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Research Article

Removal of Heavy Metals using Biocoagulants for Wastewater Treatment: Characterization and Adsorption Studies

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ABSTRACT

Wastewater is of major concern especially in developing country like Nigeria. Wastewater commonly consist of heavy metals such as Zinc, Cadmium, Chromium, Lead, and Iron which proves to be highly unwanted due to their toxicity, mutagenic and carcinogenic properties. In this work, the bioadsorbent was prepared from the biocoagulants for the removal of heavy metals in wastewater. The prepared bioadsorbent before adsorption (MOP) and after adsorption (MOP1) were characterized using, Fourier Transform Infra-Red, Energy Dispersive X-ray and Scanning Electron Microscopy to determine the functional group, surface morphology and elemental composition respectively. The resulting adsorbent were tested for the adsorption of Zinc, Cadmium, Chromium, Lead, and Iron. Furthermore, characterization showed that the presence of OH-, NH₂ and C=O functional groups present before adsorption in MOP enhance the removal of metal. The SEM images showed the presence of micro pores while the presence of high Carbon content in the prepared MOP enhanced the heavy metal uptake. A maximum adsorption capacity of 7.9 mg/g was obtained for Lead while Chromium, Iron, Zinc and Cadmium have adsorption capacities of 7.2 mg/g, 8.0 mg/g, 8.0 mg/g and 7.5 mg/g respectively.

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INTRODUCTION

Pollution is one of the major issues affecting water dearth in Nigeria. The greatest risk associated with wastewater in Nigeria is the presence of Microbial Pathogens and Heavy Metals which proves to be highly unwanted due to their toxicity, mutagenic and carcinogenic properties. Several reports have shown that the presence of heavy metals in water even at low concentrations are responsible for producing illness such as respiratory problems, dermal damage and many types of cancer (Al-Qahtanim, 2015; Pourgheysari *et al.*, 2012; Babel and Kuniawan, 2003). There are various methods of eliminating heavy metals in wastewater like Adsorption, Chemical precipitation, Membrane separation and amongst others. Of these methods, Adsorption process has proven to be more advantageous due to its efficiency, working flexibility, low cost and high quality product purification (Ghaedi *et al.*, 2012).

Due to the contamination of heavy metals, microorganism, plant nutrient and sediment, there is need to develop or produce Coagulants from natural sources for effective and low cost treatment of Wastewater. Biocoagulant are low cost materials which are non-toxic and biodegradable. The biocoagulant used in this studies are: Moringa, Okra and Pumpkin. The seeds of these biocoagulant are mostly not utilized and are disposed as waste.

Moringa is a plant that exist in the family of Moringaceae which is also known as horseradish tree family. *M. oleifera* seed, has been applied for wastewater corrections due to it non- toxicity (Bina *et al.*, 2010; Alo *et al.*, 2012; Eman *et al.*, 2014). In this way, Moringa seeds were used as alternative natural materials for wastewater treatment. Moringa seed further showed coagulant activity. A number of researchers used Moringa seed (MO) as an adsorbent for removal of heavy

metals from a solutions. It is found that MO is a good material for adsorption (Ravikumar and Sheeja, 2013). Pumpkin is one of the member of Cucurbitaceae family which is a vegetable fruit. Pumpkin seed also known as *Egusi* in West Africa is widely consumed as a diet. Several reports show that the pumpkin seed affects the uptake of heavy metals and good coagulation capabilities (Fahmi *et al.*, 2014; Swelam *et al.*, 2015, Usman, *et al.*, 2016). Okra (*Abelmoschus esculentus* L. Morench) is a vegetable that belongs to the family of malvaceae; it is mostly grown in the tropics, subtropics and warmer area. Okra is an important crop found widely in the Northern parts of Nigeria. It was mainly consumed as food in Nigeria. The seed of the okra seed can be used not only for feeding, medicine, but to be used as adsorbent in the adsorption process to remove heavy metals from wastewater (Mohsen, 2007)

The objective of this paper is to prepare a composite bioadsorbent using the seeds of Moringa, Okra and Pumpkin. In addition, the prepared bioadsorbent will be characterized using FTIR, SEM and EDX; and subsequently utilized for the adsorption of Lead, Cadmium, Zinc, Chromium and Iron in wastewater.

