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Aqueous Phase Removal of Heavy Metals from Contaminated Wastewater using Agricultural Wastes

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ABSTRACT

This study determined the presence of heavy metals in contaminated wastewater and examined their removal using agricultural wastes as bio-sorbent. Heavy metals contamination in wastewater causes severe adverse effects on human health. Huge amounts of corn cob and wheat bran are produced from maize and wheat plantations every year. The efficacy of raw corn cob (CC) and raw wheat bran (WB) were also tested for the removal of cobalt(II) and nickel(II) from metal solution and contaminated wastewater. The agricultural wastes (bio-sorbent) were characterised with Fourier transform infrared and X-ray florescence spectroscopic techniques. The FTIR result confirmed the interaction of (O-H, C-O and C-H) in (CC and WB) with heavy metals while the XRF result revealed that, both (CC and WB) contain high percent of K_2O.The batch sorption technique was conducted at room temperature. The method was applied for the removal of cobalt and nickel using Katsina youth craft village (KYCV) and Gambarawa paint cottage (GPC) contaminated wastewaters. The Microwave Plasma Atomic Emission Spectrometer (MP-AES) result revealed that corn cob is more effective removing Co(II) with (97%) removal efficiency and (77.6 mg/g) bio-sorption capacity in metal solution, (92% and 29.4 mg/g) and (80% and 3.2 mg/g) removal efficiency and bio-sorption capacity using (KYCV and GPC) contaminated wastewater while wheat bran is more effective in removing Ni(II) with (95% and 76 mg/g) removal efficiency and bio-sorption capacity from metal solution. This can serve as a cost effective and greener approach to utilize the agricultural wastes without any chemical treatment, making it user friendly bio-sorbent. From the findings of this study, concluded that corn cob and wheat bran can be used as cheap and safe bio-sorbents for uptake of cobalt and nickel from contaminated wastewater.

Keywords: Biosorption, Corn cob, Heavy metals, Wastewater, Wheat bran

INTRODUCTION

The application of bio-sorption in contaminated wastewater treatment has become a significant research area in the recent time. Contamination of wastewater with heavy metals such as cobalt, nickel, zinc, lead and chromium, is an ongoing problem that attracted attention due to the rise in metal toxicity in the living species. These toxicities also affected the soil fertility, water resource and aquatic ecosystem (Majumdar *et al.*, 2010). Heavy metals contamination in water sometimes are due to discharges from dyeing pits, pesticides, fertilizer applications, tanneries, discarded batteries, paper industries, refining ores, fixing agents, mordant and bleaching agents (Ullah *et al.*, 2013). Other sources of heavy metal pollution are the paints and pigment industries, magnetic and stainless steels, electronics, porcelain, radioisotope therapy, galvanizing, battery recharging, mining operations, nuclear power plant and grinding wheels (Anirudhan *et al.*, 2016).

Cobalt and nickel are toxic metal contaminants in water. World Health Organisation (WHO, 2010) standards, the maximum discharge limits in contaminated water are 0.50 mg/L and 0.2mg/L for cobalt and nickel respectively. Cobalt is toxic to living organism and if released into the environment can bio accumulate and enter the food chain, cobalt is known to cause vomiting, lung irritation, diarrhoea, pneumonia, weight loss, heart failure and bronchitis. Strong exposure of nickel causes dermatitis, nausea, chronic asthma and coughing (Kokkins and Economou, 2016).

The conventional methods for removing cobalt and nickel contaminants from aqueous phases are mainly biological treatment, flocculation (Jawad *et al.* 2015), membrane separation processes, chemical precipitation, adsorption with activated carbon and ion exchange (Rosales *et al.*, 2017). These methods are economically unfavourable or technically complicated, and used only on special cases of wastewater treatment.

Among these methods, bio-sorption of heavy metals is a relatively new technology for the treatment of contaminated water. Bio-sorbent material derived from low cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from contaminated water streams. The major advantages of bio-sorption

technology are its effectiveness in reducing the concentration of heavy metals to very low levels and the use of inexpensive bio-sorbent materials (Qaiser *et al.,* 2007). A variety of commercial adsorbent including chelating resins and activated carbon are available for metal sorption but are relatively expensive. In recent years, numerous low cost adsorbents have been proposed as potential bio-sorbents. This includes straw (Salem and Yakoot, 2016), wheat straw, bagasse, banana skin, walnut shell and corn cob (Tonucci *et al.*,2015), coconut shell (Tang *et al.*,2017), avocado skin (Palma *et al.* 2016).

