Sugarcane Bagasse and Orange Peels as Potential Low-Cost Bio-Sorbents for Removal of Manganese(II) In Water

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Abstract: High concentration of Mn in drinking water is a significant public health problem thereby calling for the need to reduce it to an acceptable level as required by regulatory bodies. This study was motivated by the need to evaluate the potential of low-cost and reusable bio-sorbents: Orange peels (OPs) and sugarcane bagasse (SCB) for the removal of Mn from simulated aqueous solution and water. The solid:liquid ratio of 30 mg:100 mL was applied, and the results revealed that OPs was able to remove 80.95% of Mn(II) at an optimum contact time of 10 min while SCB was able to remove 96.5% of Mn (II) at an optimum contact time of 30 min. The bio-adsorbents were characterized using, Fourier-transform infrared (FTIR) spectroscopy, scanning electron microcopy (SEM) hyphenated to energy-dispersive spectroscopy (EDS), powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA). From the findings of this study, it follows that the use of OPs and SCB could potentially yield the desired result in Mn removal from water.

***Keywords*:** bio-sorbents, Manganese, orange peels, Sugarcane bagasse, manganese, water

I. INTRODUCTION

The level of potentially toxic elements (PTEs) in drinking water is still over the limitations set by regulatory bodies in several nations globally, even in the modern period of developing technology. The elevated concentration of PTEs in drinking water causes waterborne diseases which are very significant to public health since they are sources of various pathological conditions, including cancer, neurological disorders, immunodeficiency amongst others [1].

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Specifically, drinking water with high levels of Mn lead to memory loss, learning and behaviour problems in children [2] while in adult, high level of Mn in drinking water is responsible for disorder similar to Parkinson's diseases [2]. High concentrations of manganese(ll) impact the color and taste of water, rendering its aesthetic quality unacceptable [3]. Water treatment has been designated as a global priority as a result of these pathological conditions and an increase in waterborne diseases related deaths.

Following the human health effects associated with elevated metals concentration of Mn in water, various methods are currently being used to remove Mn and other PTEs in water. These methods include chemical precipitation [4], ion exchange [5], reverse osmosis [6], membrane technology [7].However, they are not cost-effective, at time not environmentally friendly due to the generation of toxic sludge [8]. Biological adsorption using agricultural by-products is being investigated due to their availability and low cost. This study was therefore motivated by the need to investigate the potential of low-cost bio-sorbents (OPs and SCB) for the removal of Mn from simulated aqueous solutions and water.

A. Agricultural by-products (SCB and OPS) as bio-sorbents

Bio-sorbents are biological materials that are employed to actively remove contaminants from aqueous solutions. Orange peel is abundant in the soft drink industry and is typically discarded. The usage of orange peel as a bio-sorbent material has a lot of potential due to its main components, cellulose, pectin, hemicellulose, and lignin, which contain functional groups as possible metal binding sites[9], [10].

Bagasse fly ash, an industrial solid waste produced by the sugar industry, poses a significant disposal problem and is being employed as a filler in construction materials. The main components of bagasse pitch are cellulose, pentosan, and lignin. This makes it a good candidate for the removal of toxic metals [11].The oxygen functional groups in bio-sorbents are particularly significant since they control the surface properties and thus the bio-sorbents' quality.

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II. METHOD

A. Preparation of 1000 mg/L Mn(II) solution

A 1000 mg/L Mn(II) stock solution was prepared by dissolving 3.076 g of manganese(ll) sulfate monohydrate in 1000 mL and topping it to its volume with deionized water.

B. Preparation of 50 mg/L Mn(II) solution

To prepare 100 ml of 50 mg/L Mn(ll), 5 mL of 1000 mg/L was diluted to 100 mL with deionized water.

C. Investigation of the removal of 50 mg/L Mn(II) with a change in pH

The effect of pH was made at pH 3, 4,5, 6, 7 and 8. The 50 mg/L solution's original pH value was 4.87. A few drops of 65% HNO_3 were added to achieve pH 3 and 4. In order to obtain pH 5, 6, and 7, a few drops of 0.50 M NaOH were added. OPs and SCB were added to the solutions in steady doses of 30 mg each, and the mixture was allowed to react for one hour. Beyond pH 7, a precipitate was seen, hence the effect of pH could not be investigated.