MATERIALS AND METHODS

Preparation and Adsorption studies

The precursors used in this study are Moringa seed, Okra seed and Pumpkin seed as shown in Figure1. These materials were sorted and washed severally with water, dried, sieved in a No. 30 mesh according to Tyler series (0.80 mm), and was made into powdered form and subsequently stored.

Heavy metals (Cadmium, Chromium, Lead, Zinc and Iron) were removed via adsorption process. This was performed by preparing a stock solution of the Cr, Fe, Zn, Pb and Cd by dissolving the quantity of the annular grade salts in distilled

water. The stock solution was further diluted using distilled water to obtain the solutions of the various known concentration (50, 100, 150, 200, 250, 300, 350, 400 mg/L). The adsorption was carried out in batch using a series of flasks containing 50 ml solutions of wastewater at desired concentration with the mass of adsorbent. The mixture was

mixed at different ratios at 250 rpm using a shaker (jar test equipment). The Atomic Adsorption Spectrophotometer (Edibon) was used to determine the concentrations of the heavy metals. The amount of metal adsorbed was estimated at equilibrium using Equation 1:

$$q_e = \frac{(C_o - C_e)V}{m} \dots\dots\dots 1$$

Where C_o and C_e (Mg/l) are the concentrations of the heavy metals at initial and at equilibrium, V is the volume of the solution (L) and m is the mass of the adsorbent used (g).

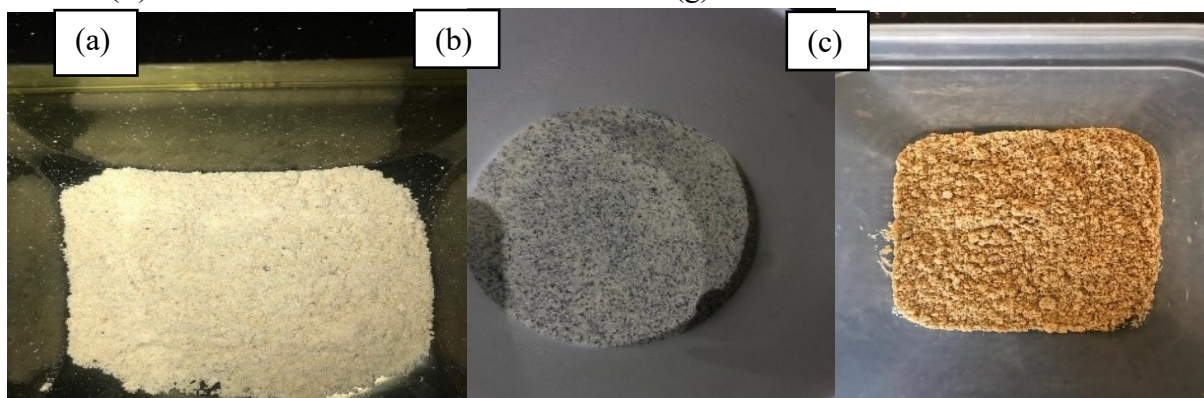


Figure 1: Precursors used in this study: (a) Moringa seed powder (b) Okra seed powder (c) Pumpkin seed powder.

Scanning Electron Microscopy (SEM)

The surface morphology of the composite of Moringa Okra and Pumpkin (MOP) were determined by the scanning electron microscopy (Phenom world Eindhoven, Netherland). The SEM analysis was carried by using the electron beam on both MOP1 and MOP in which there is interaction with the molecules of the MOP revealing the surface morphology and the composition of the MOP (ASTM, 2017).

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared spectroscopy (FTIR) is an important technique that is used to reveal the functional group present on MOP by using a Digi Lab Fourier Transform infrared spectrophotometer (Model Excalibur FTS 2000). The Functional groups composed of vibrations that shows where

the functional groups are attached in the adsorbent. These Vibrations frequencies exist with the infrared frequency array. The FTIR recorded ranges from $4000-400\text{ cm}^{-1}$ (ASTM, 2016).

Energy Dispersive X-ray (EDX)

The Energy Dispersive X-ray (EDX) is a surface analytical technique. The EDX makes use of the electron beam which hits the sample (MOP and MOP1). The electron within the nucleus of the sample are in ground state (not excited). When an incident beam is passed on the sample, the electron becomes excited so it moves to a higher energy level thus creating an electron hole. An electron from an outer, energy shell fills the hole. So the difference between the lower and the higher energy shell was released in the form of X-ray. The number of X-ray that was emitted from the sample

is then measured using the energy dispersive spectrometer (EDS). The energy of the X-rays are function of the different energy between the two shell and the atomic structure of the element being emitted. EDX allows the elemental composition of the MOP to be quantified (ASTM, 2016).