The potential of using corn cob and wheat bran as an agricultural wastes biosorbent are mainly due to the presence of organic and inorganic compounds, which are cellulose, hemicellulose, pectin and lignin present in the cell wall are the most important sorption sites. The important feature of these compound is that it contain hydroxyl, carboxyl, carbonyl, amino, and nitro groups which are important sites for metal sorption (Volesky, 2003).There is significant contribution of various research groups on use of agricultural waste for heavy metals removal through the bio-sorption. The efficacy of charred corn cob husks and charred palm nut husk for the remediation of lead from contaminated water was investigated by Agwaramgbo *et al.* (2014). The residual lead concentration was determined using atomic absorption spectrophotometer (AAS). The results indicated that, the two biosorbents were very effective in removing lead from contaminated aqueous solution with 99% removal efficiency.

Mahmudi *et al.,* (2020) conducted a research on the use of agricultural waste (corn cobs and bagasse) as an alternative to activated carbon for chromium removal using randomized factorial design method. The activated carbon from corn cobs and bagasse was able to reduce the chromium levels with the most effective dose of 2.5 g/L and a contact time of 120 minutes.

Muhammad-Razil *et al.* (2018) investigate the efficiency of sugarcane bagasse activated carbon (SBAC) modified by phosphoric acid as adsorbent for the removal of zinc (Zn) and iron(Fe) from the textile wastewater using batch method by ICP-MS.The maximum percentage removal of Fe, Zn was 80%. These findings indicated that the SBAC is an attractive alternative adsorbent material for the metal ions removal in textile wastewater.

Bandela *et al.* (2016) studied the removal of Copper from aqueous solution using local agricultural wastes as low cost adsorbent via batch adsorption method and they found that the carbons made from wheat, corn, sugarcane and *bajra* agro-wastes can be effectively used in the reduction of copper from aqueous solution. *Bajra* was one of the most efficient wastes with an ability to reduce copper by approximately 98%.Sajjanar and Kumar, (2018) also explored the removal of heavy metals such as Chromium, Copper and Zinc from industrial wastewater using low cost adsorbents like 'used tea powder' and 'saw dust', these two adsorbents were tested and was known that used tea powder and saw dust has a carbon content of 62.26% and 67.52% respectively and hence has a high probability of removing heavy metals from the waste water. In this research corn cob and wheat bran were used as low-cost, cheap and effective bio-sorbents for the removal of cobalt and nickel from metal solution, Katsina youths craft village tie-die contaminated wastewater and Katsina Gambarawa paint cottage contaminated wastewater.

MATERIALS AND METHODS

Chemical and reagents

All glassware's and plastic containers were washed with detergents, rinsed with distilled water and then soaked in a 10% HNO_3 solution for 24 hrs. They were then washed with deionised water and dried in an oven for 42 hrs at $80^{O}C$ (Todorovi *et al.* 2001)

Analytical grade reagents were used as received by BDH chemicals company England, freshly prepared metal solutions of $CoCl_2.\ 6H_2O$ and $NiCl_2.6H_2O$ with desired concentration were used as a source of heavy metals ion. Sulphuric acid (H_2SO_4) (specific gravity 1.83 g/cm^3, percentage purity 98.3% w/v), Nitric acid (HNO_3) (specific gravity 1.51g/cm^3, percentage purity 68% w/v) and Hydrochloric acid (HCl) (specific gravity 1.49 g/cm^3, percentage purity 36% w/v) were used.

Biosorbents Collection and pre-treatment

The procedure used by Hussain and Shariff, (2014) was modified and adopted. Corn cob and wheat bran were collected from a local corn mill in central market Katsina, Katsina local government area, Katsina state, Nigeria. The samples were washed thoroughly with tap water to remove the dust and other adhering particles followed by deionized water, dried in an oven at 70°C for 14 h, crushed into fine powder and sieved with a 2 mm mesh sieve for homogeneity. The samples were kept in a closed container for further analysis.

