APPLICATION OF AGRICULTURAL WASTES FOR THE AQUEOUS REMOVAL OF HEAVY METALS FROM WASTE WATER

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ABSTRACT

Heavy metals were found to have hazardous impact on man and ecosystem. The efficacy of Rice, Millet and Guinea corn husks was tested for the removal of Cu(II) and Fe(II) ions from aqueous solution. The husks were soaked in the metal ion solutions removed, dried, digested and analyzed by MP-AES. The husks were found to be effective for the removal of the targeted metal ions. The results showed the pattern of removal in the order: RH > GCH > MH and GCH > MH > RH for Cu(II) and Fe(II) respectively. The samples were also analyzed for X-ray Fluorescence (XRF) and Fourier Transform Infrared Spectrometer (FTIR). The XRF result showed oxides like SiO₂, MnO, MgO and Fe₂O₃, etc. with SiO₂ having the highest percentage. The results of the FTIR analysis showed the presence of OH, C-H, NH and C=O groups, which indicates tendencies for metal binding. Moreover, the MP-AES results showed that RH had the highest removal capacity of Cu(II) with 95% (76 mg/g), followed by GCH 92.5 % (74 mg/g), and MH has the least removal capacity of 84.5 % (67.6 mg/g). The amount of Fe(II) was found to be high in GCH with 95% (76mg/g) followed by MH, 91.5 % (73.2 mg/g) and RH having the least capacity of 60 % (48 mg/g). Generally, the results indicates that all the agricultural wastes have the capacity to remove the heavy metals significantly. This showed that, the husks can be used to remove heavy metals from wastewater without polluting the environment.

Keywords: Removal, Heavy Metals, Aqueous Solution, Bio-sorption, Agricultural Waste.

INTRODUCTION

Heavy metals are inorganic pollutants frequently found in waste waters of several industries such as electroplating, mining, metal processing, petroleum refining, textile, paint manufacture, pesticides, photographic industries and printing (Fuge et al., 2013). These inorganic pollutants have negative impact on the environment and modify the physical and chemical characteristics of water and soil (Houda et al., 2011) and the properties of aquatic fauna and flora (Das et al., 2011). Heavy metal ions get into water system through various manufacturing processes and constitute a severe risk to the environment. Like other contaminants, exceeding a threshold concentration in water, heavy metals are detrimental to human as well as other living organisms due to their toxicity and bio-accumulation. Though, trace elements are essential nutrients required by the human body, intake of high doses can lead to health problems such as irritation of the central nervous system, and kidney and liver hurt (Futalan et al., 2011). Several conventional methods have been employed for eliminating these cations from water system such as chemical precipitation, solvent extraction, vacuum evaporation, membrane technologies, adsorption, membrane separation (Rostamian et al., 2011), coagulation, flocculation, chemical precipitation, reverse osmosis, ion exchange, and ultra-filtration (O’Connell et al., 2008; Fu and Wang 2011). However, these methods have their own restrictions such as low efficiency, sensitive working environments, and production of toxic slurry (O’Connell et al., 2008). Hence, there is an urgent need for more practical and environment friendly technologies. Bio-sorption is now considered among the most effective, economic and selective methods for water treatment and analysis purposes (Fu and Wang, 2011).

There are several locally existing materials that can be used for the removal of heavy metals. Low cost bio-sorbents such as natural materials, agricultural wastes, modified biopolymers, or industrial by-products are found to be more encouraging in heavy metal removal. Agricultural waste is one of the rich sources of low-cost bio-sorbents besides industrial by-product and natural material due to its abundant availability (Abdel-Salam et al., 2011). The need for safe and economical methods for the elimination of heavy metals from waste water has necessitated research on low-cost agricultural waste products such as sugarcane bagasse, millet husk, rice husk, sawdust, coconut husk, oil palm shell, guinea corn husk, Neem bark (Madaubuchi, 2018), wheat husk, maize corn cob, banana and orange peels, soya bean hulls, grapes stalks, etc. were used as sorbents for metal removal (Muazu and Yusuf, 2017).