RESULT AND DISCUSSION

The adsorption capacity-Time profile curve for the different heavy metals is shown in Figure 2. The adsorption capacity was determined at a concentration of 100mg/L, adsorption

Temperature of 35 °C, pH of 6, Eighty minutes contact time and 0.5g adsorbent dosage. It is evident from Figure 2 that, there was a very fast adsorption of all the metals in the first 10 minutes due to the availability of more active sites on the surface of the adsorbents and extra cellular binding of the molecules (Chowdhury *et al.*, 2011). However, with increase in contact time the pores were filled and the rate of adsorption becomes slower and eventually saturated. The maximum adsorption capacity was found to be 7.2, 7.5, 7.8, 8.0 and 8.0 mg/g for Chromium, Cadmium, Lead, Zinc and Iron.

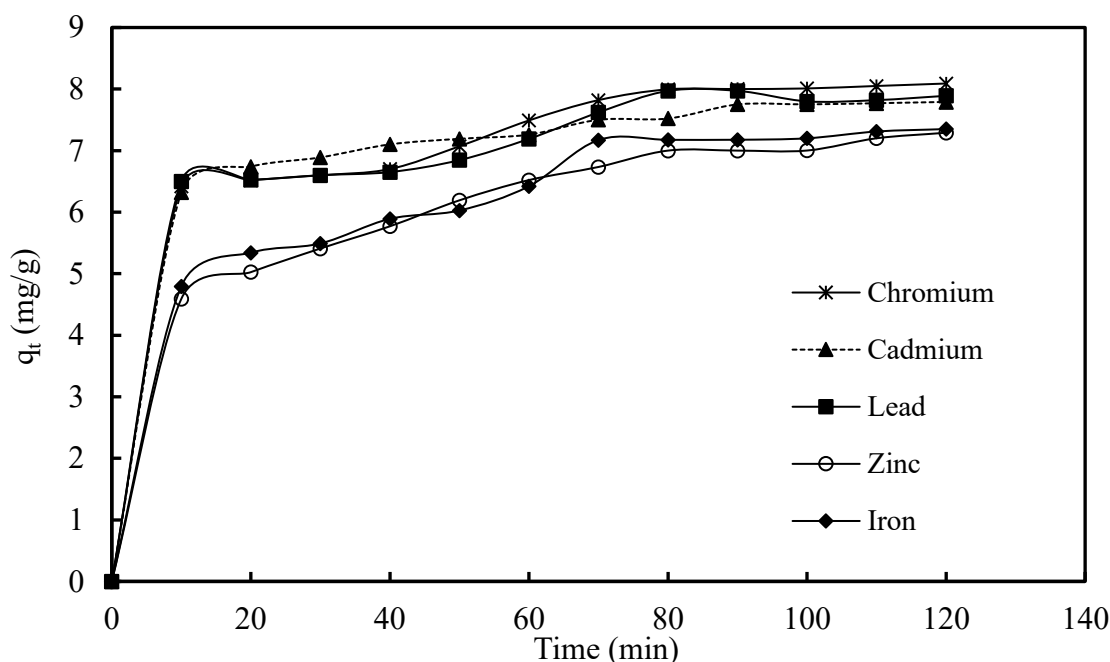


Figure 2: Adsorption capacity – Time profile of Chromium, Cadmium, Lead, Zinc and Iron.

Characterization of the Adsorbent

The characterization carried out in this study was to examine the functional group present, the surface morphology and the elemental composition on the adsorbent. The Scanning Electron

Micrographs (SEM) revealed the surface texture and morphological characteristics of the adsorbents. The SEM images of the adsorbents before and after adsorption were shown in Figures 3 (a-d) and 4 (a-d) respectively.