Contaminated Water Collection and Pre-treatment

The procedure used by Asubiojo and Ajelabi, (2008) was modified and adopted. Samples were collected from two different types of manufacturing factories in Katsina local Gov. Katsina state, Nigeria. Wastewater was obtained from tie-dye department of Katsina youth craft village, labelled as KYCV and paint contaminated water was obtained from Gambarawa paint cottage Katsina, labelled as GPC. The samples were collected into already rinsed with water followed by several washing contaminated water to be

stored. They were tightly sealed and kept in the refrigerator before use.

Preparation of Cobalt and Nickel Chloride Solution

The analytical grade Cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$) and Nickel(II) chloride hexahydrate ($NiCl_2.6H_2O$) were obtained from the laboratory without any further treatment. 4.037g and 4.049g of cobalt and nickel chloride were weighted accurately and dissolved in small volume of distilled deionised water in separate beakers and the solution were transferred to 1.0 litre volumetric flask to make 1L stock solution (Ibrahim and Jimoh, 2010). The Co(II) chloride hexahydrate ($CoCl_2.6H_2O$) solution was labelled as Co(II) solution and Ni(II) chloride hexahydrate ($NiCl_2.6H_2O$) solution as Ni(II) solution. All other experimental Co and Ni solutions of desired concentrations were prepared from the stock solution by serial dilution.

Treatment of Cobalt and Nickel Metal Solution with CC and WB

The procedure used by Agwaramgbo *et al*. (2014), was modified and adopted, where a 5g of CC powder was labelled and treated with 200ml of 2mg/L of cobalt and nickel chloride solution prepared above respectively. The mixture was shaken using laboratory shaker at a speed of 250rpm for 60 minutes and the reaction vessels were allowed to stand un-agitated for 48hr at room temperature. After 48 h the mixture was filtered and the filtrate analysed for heavy metals concentration by MP-AES while the residue was dried in an oven at a temperature of 110^{o}C for 18 h and kept in a desiccator. After which it was digested and analysed for heavy metal concentrations by MP-AES. Same procedure was repeated for wheat bran. The method was applied for removal of cobalt and nickel from Katsina youth craft village (KYCV) and Gambarawa paint cottage (GPC) contaminated water without the addition of metal solution.

Digestion of KYCV and GPC Contaminated Water Samples

The digestion method described by Srikanth *et al.* (2013) was modified and adopted, where a 100ml of KYCV wastewater was measured and transferred into Pyrex beakers containing 10ml of concentrated nitric acid (HNO_3) respectively. The sample was boiled slowly and then evaporated on a hot plate to the lowest volume (15 ml). The beakers were allowed to cool and another 5ml of concentrated Nitric acid were added. Heating was continued with addition of concentrated (HNO_3) as necessary until digestion was complete. The samples were evaporated again to dryness (but not baked) and the beakers were cooled, followed by addition of 5ml of hydrochloric acid (HCl) solution. The solution was warmed and 5ml of 5M sodium hydroxide(NaOH) solution was added and then filtered. The filtrate was transferred to 100ml volumetric flask and diluted to the mark with distilled water. It was transferred quantitatively to a capped screwed polythene plastic bottle. These solutions were then used for the elemental analysis for Co and Ni concentration determination by MP-AES. Same procedure was repeated for GPC contaminated water.

Digestion of the residue treated with metal solution and contaminated water

The procedure used by Turek *et al.* (2019) was adopted and modified, where a 1g of the corn cob residue was weighted and placed in 250cm^3 conical flasks, moistened with 4cm^3 deionised water and added 5cm^3 of concentrated sulphuric acid (H_2SO_4) and 10cm^3 of concentrated nitric acid (HNO_3). The sample was heated at a temperature of 100^{o}C in a fume cupboard until appearance of white fumes. After then, the sample was allowed to cool down at room temperature. 10 ml of deionised water was added to the sample and then filtered. The solution was made to 100cm^{3}mark volumetric flask by adding deionised water. It was transferred quantitatively to a capped screwed polythene plastic bottle. Same procedure was repeated for wheat bran. The digests were analyzed for Co and Ni 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):

$$\%\ \text{Removal Efficiency} = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

