Characterization of Water Hyacinth Powder Using FTIR Spectroscopy and the Adsorption Behaviour of Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Ni$^{2+}$ and Cr$^{2+}$ in Aqueous Solution

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Authors’ contributions

This work was carried out in collaboration among all authors. Author JOO designed the study while the author JMM performed the analysis. Author AOY wrote the protocol and read the first draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

The adsorption behavior of selected metal ions on water hyacinth powder was investigated by Fourier Transform Infrared (FTIR) spectroscopy. Water hyacinth powder was used as an adsorbent due to its popularity, low cost and ease of availability. Water hyacinth stems were dried and ground to a powder. Batch adsorption experiments were conducted at room temperature by adding known concentrations of Pb$^{2+}$, Cd$^{2+}$, Cr$^{3+}$, Zn$^{2+}$ and Ni$^{2+}$ to 5 g of water hyacinth powder in different test tubes and allowed to stand for the same time respectively. Adsorption is one of the methods used to remove heavy metals from aqueous solutions and wastewaters. FTIR analysis was performed to identify the functional groups in the water hyacinth powder using the KBr disc method. The study showed a strong broad absorption band in the region of 3300-3200 cm$^{-1}$ which is characteristic of O-H stretching vibrations of the adsorbed water molecules at the surface of raw water hyacinth powder particles. Other peaks appeared at 1732 cm$^{-1}$ which corresponded to C=O stretching vibrations while the band at 1396 cm$^{-1}$ could be attributed to C-H bonds. The functional groups identified were: C-H; O-H; C=O or C-O. After adsorption there was a disappearance, reduction or a shift in the adsorption bands depending on the type of metal ion. Lead for example showed a strong absorption band in the region of 1732 cm$^{-1}$ which is characteristic of C=O stretching bond.

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structure which is found in esters and carboxylic acids. The disappearance of the peaks indicated that the H atom present in the functional groups of the raw water hyacinth powder could have been substituted with lead ion. The intensity of the adsorption bands reduced for all the metals confirming that functional groups were responsible for adsorption of the heavy metal ions on to the material.

Keywords: Water hyacinth powder; characterization; biosorption; functional group; heavy metal.

1. INTRODUCTION

FTIR spectroscopy is a powerful technique that can be used in diagnostic analysis of water hyacinth powder before and after adsorption of metal ions. It is a rapid and non-destructive technique that has been used to characterize the functional groups responsible for adsorption of heavy metal ions [1,2]. This is because the peaks in the spectral regions are characteristic of specific bonds that can be used to identify the presence of a particular functional group or changes in that particular functional group. Peaks are believed to arise from molecular deformations. These may be characteristic of molecular symmetry or may involve several bands from the multiple bonds which are deforming simultaneously. The hazardous heavy metals can affect the human physiology and biological systems [3] hence it is important to frequently evaluate their occurrence in the environment. Heavy metals are introduced to aquatic systems through wastewater and are a major health concern due to their toxic impacts on living organisms. The concentrations which accumulate within bodies of fish etc are a threat to food security. FTIR technique helps to elucidate the functional groups that participate in the heavy metal adsorption. The use of plant materials in the removal of heavy metals from wastewaters has been reported [4,5]. Adsorption is one of the remediation technologies that has proved effective in the removal of pollutants from aqueous solutions and wastewater. Activated carbon is the most commonly used adsorbent however it is too expensive hence its usage will depend on its local availability [6]. Water hyacinth (Eichhornia crassipes) is a common aquatic plant in Lake Victoria and dams in Kenya. It is readily available and therefore in this study it has been used as a low cost adsorbent to evaluate its adsorption behaviour in the presence of metal ions in aqueous solution. This is also because biomaterials have been reported as low cost and sustainable adsorbents that could be used for water treatment applications [7].

FTIR spectroscopy was used to identify the functional groups in water hyacinth powder that are responsible for heavy metal adsorption. FTIR was used because it has a high reliability even with small amounts of material and it is analytically sensitive.

The presence of heavy metals in the environment which are toxic even at low levels has raised a lot of health concerns. The objective of this study was therefore to characterize the water hyacinth powder before and after heavy metal absorption using FTIR spectroscopy in order to elucidate the adsorption capacity of the water hyacinth powder. The spectra of the water hyacinth powder (unloaded) and that which is loaded with the heavy metal ions (Pb\(^{2+}\), Cd\(^{2+}\), Cr\(^{3+}\), Zn\(^{2+}\) and Ni\(^{2+}\)) were compared in order to establish any structural changes in the functional groups due to adsorption.