D. Investigation of the removal of 50 mg/L Mn(II) with a change in contact time

Investigations into the impact of contact time were conducted for contact times of 30 min, 1 h, 1 h and 30 min, 2 h, and 3 h. The pH of the solutions was adjusted to pH 5. Orange peels and SCB were added to the solutions in steady doses of 30 mg each.

E. investigation of the removal of Mn(ll) with a change in adsorbent dosage

The following dosages of OPs and SCB were utilized to examine the impact of adsorbent dosage on the percentage The TGA results demonstrate the moisture loss as well as the evolution of various light molecules, such as water, up to 200 °C for OPs. The mass loss for OPs was 6.887% and this is consistent with the degradation of cellulose and hemicellulose components in OPs. The last region of degradation shows that there is 81.46 % volatile matter in OPs, and this corresponds to the sample's lignin content degrading. The digestion is enhanced by the fact that cellulose is the easiest natural polymer to break down into its constituent monomers. The **Fig 1** also depicted that there are two regions for both raw and Mn (II) reacted SCB. The first region of the TGA curve ranges from 30 to 200 ˚C for both graphs and this can be attributed to the removal of free moisture and mass loss and the removal of bound moisture and evaporation of small amounts of volatile matter, totalling 4.084% of the weight loss of SCB. The greatest devolatilisation and greatest mass loss take place in the second region. It exists between 200 and 850 ˚C. According to [12]**,** the degradation of hemicellulose and cellulose occurs between temperatures of 200 and 350 ˚C. The subsequent mass loss in this part represents the breakdown of cellulose followed by the degradation of lignin and

removal of Mn: 10, 30, 50, 100, 150, 170, and 200, mg. The pH of the solution was adjusted to pH 5 for 10 min when using OPS and 30 min when SCB was used.

The solutions were then filtered using filter paper with a 0.45 µm diameter. The filtrate was then put through an FAAS analysis with the prepared standard solutions utilizing an air/acetylene flame, an analytical wavelength of 279.5 nm, and a slit width of 0.5 nm. The optimum Ph, contact time and adsorbent dosage for removing Mn(II) with SCB and OPS was subsequently established [12].

III. RESULTS AND DISCUSSION

F. Thermogravimetric results of orange peels

The TGA results of bio-sorbents are shown in the following Fig 1

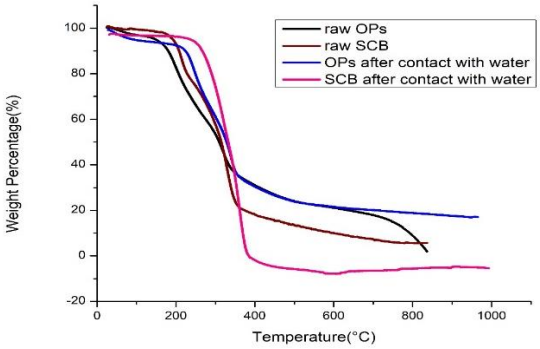

Fig 1: TGA results of SCB and OPs

Pentosan. This devolatilisation totals 90.94 % mass loss. The remainder of the sample weight, (4.976%), is left as waste.