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) (Puglla *et al.* 2020).

$$q_e = \frac{(C_o - C_t)V}{W} \quad (2)$$

Where: V= Volume of the solution
W= Mass of the bio-sorbent

X-ray Fluorescence (XRF) Analysis

X-ray fluorescence spectroscopy is a non-destructive analytical technique, it was used to determine the oxide content (wt. %) in raw (CC and WB) in the samples and the samples was run using EDXRF Analyser. 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 samples were run using Agilent/MP Expert MY17380004 to determine the

concentration of cobalt and nickel in contaminated wastewater and metal salt solution before and after bio-sorption with the CC and WB bio-sorbents.

Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-transform infrared (FTIR) spectroscopy analysis was used to reveal the functional groups of the CC and WB before and after treatment with Co(II) and Ni(II)aqueous solution, dye and paint wastewater respectively. The absorption spectra were obtained using VERTEX $70/70_V$ Spectrophotometer (Agilent Technologies) within wavenumber range of 4000-650cm^{-1}.

RESULTS AND DISCUSSION

X-ray Fluorescence (XRF) Analysis Result

The oxides composition of agricultural wastes(CC and WB) were analysed by X-ray fluorescence (XRF) and the result revealed that, the major components are K_2O, MgO, $Fe_2O_3$and CaO while the minor components are MnO, Na_2O and Al_2O_3as shown in Figure 1. That may have given the bio sorbents ability to pick or remove metal ions from contaminated water by interacting with them. The percentages of the elements varied. The higher percent of K_2O in (CC and WB) biosorbents are due to application of potassium in fertilizer as macro nutrients to regulate stomatal opening and closing and to regulate plant structure. In addition to this, may be attributable to the nature of the specie, soil composition, season and geographical area of the farmland and also has a favourable effect on soil physical property and permeability as contained in a similar report of Chaudhari, (2013).

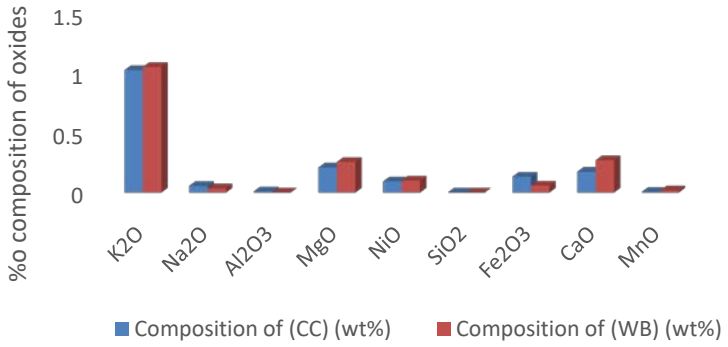

Figure 1: % Oxides composition of CC and WB powder

Microwave Plasma Atomic Emission Spectrometry (MP-AES) Result

The agricultural wastes CC and WB bio-sorbents were treated and digested for cobalt and nickel removal using metal solution, KYCV and GPC contaminated wastewater respectively, and the resulting solutions were analysed by MP-AES. The analytical results were provided in Figures 2 - 5 respectively. The MP-AES result of metal solution treated by agricultural wastes CC and WB bio-sorbents show that CC shows higher efficacy of Co(II) removal in filtrate solution after treatment (0.06mg/L) and it also contain higher residue concentration of (0.95mg/L) followed by WB has the least cobalt removal with (0.17mg/L) filtrate concentration after treatment and residue concentration of (0.42mg/L), while WB shows higher efficacy of Ni(II) removal (0.10mg/L) concentration in it filtrate solution and it contain higher residue concentration of Ni(II) (0.85mg/L), all in the order CC>WB. The result indicates that (CC) has higher efficacy of Co(II) removal while WB shows higher efficacy of Ni(II) removal. Also the result shows higher absorption of Co(II) ion when compared to Ni(II) ion, signifying higher affinity of Co(II) ion toward CC and WB biosorbents, some bio-sorbents tended to prefer some metals more than others, the agricultural wastes capacity for metal removal depends on metallic elements and operating conditions (Nguyen *et al.* 2013). The result is similar to the reported of Benaissa, (2006) on the capacity of four inexpensive materials which are peels of peas, broad bean, medlar and fig leaves, to remove Cd from aqueous solutions; it was noted that the broad bean peel has the maximum adsorption capacity for Cd.