2. MATERIALS AND METHODS

Water hyacinth (Eichhornia crassipes) was collected from a beach point on Lake Victoria and the stems were sliced into pieces and cleaned thoroughly with tap water in order to remove dust and any other contaminants. The stems were then rinsed with distilled water and dried until sufficiently dry. The water hyacinth pieces were further oven dried at 110°C for a day to remove moisture completely. The dry fractions of the water hyacinth stem were ground into powder using mortar and pestle and the particles were sieved using 300µm sieve and stored for subsequent use.

2.1 FTIR Analysis of Raw Water Hyacinth Powder

A 0.5 g water hyacinth powder was ground until it was fine. The sample was mixed with KBr and pressed to form a pellet and examined with FTIR spectrometer (Model: IR Afinity IS Class 1) according to standard procedures. The scanning was performed in the range of 4000-400 cm\(^{-1}\) wave numbers to determine the functional groups responsible for metal ion adsorption.
2.2 FTIR Analysis of Metal Loaded Water Hyacinth Powder

The metal loaded adsorbent was obtained after a series of batch adsorption studies performed at room temperature. The maximum pH value for metal adsorption was considered. The water hyacinth (adsorbent) residue after adsorption of metal ions (Pb$^{2+}$, Cd$^{2+}$, Cr$^{3+}$, Zn$^{2+}$ and Ni$^{2+}$) was filtered and dried in an oven at 110°C for a day to remove moisture completely. A 0.5 g of dry fractions of metal loaded adsorbent were ground into fine powder using mortar and pestle and examined using FTIR spectroscopy according the FTIR standard procedures. The scanning was done in the range of 4000-400 cm$^{-1}$. The structural changes in the spectra of the functional groups were compared with those of the raw water hyacinth powder to assess the adsorption behavior of the different heavy metal ions.

3. RESULTS AND DISCUSSION

The Fourier transform Infrared spectroscopy (FTIR) showed changes in the functional groups present in the adsorbent in the 4000-400 cm$^{-1}$ range. The FTIR spectra of the adsorbent after adsorption of the metal ions (Ni$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Zn$^{2+}$ and Cr$^{3+}$) are give in Figs. 1-5. For all the metals after adsorption, there was a shift, reduction or a disappearance of the spectra depending on the type of the metal. In Figs. 1a and 1b the spectra of Pb before and after adsorption are compared.

The study showed that there was a strong broad absorption band in the region of 3300-3200 cm$^{-1}$ (Fig. 1a) for the raw water hyacinth powder before adsorption. The presence of this band is characteristic of O-H stretching which is attributed to alcohol, water, acid and phenols [5]. After adsorption the peak is absent (Fig. 1b). The disappearance of the peak could be attributed to H atom in the functional groups which has been substituted with Pb$^{2+}$ ion [8]. The strong absorption band in the region of 1732 cm$^{-1}$ (Fig. 1a) is characteristic of C=O stretching bond structure which could be attributed to esters and carboxylic acids [7]. After adsorption the peak is absent (Fig. 1b). The strong band in the region of 1396 cm$^{-1}$ is characteristic of bending of the C-H bond in structures that contain alkanes or both C-O stretch and O-H deformation in carboxylic acids [8]. The disappearance of the peaks (1732 cm$^{-1}$ and 1396 cm$^{-1}$ in Fig. 1b) could be because lead ions are bound to hydroxyl, carboxyl and carboxylic functional groups [9]. The strong band at 1033 cm$^{-1}$ is characteristic of C-O stretch in

![Fig. 1. a= Water hyacinth powder before adsorption; b= spectrum of water hyacinth after Pb$^{2+}$ ions adsorption](image-url)
structures which contain carboxylic acids, reduced in intensity upon adsorption of lead ethers, ethers and alcohol [10]. The band ions.

Fig. 2. Water hyacinth powder before adsorption; b= spectrum of water hyacinth loaded with Cd\textsuperscript{2+} ions

Fig. 3. Water hyacinth powder; b= spectrum of water hyacinth loaded with Ni\textsuperscript{2+} ions
The spectra for Cd$^{2+}$ ions adsorbed on the water hyacinth powder (Fig. 2b) showed that the bands for O-H (3300-3200 cm$^{-1}$) and C=O (1732 cm$^{-1}$) band disappeared. This could be due to participation of hydroxyl, and Carbonyl groups during cadmium adsorption [11].
The strong band in the region of 1396 cm\(^{-1}\) is a characteristic of bending of the C-H bond in structures that contain alkanes or both C-O stretch and O-H deformation in carboxylic acids [8]. The band reduced in intensity upon adsorption of cadmium ions.