G. Scanning Electron Microscopy – Energy Dispersive Spectroscopy

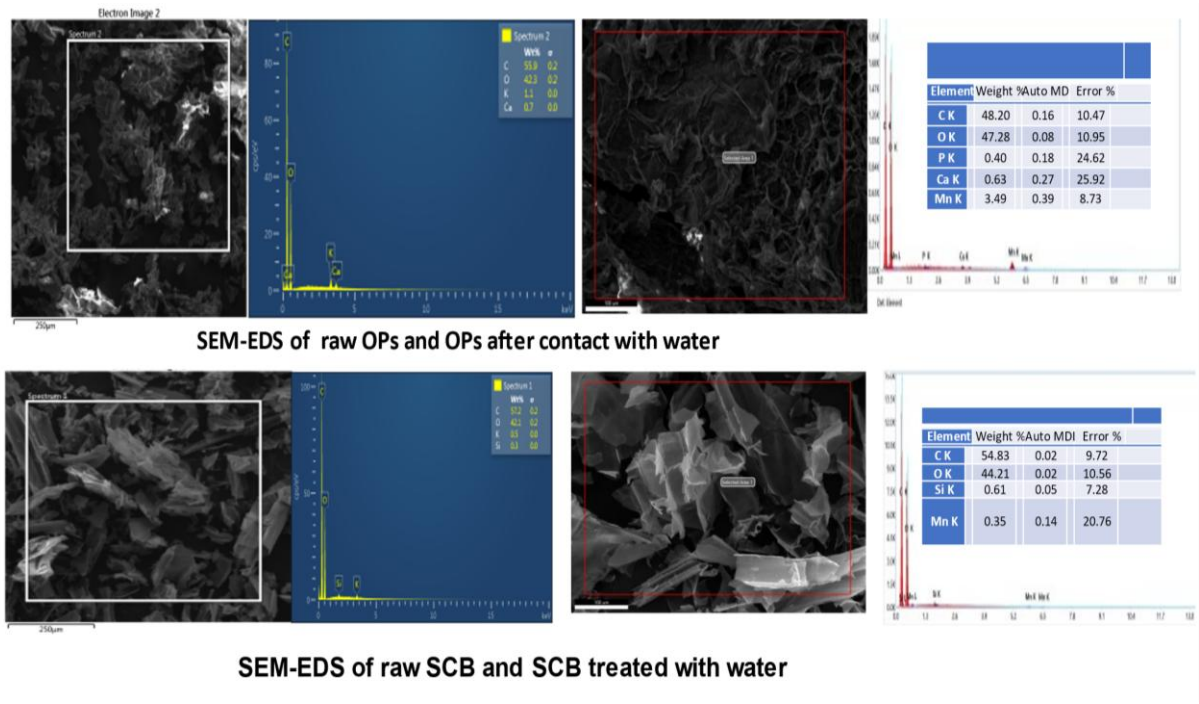

Fig 2: SEM EDS of OPS and SCB before contact with water

The **Fig 2** demonstrated the irregular and porous surface of OPs. The SEM-EDS of OPs after contact with Mn (II) shows an irregular and porous surface while the SEM of raw OPs shows a sort of large mass occupying the entire surface. The EDS results show that the elements C, O, K, and Ca were present in both raw and Mn (II) reacted OPs while Mn was only present in Mn (II) reacted OPs thereby confirming that OPs adsorbed Mn (II) from water.

The EDS results of SCB shows that C, O, Si, and K were found in raw SCB while C.O. Si and Mn were found in water reacted SCB. This also confirms that Mn was indeed adsorbed onto the surface of SCB, but the low percentage (0.35%) of Mn shows that SCB is a weaker adsorber compared to OPs (over 3%).

Fig 2 also shows the morphological characteristics of the raw SCB and Mn (II) reacted SCB. The SEM image of raw SCB demonstrate an uneven structure while the SEM image of water reacted SCB show a sort of palette occupying the entire surface.