Agricultural waste is one of the inexpensive bio-sorbent for heavy metal removal, which contains 50 – 90% of silica (SiO₂). In addition to being cost-effective and environmental friendly, agricultural waste is abundant and renewable (Da’na, 2017). The application of agricultural wastes in removing heavy metals from wastewater has attracted much attention owing to its economic advantages and high removal efficiency which is attributed to different functional groups (Alalwan et al., 2020). Agricultural wastes especially those with high percentage of cellulose and lignin contains polar functional groups like amino, carbonyl, alcoholic, phenolic, and ether groups having high potential for metal binding (Hossain et al., 2012). These groups donate a lone pair of electrons and
form complexes with metal ions in the solution (Demirbas, 2008). Due to their unique chemical composition (the presence of hemicellulose, lipids, lignin, water hydrocarbons, simple sugars, and starch having a variety of functional groups) and availability, the use of agro-wastes seems to be a viable option for heavy metal remediation (Sri Lakshmi et al., 2018). Madubuchi (2018) used Agricultural Waste Materials (banana peels and peanut shells) as a Potential bio-sorbent for Removal of Heavy Metals (lead and manganese) in Waste Water. Muazu and Yusuf, (2017) investigate the utilization of millet husk as a low-cost bio-sorbent for removal of Lead (II), Cadmium (II) and Nickel (II) ions from aqueous solution, in which the FTIR and SEM characterizations were carried out on the samples. Therefore, the objective of this research is to study the utilization of rice, millet and guinea corn husks for the removal of Cu and Fe from aqueous solution.

MATERIALS AND METHOD

Chemical and reagents

All reagents were analytically grade purchased from Sigma Aldrich and used without further purification. freshly prepared metal solutions of CuCl₂.2H₂O and FeCl₃.4H₂O with desired concentration were used as a source of heavy metals ion. Sulphuric acid (H₂SO₄) (specific gravity 1.83 g/cm³, percentage purity 98.3% w/v), Nitric acid (HNO₃) (specific gravity 1.51g/cm³, percentage purity 68% w/v) and Hydrochloric acid (HCl) (specific gravity 1.49 g/cm³, percentage purity 36% w/v) were used. All glassware’s and plastic containers were washed with detergents, rinsed with distilled water and then soaked in 10% HNO₃ solution for 24 hrs. They were then washed with deionised water and later dried in an oven for 28 h at 80°C (Todorovi et al., 2001).

Sample collection and pre-treatment

Adopting a modified pretreatment method reported by (Ahmed, 2013). The bio-sorbents (rice, millet and guinea corn husks) were obtained from a farmland where the milling activities were carried out and the husks being dumped at Tinga village of Batagarawa Local Government, Katsina State, Nigeria. All the samples were collected in a clean polyethylene sample bag, labeled appropriately as Rice husk (RH), Millet husk (MH), Guinea Corn husk (GCH) and brought to the laboratory for further treatment. The biomass were washed several times with tap water to remove adhering particles and finally soaked in distilled water for 6 h, drained, rinsed and oven dried at 110°C for 24 h. The wastes were then ground using pestle and mortar, sieved using 300 μm mesh sieve, stored in clean polyethylene sample bags and labeled appropriately. Each of the three husks was divided into three more portions. The first portion was taken for FTIR analysis to evaluate the functional group present, the second portion was taken for XRF analysis to determine the elemental composition and the third portion was utilized for bio-sorption of heavy metals.

Preparation of Standard Solutions for the heavy metals used

Stock solutions 1000 cm³ of the metal solution was separately prepared by dissolving calculated gram of metal salts (CuCl₂.2H₂O and FeCl₃.4H₂O) in 100 cm³ beaker and made up to 1000 cm³ in a volumetric flask with deionized water. All other experimental solutions of 0.0ppm were prepared by serial dilution of the stock solution similar to the report of Adeyi et al., (2019).

Experimental Method

Fourier Transform Infrared (FTIR) Spectroscopic Analysis

Fourier transform infrared (FTIR) spectroscopic analysis was used to know the functional groups of the agricultural wastes (RH, MH and GCH) before and after treatment with Cu (II) and Fe (II) aqueous solutions. The machine used was Agilent Technology, FTIR (Cary 630) Fourier Transform Infrared Spectrophotometer. 650 – 4000 cm⁻¹ wave number was used to scan the sample during the analysis.

X-ray Fluorescence (XRF) Spectroscopic Analysis

The X-ray Fluorescence (XRF) Analysis is a non-destructive analytical technique, it was carried out to determine the oxide content (wt. %) of the raw RH, MH and GCH. The machine used for the analysis was EDXRF Analyzer (PW 2400) Energy Dispersive X-ray Fluorescence Spectrophotometer. It works by measuring the fluorescence (secondary) X-rays emitted from a sample when excited by a primary X-ray source.