The strong peak at 1033 cm\(^{-1}\) is ascribed to the C-O stretch in structures which contained carboxylic acids, ethers, ethers and alcohol [12,13]. The band disappeared due to adsorption of cadmium ions.

The spectra of the water hyacinth powder before and after adsorption of Ni\(^{2+}\) ions are presented in Fig. 3.

Fig. 3a is the spectra of the raw water hyacinth powder. It showed a strong broad absorption band in the region of 3300 to 3200 cm\(^{-1}\). The adsorption of Ni\(^{2+}\) ions caused O-H (3300 to 3200 cm\(^{-1}\)) and C-H bands (1396 cm\(^{-1}\)) to disappear. Ni\(^{2+}\) ions adsorption was observed to cause a shift of the C=O peak from 1732 cm\(^{-1}\) to 1724 cm\(^{-1}\).

The adsorption peak 1033 cm\(^{-1}\) reduced in intensity after adsorption of nickel ions.

The spectral changes during the adsorption of Cr\(^{3+}\) ions are shown in Fig. 4. The study showed that adsorption of Cr\(^{3+}\) caused the O-H band peak at 3300-3200 cm\(^{-1}\) to disappear (Fig. 4b). It was also observed that the peaks at 1732 cm\(^{-1}\) and 1396 cm\(^{-1}\) disappeared while the peak 1033 cm\(^{-1}\) reduced in intensity. The observation was in agreement with the studies conducted by [14] using other biological materials. The presence of functional groups in an adsorbent had also been reported [15] to be responsible for complex formation of Cr (VI) ion during the FTIR analysis of rice waste. The changes in the spectral bands for Zn\(^{2+}\) ions are shown in Fig. 5.

The O-H band in the region of 3300-3200 cm\(^{-1}\) (Fig. 5a) reduced in intensity after adsorption of Zn\(^{2+}\) ions (Fig. 5b). The reduction in intensity could be attributed to zinc ions being attached to the functional groups in the region 3300-3200 cm\(^{-1}\) which reduced the peak height hence the absorption band stretching to a lesser degree [16]. The adsorption of Zn\(^{2+}\) ions caused C=O to shift from 1732 to 1720 cm\(^{-1}\) while the band at 1396 cm\(^{-1}\) shifted to 1395 cm\(^{-1}\). The shifting of bands showed that Zn\(^{2+}\) ions were adsorbed by the relevant functional groups [4]. The adsorption of zinc ions caused the C-O band to reduce in intensity [16,17].

The use of FTIR spectroscopy has shown that during adsorption of heavy metal ions by water hyacinth powder, absorption bands either disappeared or reduced in intensity. The observations are summarized in Table 1.

In Table 1, it is observed that during the heavy metal adsorption on the water hyacinth powder, there was a reduction in the intensity, disappearance or a shift in the functional groups confirming that the functional groups are responsible for the metal ion adsorption [18,19].

| Wave number(cm\(^{-1}\)) | Functional groups identified in the raw water hyacinth | Changes in spectral structure after adsorption of the metal |
|--------------------------|-------------------------------------------------------|-------------------------------------------------------------|
| 3300 - 3200              | O-H, carboxylic acid, alcohol, water, phenols         | Disappeared | Disappeared | Reduced intensity | Disappeared | Disappeared |
| 1732                     | C=O acid, esters                                      | Disappeared | Shifted (1724 cm\(^{-1}\)) | Shifted (1720 cm\(^{-1}\)) | Disappeared | Disappeared |
| 1396                     | C-H bending (alkanes) or C-O stretch and O-H deformation (acids) | Disappeared | Disappeared | Shifted (1395 cm\(^{-1}\)) | Reduced intensity | Disappeared |
| 1033                     | C-O Alcohols, Acids, Esters, Ether                    | Reduced intensity | Reduced intensity | Reduced intensity | Disappeared | Reduced intensity |

Table 1. Changes in spectral structure when various heavy metals are adsorbed on the water hyacinth
4. CONCLUSION