H. Fourier Transform InfraRed

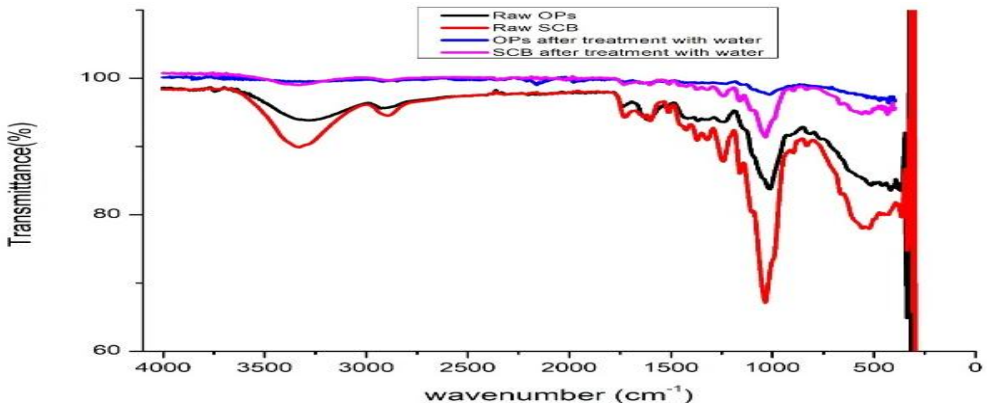

Fig 3: FTIR of the bio-sorbents before and after treatment with water

From **Fig 3**, it follows that numerous functional groups were present on the surface of the bio-sorbents. The spectra show bands shifting and potential hydroxyl group involvement near the wide peaks 3450 cm^{-1} which could be from a carboxylic acid. the result of The two spectra show that there are many functional groups present in raw OPs and SCB. After reaction with water, very few functional group appears with the first peak at 1235.04 cm^{-1} characteristic of a C-O carboxyl band. The peaks below 1000 cm^{-1} could be showing the presence of Mn as metals appear in the lower regions of the spectra revealed the presence of hydroxyl groups of carboxylic acid, in cellulose, hemicellulose, and pectin.

I. Powder X-ray Diffraction results

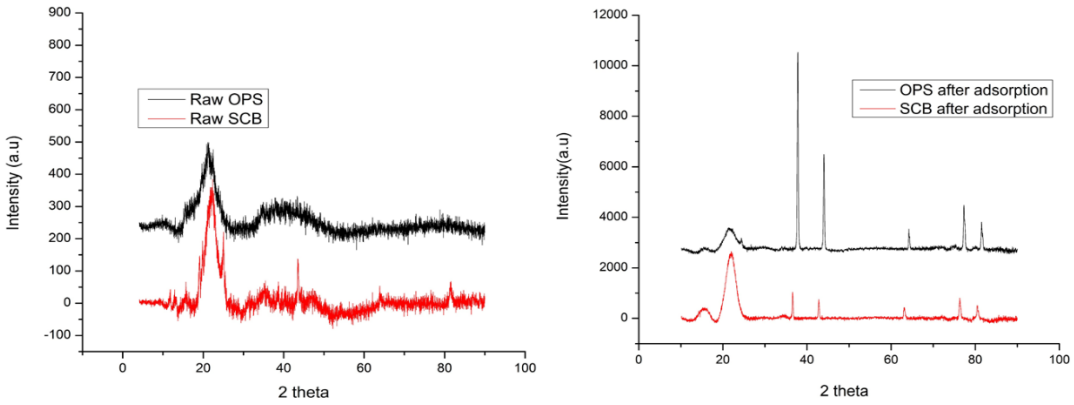

Fig 4: pXRD of SCB and Ops before and after treatment with water

The results from **Fig 4** revealed that Cu served as the anode material, and the elevation ranged from 2θ = 10° to 80°. There are 2 distinct peaks in the PXRD spectra at 2θ= 25˚ and 39˚. As expected for organic materials, the OPs structure is almost entirely amorphous. The diffractogram peaks at about 2θ = 19° may be hemicellulose, and the sharp peaks at about 2θ = 22° are characteristic for cellulose.

Fig 4 is a depiction of the diffraction pattern of SCB, which reveals an intensity peak between 2θ=25˚, which is typical of amorphous material (undoubtedly evident of solid material, which is classified as stable, solid, and non-crystalline material). Cu served as the anode material, and the elevation ranged from 2θ = 10° to 80. The diffraction peak at 22.5˚ is characteristic of amorphous cellulose. The long peaks appearing in OPs and SCB after reaction with water could be indicative of Mn (II) potentials of OPs and SCB show all negative values across the studied pH range, indicating that the surface of bio-sorbents are well-suited for interacting with metal cations.