Microwave Plasma Atomic Emission Spectrometry (MP-AES)

The microwave plasma atomic emission spectrometry is an analytical technique used to determine the concentration of heavy metals in the samples. The machine used was Agilent/MP Expert MY17380004 it was carried out to determine the metal ion concentration before and after bio-sorption process.

Treatment of Heavy Metal Solutions with RH, MH and GCH

Applying and modifying a treatment method used by Agwaramgo et al., (2016) provides as follows: 5g of the samples (RH, MH and GCH) where weighted separately into each conical flask containing 200 cm³ of 2.00ppm of copper ion (Cu²⁺) solution. The flasks and their contents were shaken using a mechanical shaker for 30 minutes at 250rpm and the reaction vessels were allowed to stand un-agitated for 48 h at room temperature. After then, the mixture from each reaction flask was filtered. The filtrates were digested and analyzed for heavy metals and compared with the concentration of heavy metal in untreated sample using Micro Plasma Atomic Emission Spectrophotometer (MP-AES), while the residues were kept overnight in a desiccator, and later dried in an oven for 3days at 110°C. After drying, they were divided into two different labeled portions. The first portion were taken to FTIR analysis for functional group determination and the second portion was digested and analyzed for metal ion concentrations. Correspondingly, the same method was applied for the treatment of Fe²⁺ solution.

Digestion of residue obtained after bio-sorption process

The method used by Turek et al., (2019) was modified and adopted. Accordingly, 1.0 g each of the husks were ground and its powder placed in 100 cm³ conical flasks moistened with 4 cm³ distilled water, and followed with the addition of 5 cm³ concentrated H₂SO₄ (specific gravity 1.83 g/cm³, percentage purity 98.3% w/v) and 10 cm³ concentrated HNO₃ (specific gravity 1.51 g/cm³, percentage purity 68% w/v). Each flask was slightly heated at a temperature of 100°C for 2 h and then allowed to cool. After cooling, the solutions were diluted with 10 cm³ distilled water and then filtered. The solution was then made to 100 cm³ mark by adding distilled water and then transferred quantitatively to a clean sample bottles for MP-AES analysis. The procedure was used as prototype for all other samples.

The digests were analyzed for Cu and Fe concentration by MP-AES. The percentage of bio-sorption removal (%R) known as
bio-sorption efficiency for the metal ion was evaluated from the following equation (1):
\[
\%\text{Removal\ Efficiency} = \frac{C_0 - C_t}{C_0} \times 100
\]
where \(C_0\) and \(C_t\) are the initial and final bio-sorbents concentrations respectively.

The gram of a particular metal adsorbed per unit gram of bio-sorbents otherwise known as bio-sorption capacity after a given time was calculated using the equation (2): (Puglia et al. 2020).
\[
q_e = \frac{(C_0 - C_t)W}{V}
\]
where \(V\) = Volume of the solution \\
\(W\) = Mass of the bio-sorbent

RESULTS AND DISCUSSION

X-ray Fluorescence (XRF) Analysis

The resulting filtrate obtained after the bio-sorption process was digested in line with the literature report with some modifications (Srikanth et al., 2013). Accordingly, 100 cm³ of each of the filtrate was transferred into labeled beaker each containing 10 cm³ of conc. HNO₃. The sample was boiled slowly and then evaporated on a hot plate to the lowest possible volume (about 20 cm³). After cooling, 5 cm³ of conc. HNO₃ was added and the heating continues until digestion was completed. The sample was then vaporized to dryness, cooled and followed by addition of 5 cm³ of HCl (specific gravity 1.49 g/cm³, percentage purity 36% w/v) solution. The solution was warmed and 5 cm³ of 5M NaOH was added and then filtered. The filtrate was transferred to 100 cm³ volumetric flasks and diluted to the mark with distilled water. This was used as a prototype procedure for all other preparations before analyzing for MP-AES analytical technique.