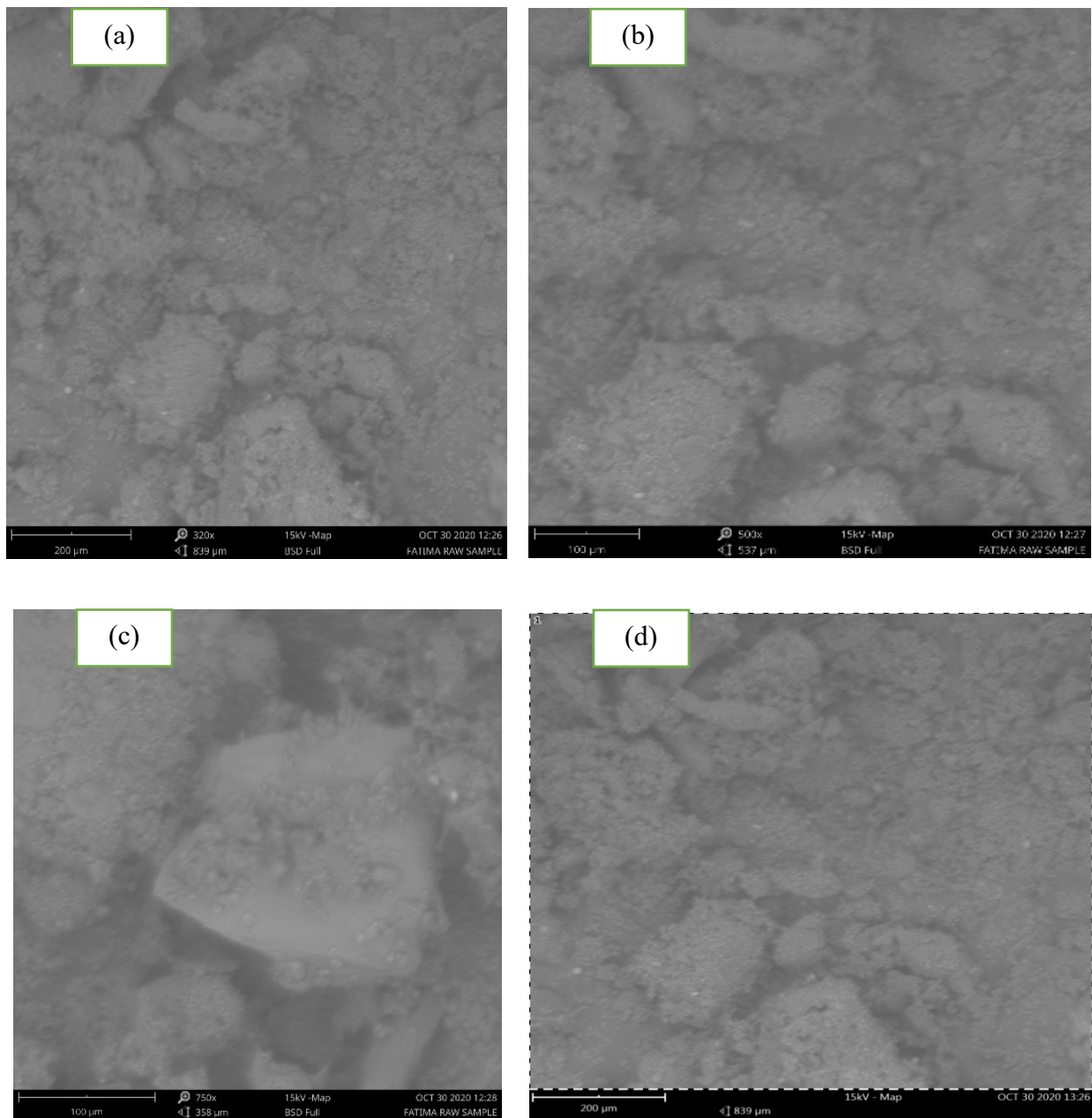


Figure 3: SEM images before adsorption: (a) MO (b) PM (c) OK (d) MOP

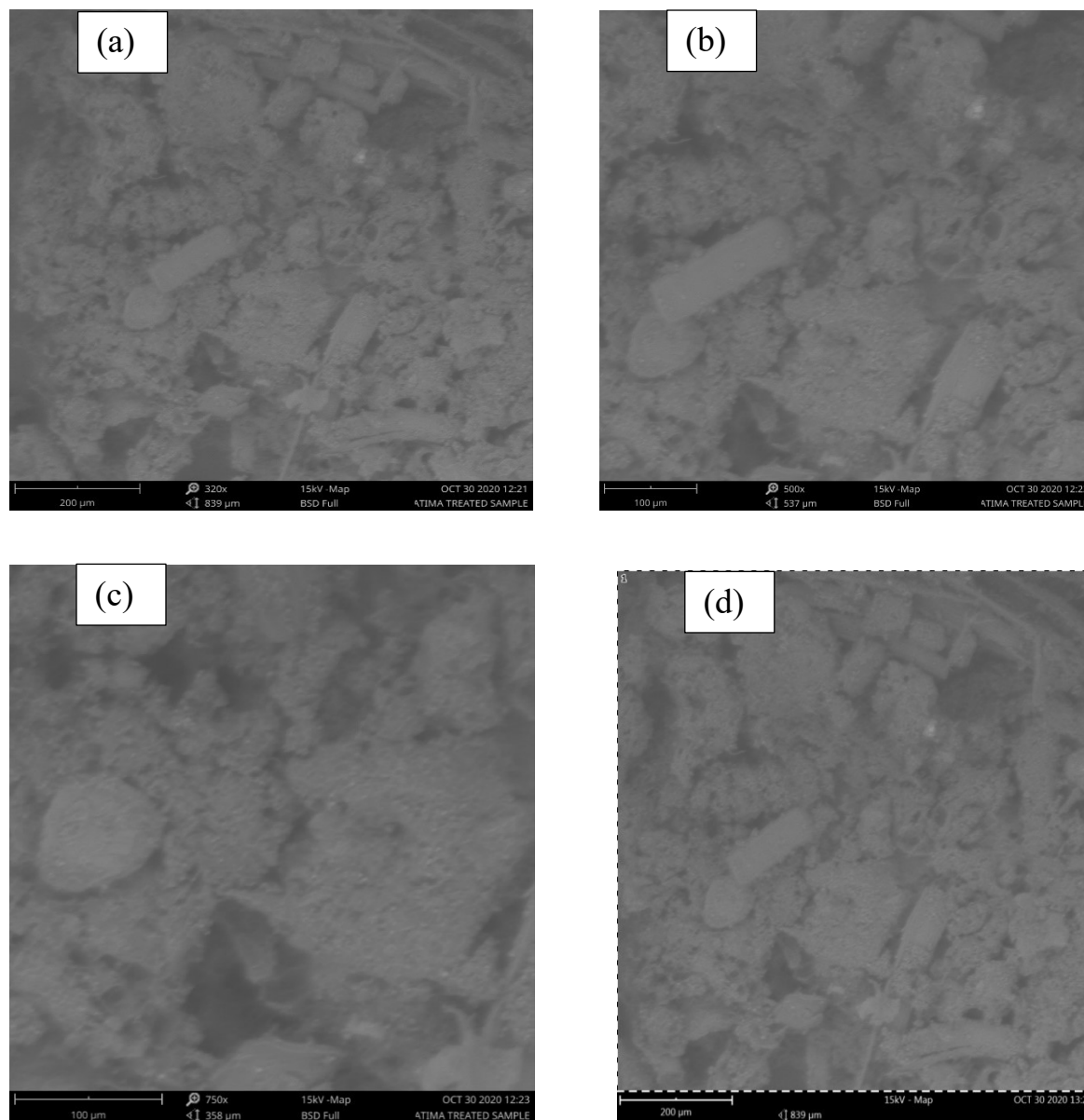


Figure 4: SEM images after adsorption (a) MO (b) PM (c) OK (d) MOP

The SEM images of the prepared material in Figures 3 (a, b, c, d) show agglomeration of the particles with distinctive irregular surfaces. The various pores on the surface of the adsorbent indicates the presence of micro pores structures with defined pores for adsorption. While the SEM image of the MO, OK, PM and MOP (Figures 4 a, b, c and d) shows a partially blocked surface with poor

morphology which may be due to the adsorption of the adsorbate (Rápó *et al.*, 2020). These results can be further proven by the results of previous research for the SEM characterization of the mass transfer for Cr during the adsorption on used black tea leaves (Hossain *et al.*, 2010) shows a partially blocked surface due to the deposition of the adsorbed heavy metal on the pores of the material after adsorption.