The percent removal efficiency and bio-sorption capacity of Co(II) and Ni(II) ions by bio-sorbents indicates that CC possess highest percent removal efficiency and bio-sorption capacity (97% and 77.6mg/g) while WB has highest percent removal and bio-sorption capacity of Ni(II) (95% and 76mg/g) then CC has the least removal efficiency of Ni(II) and (WB) has the least removal of Co(II).The result shows that, the bio-sorbents demonstrate good efficacy and bio-sorption capacity of heavy metals removal from metal solution as shown in Fig. 4 data. These results are consistent with those reported by Abdelfattaha *et al.* (2016) in which peanut husk removed cobalt

and nickel from metal solution with 90% removal efficiency.

The MP-AES result also revealed the presence of the heavy metals [Co(II) and Ni(II)] in the KYCV and GPC contaminated wastewater, the varied concentration of the heavy metal indicates that the contaminated wastewater from KYCV has highest concentration of 0.80mg/L and 0.90mg/L for Co (II) ion and Ni(II) respectively while GPC has the lowest concentration of 0.10mg/L and 0.78mg/L for Co and Ni respectively as shown in Figure 3. The result shows that CC and WB biosorbents were able to reduce cobalt and nickel concentration from KYCV and GPC contaminated wastewater to lowest level after treatment. WB has the highest removal efficiency and biosorption capacity of Co(II) (92.5% and 29.6 mg/g) and it has higher Ni(II) removal and biosorption capacity of 52.2 mg/L and18.8 mg/g than CC using KYCV contaminated wastewater respectively while using GPC contaminated wastewater shows that WB has the highest Co(II) removal efficiency and biosorption capacity (80% and 3.2 mg/g) while CC the highest Ni(II) removal efficiency and bio-sorption capacity than WB as shown in Figure. 5.

The result shows that WB has high Co removal efficiency while CC has high Ni removal efficiency from contaminated wastewater. The concentration of heavy metals in (digested) residue revealed that WB has higher removal of Ni in both the contaminated wastewater. The agricultural wastes CC, WB manifested a good efficacy of heavy metal removal from contaminated wastewater. The higher percent removal of WB may be attributed to its powdery nature which makes it more porosity with larger surface area and thus making its particles compact easy to participate in the bio-sorption of the metal ions. Furthermore, the efficacy of these agricultural wastes materials in cobalt and nickel removal from contaminated water is similar to the reported of Farajzadeh and Monji, (2004) on cadmium and copper removal using wheat bran in contaminated water. This result seems to be less than the removal obtained using the standard single metal solution investigated. Since KYCV and GPC contaminated water samples may contain other ions, the reason is may be due to the possibility of competition for sorption sites. The level of cobalt and nickel in KYCV and GPC exceeded the permissible exposure limit of 0.50 mg/L for cobalt and 0.20 mg/L for nickel set by WHO (2010) for effluent water.

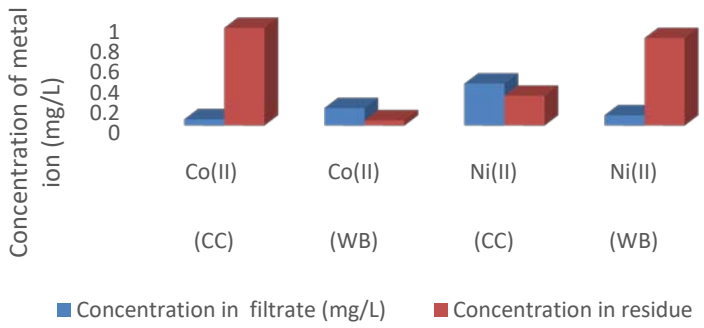

Figure 2: Concentration of Co(II) and Ni(II) after treatment with (CC and WB) biosorbents using metal solution

