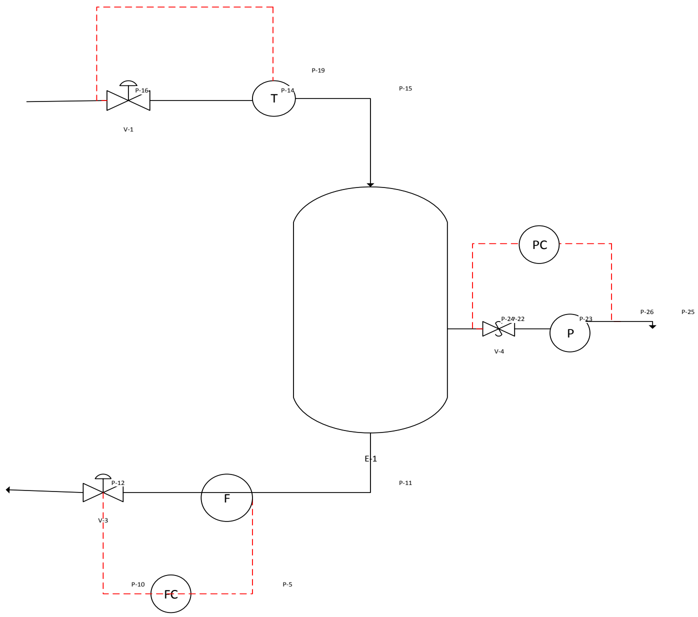

Fig. 6. Process control over the adsorption column

Key: FC-Flow control, PC-Pressure control, TC-Temperature control

Hazard Operability Analysis for an Adsorption Column

The Hazard Operability Analysis (HAZOP) for the adsorption column is indicated in Table 2.

Table 2. HAZOP Analysis for the Adsorption Column

Para-meter	Guide word	Possible cause of disturbance	Consequence of disturbance	Correction of the disturbance
Temper-ature	More of	Very high temperatures experienced due to very high atmospheric conditions	It leads to evaporation of water and therefore low water output	An automated temperature control
	Less of	A high flow rate of the cold untreated water	It slows the rate of the adsorption of the zinc	An automated temperature control
Pressure	More of	Over pumping	Less contact time for the activated carbon and water hence less adsorption will take place	Relief valves and pressure alarms
	Less of	Valve not fully opened, blockage in the pump hindering pumping	The required amount of water to be treated an hour will not be treated thus less water	Clean the pumps regularly and constantly check the valve.
Flow	High	Over pumping	Leads to pressure build up in the adsorption column	Controlling the valves to allow the correct amount of water in the adsorption column
	Low	Non porous backed bed and blocked pumps. Closed valve	Less water is treated than the required amount of water	Cleaning the pumps and changing the packing's frequently as well as checking the valves

ECONOMIC ANALYSIS

Capital Cost Estimation

The capital cost estimation of the project was done using a factorial method for estimation of material cost from prices in the local market. The equation below was used for calculating the total capital cost.

Total capital cost = Fixed capital + working capital.

Calculation of Equipment Cost

The cost of equipment was calculated using the six-tenths rule. The formula that was used is given below in accordance to Lang (1948), as cited in Sinnot (2006),

$$C_1 = C_2\,(S_2/S_1)^n(I_C/I_o)$$

where C_1 is the cost of the equipment in a certain given year, C_2 is the current cost of equipment to be calculated, S_1 is the equipment size for the known cost, S_2 is the equipment size of current equipment, I_C is the current cost index, and I_o is the cost index of the other year of known equipment cost. Values of these quantities were as follows: n =0.6; C_1 = $55 000; S_1 = 1200 000 tonnes per year; S_2 =1 642 500 tonnes per year; I_o = 550.8; and I_C = 567.3.

Since the plant in this project is for treating 4500 m^3 of water per day, then according to calculations it treats 1,642,500,000 litres per year. Then converting that to tonnes to equal units with the equipment used for estimation it becomes 1,642,500 tonnes per year.

$$C_2 = 55\,000(1{,}642{,}500/1{,}200{,}000)^{0.6}(567.3/550.8) = \$68{,}387.39$$

Thus the cost of the adsorption column is $68,387.39

The Factorial Method of Cost Estimation

Capital cost estimates for chemical process plants are often based on an estimate of the purchase cost of the major equipment items required for the process and in this process the major equipment is the adsorption column. The other costs are then estimated as factors of the equipment cost.

The factorial method of cost estimation is often attributed to Lang (1948) cited in Sinnot (2006). The fixed capital cost of the project is given below,

$$C_f = f_L C_e$$

where C_f is fixed capital cost, C_e is the total delivered cost of all major equipment items like the adsorption column, F_L is the Lang factor which depends on the type of process, F_L = 3.1 for a predominantly solids processing plant, F_L = 4.7 for predominantly fluids processing plant, and F_L = 3.6 for a mixed fluids solids processing plant.