Table 1: Elemental composition of MOP and MOP1

Adsorbent	% Element															
	C	O	K	S	P	Ca	Cl	Al	Mg	Si	Na	Cr	Zn	Fe	Pb	Cd
MOP	49.2	10.8	15.7	9.4	3.6	1.5	2.3	1.2	1.9	2.4	1.8	-	-	-	-	-
MOP1	43	17.3	10.2	5.0	2.0	3.1	4.9	1	1.8	1.1	1.1	2.0	2.1	1.2	2.3	1.9

Table 1 presents the Elemental Chemical Composition of the MOP and MOP1. The result indicates the presence of Potassium, Carbon, Aluminum, Oxygen, and Magnesium in both MOP and MOP1. However, the MOP and MOP1 shows the presence of high amount of Potassium and carbon, this may be due to the content of the element found in both MOP and MOP1 which resulted in increased surface pores. The porosity and particle size of MOP particles enhance metal uptake and encourages mass transfer of heavy metals within the sorbent (Zhang *et al.*, 2009; Alayande *et al.*, 2011; Edwin, 2008). The presence of element such as Carbon, Aluminum, Silicon, and potassium, Calcium, Phosphorus, Chlorine, Magnesium and Oxygen have been reported to enhance adsorption (Michaud, 2011). Element such as Al, K, Ca, and Mg could exchange for the heavy metals while elements like Si, O, P could prompt chelation, coordination and complexation (Michaud, 2011).

The FTIR spectra for MOP and MOP1 are depicted

in Figures 5 (a and b). After adsorption, the FTIR spectra showed new peaks (shift) at the characteristic peaks 2864 cm^{-1} and 2401 cm^{-1} which may be assigned to C-H asymmetric stretching and -OH and NH stretching vibrations respectively. Meanwhile, these FTIR peaks are absent in the adsorbent before adsorption which indicates the presences of new groups assigned to hydroxyl and amine groups. FTIR results suggested that the surface functional groups and the structure of adsorbent after adsorption were changed significantly by the effect of the adsorption process, similar finding has been reported earlier (Wang *et al.*, 2018; Maina *et al.*, 2016). It can be speculated that the present of functional groups found on the adsorbent could be the principal mechanism in the removals of metals (Yang & Ren, 2009). The peak positions on the spectra illustrates the presence of a certain functional group with the form of vibration it exhibits. Figures 5 shows the functional groups in $4000\text{--}1000\text{ cm}^{-1}$ peak positions and its vibration forms for the adsorbent before and after adsorption.