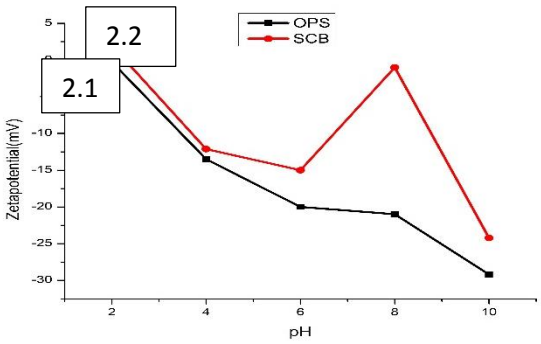

Fig 5: Zeta potential of OPs and SCB

Influence of pH, contact time and adsorbent dosage on Mn(II) removal from aqueous solutions

J. Effect of pH on Mn(II) removal

The pH effects on Mn(II) removal are presented in **Fig 6.** It shows that pH 5 produced the greatest percentage removal of Mn(II) for both OPs and SCB. Removal of Mn(II) using OPs was 77.61% at pH 5 while Mn (II) removal by SCB was 83.10%. Therefore, pH 5 was chosen as the optimum pH for the removal of Mn(ll) for both OPs and SCB. In an aqueous solution, Mn(ll) exists as the ion Mn^{+2}, which interacts with a negatively charged adsorbent. Due to the formation of positive charge on the adsorbent's active sites, Mn(II) adsorption at lower pH was minimal. Since there is a significant concentration of H^{+} ions at low pH levels, they compete with the Mn^{2+} ions for binding to the negatively charged surface of the adsorbent in most of the solution.

K. Zeta potentials results

The adsorbent's surface charge density is represented by the zeta potential. The zeta

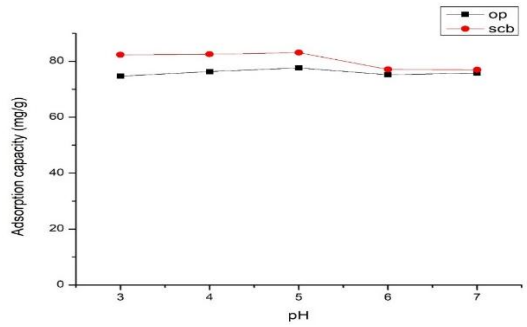

Fig 6: results of the influence of pH on the adsorption capacity

The results of Mn(ll) adsorption on OPs demonstrated that equilibrium could be reached in just 10 min and that further increases in time had no effect on adsorption. In the case of SCB, equilibrium is reached after 30 min, and adsorption continued for only a brief while after this due to more free adsorption sites in the beginning, but over time, those sites will diminish, and the rate of adsorption will stabilize or slow down because of the solute's slower diffusion inside the adsorbent. This study shows that OPs had a higher Mn(ll) removal efficiency than SCB while using less time.

L. The effect of adsorbent dosage on the removal of Mn(II)

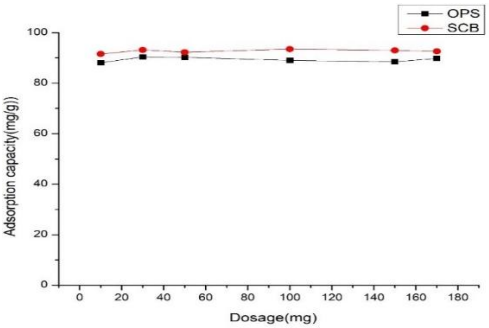

Fig 8: Effect of adsorbent dosage on Mn removal

Fig 8 shows that as bio-sorbent dosage is increased, more adsorbent sites are created, increasing the surface area in contact with Mn (ll). At the optimum dose of 30 mg for the OPs adsorbent, 90.40% removal was seen, while at the optimum dosage of 30 mg for the SCB adsorbent, 93.18% removal was shown. With less adsorbent, SCB has a higher removal efficiency than OPs. The lowest percentage of Mn(ll) ions was achieved by both bio-sorbents at an adsorbent dosage of 10mg and this is because of the few active sites on the bio-sorbents associated with a small dosage. High percentage removal was seen at higher adsorbent dosages for OPs, although only 100 mg of SCB and 150 mg of OPS guarantee the preservation of the water's aesthetic quality because the color of water becomes yellow when OPS are used at high dosages and white when SCB is used at high dosages when you exceed these values.

IV. CONCLUSION

The findings revealed that OPs and SCB were efficient in removing Mn (II) in simulated water samples. However, more investigations must be conducted to assess their feasibility in large scale.

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