Digestion of filtrate obtained after bio-sorption process

The XRF results indicates the oxides composition of the bio-sorbents (RH, MH and GCH) contain traces of some elemental oxides, their percentage composition varies which is the decreasing order; SiO₂ > P₂O₅ > MgO > CaO > K₂O > Fe₂O₃ > MnO (Figure 1). SiO₂ has the highest composition which is due to the application of silicone fertilizer to enhance the plant’s ability to resist micronutrient and other metal toxicity and also to improve stem strength, drought tolerance to delay wilting in certain crops where irrigation is withheld. Additionally, it may be attributed to soil composition, nature of the specie and irrigation area. This XRF results recorded, corresponds to the literature reports (Hammajam et al., 2017; Bello et al., 2018; Hasson, 2013) which also confirmed the possibility of the agricultural waste to be used as bio-sorbent to remove the heavy metal from the aqueous solution.

Micro Plasma Atomic Emission Spectroscopic (MP-AES) Analysis

Table 1: Metal ions (Cu²⁺ and Fe²⁺) Concentrations (ppm) in the free (untreated) agricultural wastes

| Metal ion | Agricultural wastes | Concentration (ppm) |
|-----------|---------------------|---------------------|
| Cu        | RH                  | 0.08                |
|           | MH                  | 0.06                |
|           | GCH                 | 0.08                |
| Fe        | RH                  | 0.57                |
|           | MH                  | 1.36                |
|           | GCH                 | 2.56                |
The MP-AES analysis is an important spectroscopic technique that was conducted to determine the concentrations of the metal ions in the agricultural wastes (bio-sorbens) before and after the bio-sorption study. Table 1 shows the initial concentration of the bio-sorbens before the bio-sorption process, the result indicates the presence of the metal ions (Cu and Fe) in the bio-sorbens (RH, MH and GCH) with varying concentrations; 0.08ppm (RH and GCH), 0.06ppm (MH) with respect to Cu(II) and 0.57ppm, 1.36ppm, 2.56ppm for RH, MH and GCH respectively with respect to Fe(II), the presence of these metal ions is associated with pesticides and fertilizer application, nature of the irrigation water and irrigation area. The agricultural wastes on the other hand, manifested good efficacy for the removal of metal ions from aqueous solution and the analytical results were presented in Figure 2 and 3 respectively. The result of the MP-AES analysis indicates that RH shows higher efficacy of Cu(II) removal in filtrate solution after treatment (0.10ppm) with a residue concentration of (0.30ppm) followed by GCH with filtrate concentration (0.15ppm) and residue concentration (0.21ppm) followed by MH which has the least Cu removal with (0.31ppm) filtrate concentration after treatment and residue concentration (1.99ppm), all in the order; RH > GCH > MH. While GCH shows higher efficacy of Fe(II) removal having (0.07ppm) concentration in its filtrate solution and a higher residue concentration (0.31ppm), the removal efficacy of all the bio-sorbens for Fe(II) removal is in the order GCH > MH > RH. The whole result indicates that RH has higher efficacy of Cu(II) removal with 95% removal rate and 76mg/g bio-sorption capacity, while GCH shows higher efficacy of Fe(II) removal with 96.5% removal efficiency and 77.2mg/g bio-sorption capacity. Also, the result shows higher absorption of Fe(II) ion when compared to Cu(II) ion, demonstrating higher affinity of Fe(II) ion toward GCH, MH and RH bio-sorbens.

The removal efficiency (percent) and bio-sorption capacity of Cu(II) ion by the bio-sorbens shows that RH has highest percentage removal efficiency and bio-sorption capacity; 95% and 76mg/g. followed by GCH (92.5% and 74 mg/g), and MH has the least removal efficiency and bio-sorption capacity (84.5% and 67.6 mg/g). While GCH has highest percentage removal and bio-sorption capacity of Fe(II) (95% and 76mg/g) followed by MH with (91.5% and 73.2 mg/g) then RH has the least removal efficiency; 60% and 48 mg/g. The result shows that, the bio-sorbens possessed good efficacy and bio-sorption capacity of removing heavy metal ions from aqueous solution as shown in Figure 2. These results are similar to the literature reported by Ahmad, (2013) on the removal of heavy metals from wastewater using agricultural and industrial wastes as bio-sorbens, in which rice husk removed Fe(II) and Fe(II) with more than 80% removal efficiency.