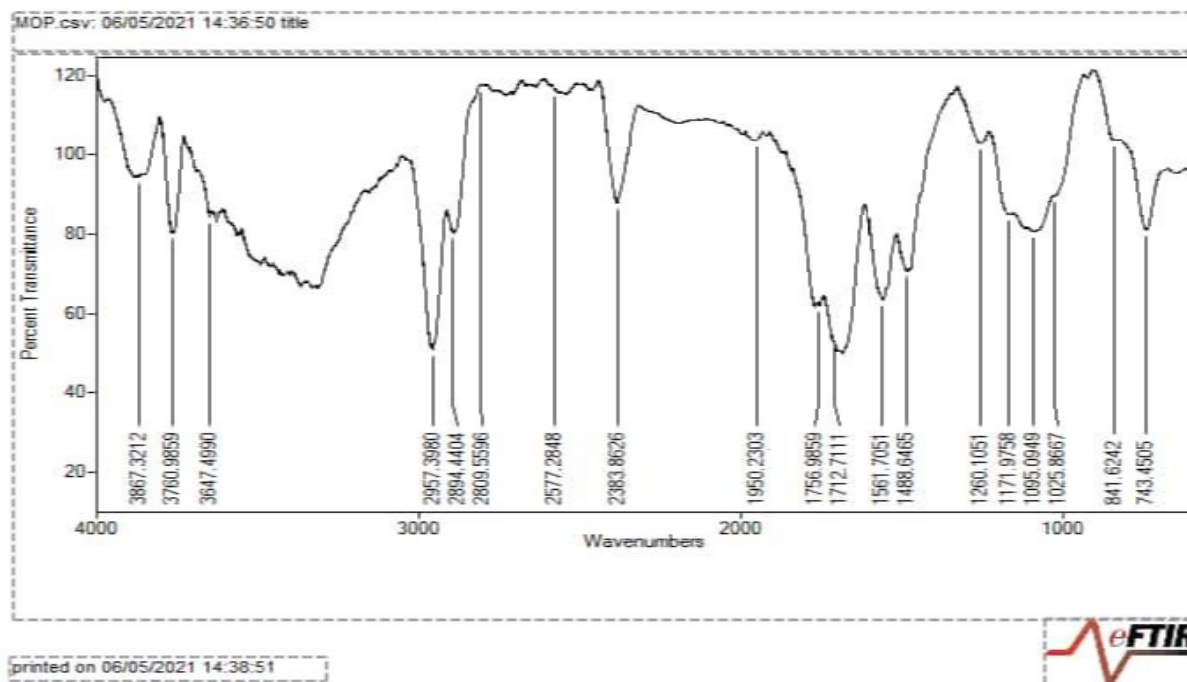
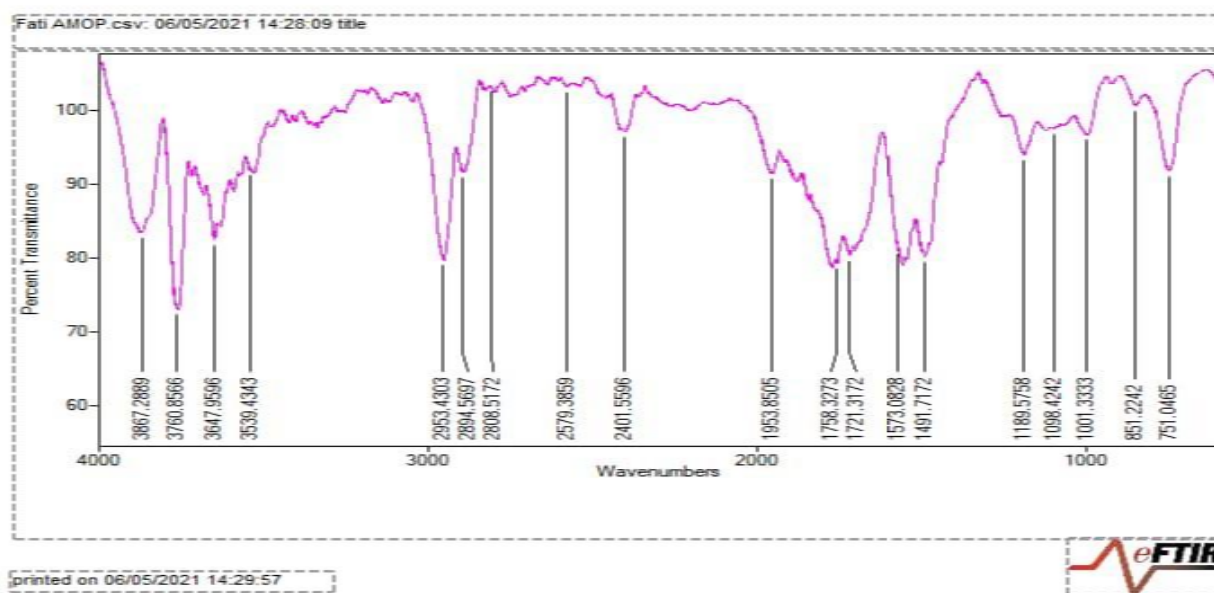


FIGURE 5: (a) FTIR spectra of MOP



Figures 5(b) FTIR spectra of MOP1

CONCLUSION

In this study, a composite bioadsorbent was prepared using the seeds of biocoagulant (MOP) for the adsorption of heavy metals and subsequent characterization of the bioadsorbent. The adsorption studies shows that there was a very fast adsorption of all the metals at the stage due to availability of more active sites on the surface of the adsorbents. However, with increase in contact time the pores were filled and the rate of adsorption becomes slower and eventually saturated. In addition, the removal efficiency of the metals was enhanced due to improved surface morphology and presence of functional groups that aided in the removal of the

heavy metals. The elemental analysis reveals the presence of Carbon, Potassium, Silicon, Sodium, Magnesium, Oxygen and calcium which are element contained in the MOP. This analysis also shows that MOP has a high carbon content which plays a role in the heavy metal uptake. The FTIR spectra shows that a characteristic peaks at 3867 cm^{-1} on the surface of the MOP may be attributed to OH and NH Stretching vibration while the peak at 3647 cm^{-1} and 2953 cm^{-1} may be attributed to Amide (N-H) and carboxylic acid OH stretching groups respectively in both MOP and MOP1. Therefore, biocoagulants can be effectively used to reduce the concentration of heavy metals in wastewater.

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