FTIR spectroscopy confirmed the presence of various functional groups in the water hyacinth powder which are capable of adsorbing metal ions. The study showed that during adsorption, spectral bands were reduced, disappeared or shifted their positions depending on the nature of the metal. The differences in spectral intensities after adsorption could be attributed to the size of the metal ions, availability of metal ions at the sight or on the electronegativity of the metal. The spectral intensities were observed at different frequencies indicating that bonds formed could have different energies [19]. The reduction in spectral intensities could have contributed to adsorption process. Further, the study showed that water hyacinth (*Eichhornia crassipes*) is a promising low cost adsorbent and could play an important role in the removal of heavy metals from water.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Csernatoni F, Socaciu C, Pop MR, Bunghez F. Application of FTIR spectroscopy for fingerprinting bioactive molecules in a nutraceutical PROMEN, comparatively with plant ingredients. Journal of Food Science and Technology. 2013;70(1):68-69.
2. Sahira J, Pokharel BP. preparation and characterization of activated carbon from lapsi (*Choerospondias axillaris*) seed stone by chemical activation with potassium hydroxide. Journal of the Institute of Engineering. 2012;9(1):79–88.
3. Ayhan D. Heavy metal adsorption onto agro-based waste materials: A review. J. Hazard. Mater. 2008;57:220-229.
4. Njoki MA, Mercy G, Nyagah G, Gachanja Fourier transform infrared spectrophotometric analysis of functional groups found in *Ricinus communis*. L and *Cucurbita maxima Lam.* Roots, Stems and Leaves heavy metal adsorbent. International Journal of Science Environment. 2016;5:861-871.
5. Monteiro SN, Margem FM, Loiola RL, Assis, Oliveira MP. Charaterization of banana fibers functional groups by infrared spectroscopy. Materials Science Forum. 2014;775-776.
6. Bailey SE, Olin TJ, Brickaz RM, Adrian A review of potentially low-cost sorbents for heavy metals, Water Res. 1999;33:2469-2479.
7. Ali HR, Hassaan MA. Applications of bio-waste materials as green synthesis of nanoparticles and water purification Advances in materials chemistry. 2017; 1(1):6-22.
8. Ibrahim M, Nada A, Kamal DE. DFT and FTIR spectroscopic study of carboxyl group. Indian Journal of Pure and Applied Physics. 2005;43:911-917.
9. Ibrahim M, Kuhn O, Scheytt T. Molecular spectroscopic study of water hyacinth dry matter. The Open Chemical Physics Journal. 2009;2:1-6.
10. Mathias E, Evangelou MWH, Scaeffer A. A cyanide phytoremediation by water hyacinth (*Eichhornia crassipes*). Chemosphere. 2007;66:816-823.
11. So LM, Chu LM, Wong PK. Microbial enhancement of Cu**2+** removal capacity of *Eichhornia crassipes* (Matt) Chemosphere. 2003;52:1499-1503.
12. Nuhoglu Y, Malkoc E. Thermodynamics and kinetics studies for the enviromentaly friendly Ni (II) biosorption using waste pomance of olive oil factory. Bioresources Technology. 2009;100:2375-2380.
13. Hasan SH, Talat M, Rai S. Sorption of cadmium and zinc from aqueous solution by water hyacinth (*Eichhornia crassipes*) Bioresources Technology. 2007;98:918-928.
14. Gobran A, Siddig TK, Hago A. Determination of heavy metals in soil samples from Tuti Island Khartoum, Sudan. Red sea. University Journal of Basic and Applied Science. 2017;2(3):1-12.
15. D'Souza L, Devi P, Shridhar DM, Naik CG. Use of fourier transform infrared (FTIR) spectroscopy to study Cadmium-induced changes in Padina tetrastromatica (Hauck) Analytical Chemistry Insights. 2008;3:135–143.
16. Hasan SH, Talat M, Rai S. Sorption of Cadmium and zinc from aqueous solution by water hyacinth (*Eichhornia crassipes*). Bioresources Technology. 2007;98:918-928.

17. Durwe A, Chandra N. FTIR analysis of bacteria biomass in response to heavy metals stress. International Journal of Biotechnology Photon. 2014;112:386-391.

18. Liu T, Hou JH, Wang JB, Wang W, Wang, XY, Wu JL. Bio-sorption of Heavy metals from aqueous solution by the novel Biosorbent Pectobacteriu; 2017.

19. Naiya TK, Singha B, Das SK. FTIR study for the Cr(VI) removal from aqueous solution using rice waste. International Conference on Chemistry and Chemical Process, IPCBEE. IACSIT Press, Singapore. 2011;10.

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