Figure 2: Concentrations (ppm), % Removal and Bio-sorption capacity (mg/g) of Cu and Fe in the Filtrates

Figure 3: Concentrations (ppm), % Removal and Bio-sorption capacity (mg/g) of Cu and Fe in the digested residue
Fourier Transform Infra-red (FTIR) Characterization

Table 2: FTIR Absorption bands of raw (RH, MH and GCH) before and after bio-sorption of Cu(II) and Fe(II)

| Assignment | RH    | Cu-RH | Fe-RH | MH    | Cu-MH | Fe-MH | GCH   | Cu-GCH | Fe-GCH |
|------------|-------|-------|-------|-------|-------|-------|-------|--------|--------|
| O-H (cm⁻¹) | 3286  | 3279  | 3294  | 3286  | 3339  | 3275  | 3279  | 3280   | 3264   |
| C-H (cm⁻¹) | 2921  | 2921  | 2921  | 2918  | 2921  | 2918  | 2921  | 2992   | 2921   |
| N-H (cm⁻¹) | -     | 1514  | 1562  | 1514  | 1599  | 1514  | 1544  | 1544   | 1562   |
| C=O (cm⁻¹) | 1741  | 1737  | 1737  | -     | -     | -     | -     | -      | -      |

The FTIR analysis is a useful spectroscopic technique that was conducted to determine the presence of functional groups and any change’s takes place after the bio-sorption study. Figure 4 shows the FTIR spectra of the bio-sorbents; RH, Cu-RH, Fe-RH, MH, Cu-MH, Fe-MH, GCH, Cu-GCH and Fe-GCH before and after bio-sorption of the metal ions, the results shows the presence of -OH, C-H, N-H and C=O functional groups.

The RH and MH shows the characteristic band of -OH group at 3286 cm⁻¹ while GCH was at 3279 cm⁻¹, some of these bands have been shifted to the lower wavenumbers of 3279 cm⁻¹ (Cu-RH), 3275 cm⁻¹ (Fe-MH) and 3264 cm⁻¹ (Fe-GCH) and some to higher wavenumbers; 3294 cm⁻¹ (Fe-RH), 3339 cm⁻¹ (Cu-MH) and 3280 cm⁻¹ (Cu-GCH) after bio-sorption of the metal ions which is due to OH stretching vibration of water molecule. The spectra show presence of C-H group at 2921 cm⁻¹ (RH and GCH) and 2918 cm⁻¹ (MH), there is no any shift of band in Cu-RH, Fe-RH, Fe-MH and Fe-GCH, but other bands have been shifted to the higher wavenumbers of 2921 cm⁻¹ (Fe-MH) and 2992 cm⁻¹ (Cu-GCH) these are due to C-H stretching vibration.

The peaks at 1514 cm⁻¹ (MH) and 1544 cm⁻¹ (GCH) indicates the presence of N-H bending vibration, some of these peaks have been shifted to 1599 cm⁻¹ and 1562 cm⁻¹ in Cu-MH and Fe-GCH respectively, no any significant shift in Fe-MH and Cu-GCH, new peaks have been formed at 1514 cm⁻¹ and 1562 cm⁻¹ after the bio-sorption of Cu²⁺ and Fe²⁺ with RH. C=O group appeared at 1741 cm⁻¹ and this band was shifted to the lower value of 1737 cm⁻¹ after bio-sorption of the metal ions, these is attributed to C=O stretching and angular vibration of water molecules. These FTIR results correspond to the literature reported by Baby et al., (2019). Presumably, the formation of new absorption bands, the change in absorption intensity and the shift in wavenumber of functional groups could be attributed to complexation between metal ions and binding sites of the bio-sorbents, and indicates the successful bio-sorption of the metal ions on the bio-sorbents (the agricultural wastes). Detailed FTIR absorption bands of the bio-sorbents before and after bio-sorption of metal ions were shown in Table 2.

Figure 4: FTIR spectra of raw Bio-sorbents before and after bio-sorption of Cu(II) and Fe(II)

CONCLUSION

This study was conducted to test the efficacy of agricultural wastes (RH MH and GCH) bio-sorbents as natural, cheap and effective material for the removal of Cu(II) and Fe(II) ions from aqueous solution. The removal ability of the agricultural wastes has been tested and further confirmed by MP-AES analysis. The result demonstrated that all the selected agricultural waste bio-sorbents have successfully remove Cu(II) and Fe(II) from the aqueous solution with more than 90 % removal efficiency and 50 mg/g bio-sorption capacity. Among these selected bio-sorbents GCH possess higher removal efficiency. Their key property is the presence of functional groups that can bind metal ions through complexation. Finally, the result demonstrate that all the agricultural wastes used were good in the removal of heavy metal ions from aqueous solution, the use of such materials will not only convert waste materials into low-cost effective bio-sorbents, but also provide a solution to their disposal.

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