In this case it's a fluid-solid system, so the factors to be used are for the fluid-solid system. A summary of the economic indicators is given in Table 3.

Table 3. Economic Indicators for Lake Water Treatment Using Bio-Charcoal

Item	Cost (US$)
Direct costs	215420.28
Labour costs	86168.11
Total capital investment	331747.23
Utilities cost	11162.34
Maintenance and repair	21542.03
Operating labour cost	5581.71
Supervision cost	558.12
Total direct production cost	94655.37
Fixed costs	32313.05
Plant overheads	9465.54
Total manufacturing cost	136433.96
Total production cost	140526.98
Net profit	107757.07
Rate of return	32.5%
Payback period	3.08
Cost of water	$0.18/L

CONCLUSIONS

1. Corn stover has potential to be used as bio-adsorbents in water treatment.
2. Maize corn stover bio-charcoal can remove about 25% of zinc from Lake Water.
3. Preliminary cost estimation for a plant which can treat 4500 m^3 of water per day was found to be economically viable with a rate of return on investment of 32.5% and a payback period of 3.08 years.
4. In addition to that a packed bed adsorption column with two packings was designed as the major equipment of the process. Some vital operational considerations such as the process control and safety of the plant were taken into consideration and operational studies as HAZOP study were thoroughly done on the major equipment so as to ensure the major equipment ‘s safe operation in the plant.

ACKNOWLEDGEMENT

Harare Institute of Technology is thanked for funding this work.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES CITED

Adegoke, K. A. and Bello, O. S. (2015). "Dye sequestration using agricultural wastes as adsorbents," *Water Resources and Industry* 12, 8-2. DOI: 10.1016/j.wri.2015.09.002

Adil, S., Mashiatullah, A., Asma, M., Abid, J., and Ghaffar, A. (2014). "Heavy metal removal efficiency of paper mulberry biochar and commercially available silica powder from simulated industrial wastewater," *Iranica Journal of Energy and Environment* 5(4), 446-452.

Bailey, S. E., Adrian, D. D., Bricka, R. M., and Olin, T. J. (1999). "A review of potentially low cost sorbents for heavy metals," *Water Research* 33(11), 2469-2479.

Behazia, E., Ogunsona, E., Rodriguez-Uribe, A., Mohanty, A. K., Misra, M., and Anyia, A. O. (2016). "Mechanical, chemical and physicochemical properties of wood and perennial grass biochars for possible composite application," *BioResources* 11(1), 1334-1348.

Coulson and Richardson (2002). *Chemical Engineering,* Vol.2, 5th Edition, 225 Wildwood Avenue, Woburn, Butterworth-Heinemann, pp. 902-903.

Inyang, M., Gao, B., Yao, Y., Xue, Y., Zimmerman, A. R., Pullammanappallil, P., and Cao, X. (2012). "Removal of heavy metals from aqueous solution by biochars derived from anaerobically derived biomass," *Bioresource Technology*, 1-7.

Kativhu, C. C. (2013). "Potability of borehole, bottled, and municipal water in Harare," A dissertation submitted in partial fulfillment of the requirements for the Bachelor of Science Honours Degree in Biological Sciences Department of Biological Sciences Faculty of Science and Technology Midlands State University November 2013.

Peters, M. S., and Timmerhaus K. D. (1993). *Plant Design and Economics for Chemical Engineers*, 4th Edition, Singapore.

Perry, R. H., and Green, D. (1984). *Perry's Chemical Engineering Handbook*, 6th Ed., McGraw-Hill, New York.

Sinnot, R. K. (2006). *Chemical Engineering Design, Coulson and Richardson's Chemical Engineering Series*, 4th Edition, Elsevier, India.

Tau, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y. and Yang, Z. (2015). "Application of biochar for the removal of pollutants from aqueous solutions," *Chemosphere* 125, 70-85.

www.chemengonline.com

Zhang, Y., and Luo, W. (2014). "Adsorptive removal of heavy metal from acidic wastewater with biochar produced from anaerobically digested residues: Kinetics and surface complexion modelling," *BioResources* 9(2), 2484-2499.

Zvinowanda, C. M., Agyei, N. M., Okonkwo, J. O., and Shabalala, P.N. (2009). "A novel adsorbent for heavy metal remediation in aqueous environment," *International Journal of Environmental Science and Technology* 6(3), 425-434.

Article submitted: June 13, 2016; Peer review completed: August 5, 2016; Revised version received and accepted: October 10, 2016; Published: December 20, 2016.