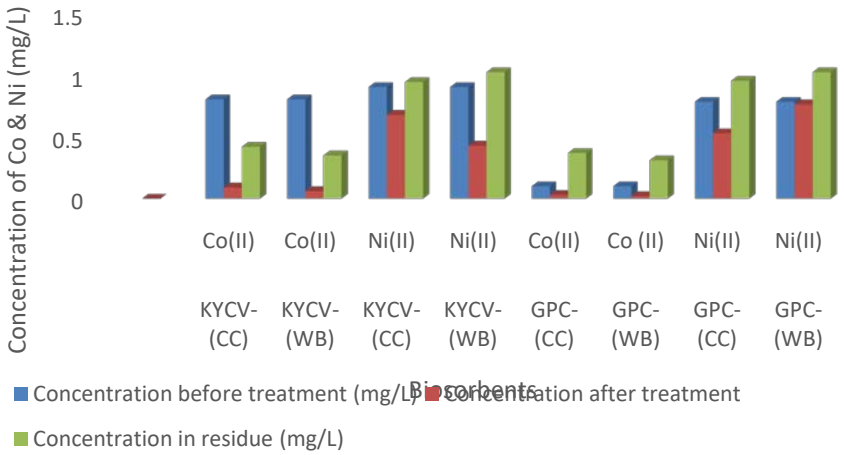

Figure 3: Concentration of Co(II) and Ni(II) after treatment with (CC and WB) biosorbents using (KYCV and GPC) contaminated wastewater

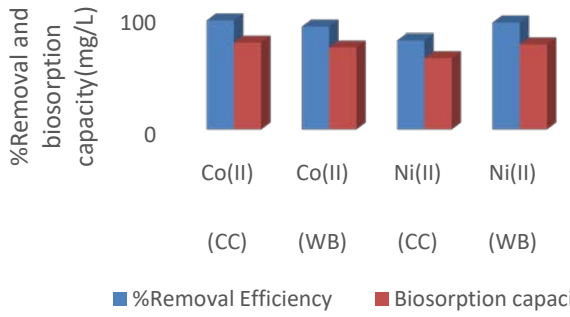

Figure 4: Removal and Bio-sorption capacity (mg/g) of Co(II) and Ni(II) by (CC and WB) as bio-sorbents using metal solution

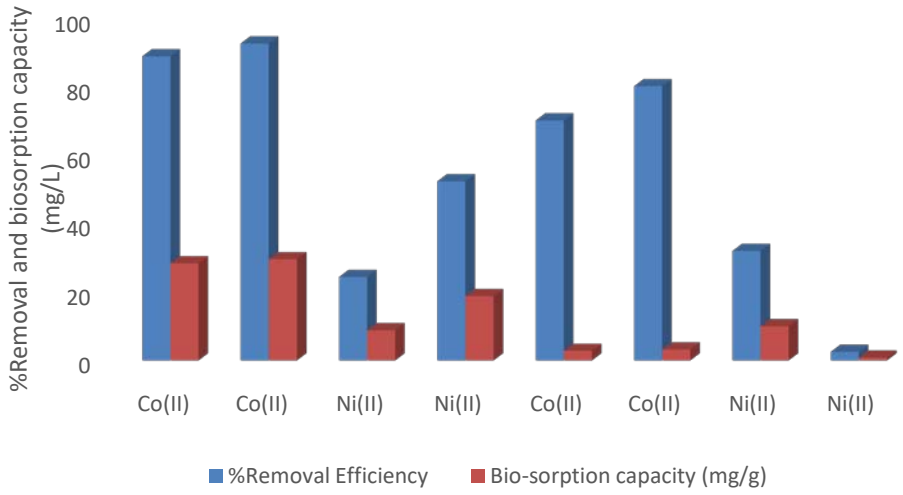

Figure 5: Removal and Bio-sorption capacity (mg/g) of Co(II) and Ni(II) by (CC and WB) as bio-sorbents using (KYCV and GPC) Contaminated Wastewater

Fourier Transform Infra-red (FTIR) Analysis Result

Infrared spectroscopy is a useful technique for the determination of functional groups and any changes taking place in the functional groups of any compounds. Figure 6 and 7 shows the Fourier Transform infrared (FTIR) of the CC and WB.

The Figure 6 shows the interpretation of raw-(CC) spectra before and after bio-sorption with Ni(II),Co(II), (KYCV and GPC) contaminated water uptake respectively. The spectra of raw-(CC) exhibited a sharp absorption band at 3398 cm^{-1} assigned to vinyl (O-H) stretching vibrations of carboxylic group, the band at2834 cm^{-1}, 2921 cm^{-1}, due to C-H stretching indicate presence of methyl and methylene groups, the 899 cm^{-1} and 668 cm^{-1} band are due C-H bending in aromatic compounds, the region at 1637 cm^{-1} indicate the presence of N-H bending in secondary amine, the peak at 1240cm^{-1}, 1320cm^{-1} due to C-O stretching vibration in alky aryl ether and aromatic ester, the band at 1715cm^{-1} indicate the C=O stretching in α,β-unsaturated ester and the peak at 1033 cm^{-1}indicate the stretching band of C=C. After interaction of raw-(CC) with Co(CC), Ni(CC), KYCV-(CC) and GPC-(CC), the spectra shows that, the characteristic bands of OH groups were shifted to lower wavenumber from 3398 cm^{-1} to 3301 cm^{-1} to 3312 cm^{-1} 3335 cm^{-1} and 3286 cm^{-1} in raw-(CC), Co-(CC) and Ni-(CC), KYCV-(CC) and GPC-(CC) respectively after bio-sorption, due to interaction of bio-sorbents functional groups with heavy metal ions as shown in Table 1. The band of C-H stretching vibration of methyl and methylene has also shifted from 2921 cm^{-1} to 2948 cm^{-1} to 2899 cm^{-1} to 2918 $cm^{-1}$$cm^{-1}$ to 2903 cm^{-1} in raw-(CC), Co-(CC) and Ni-(CC), KYCV-(CC) and GPC-(CC) respectively due to loading of heavy metals. The N-H band was also shifted in from 1637$cm^{-1}$to 1607$cm^{-1}$to 1592cm^{-1} to 1629$cm^{-1}$for Co, Ni, KYCV and GPC respectively, the carbonyl peak at 1715cm^{-1} were shifted and disappeared in KYCV spectra, the C-O band at 1240cm^{-1}were shifted to 1240cm^{-1}, 1236cm^{-1}, 1238cm^{-1}, 1246cm^{-1}, and 1242cm^{-1}, after bio-sorption with Co-(CC), Ni-(CC), KYCV-(CC) and GPC-(CC) respectively, the C=C stretching band at 1033cm^{-1} stretching band were not significantly shifted. Table 1 shows

the infrared bands of (CC) before and after the bio-sorption.

The spectra of raw-(WB) exhibited a sharp absorption band at 3398 cm-^{1} assigned to O-H stretching vibrations in alcohols, C-H stretching regions were observed at 2899 cm-^{1},due presence of methyl and methylene groups, 899cm-^{1} and 665cm^{-1}are due to trans-C-H out of plane bend and C-H stretching in aromatic compounds, the peak at 1640cm-^{1} indicate presence of N-H bend in secondary amine, the region at 1242cm-^{1}due to C-O stretching vibration in alky aryl ether, the band at 1707cm-^{1} indicate the C=O stretching in α, β-unsaturated ester and the peak at 1022 cm-^{1}indicate the stretching band of C=C. As shown in Table 2. After sorption process, the bio-sorbents spectra showed that, the main characteristic peaks have shifted to lower frequencies, the stretching bands of the OH groups were shifted to 3875 cm-^{1} to 3279 cm-^{1} to 3276 cm-^{1} to 3275 cm-^{1} and 3257 cm-^{1} in raw-(WB), Co-(WB) and Ni-(WB), KYCV-(WB) and GPC-(WB) respectively. The C-H stretching vibration of methyl and methylene has also shifted from 2899 cm-^{1} to 2921 cm-^{1} to 2918 cm-^{1} to 2921 cm-^{1} to 2921 cm-^{1} in raw-(WB), Co-(WB) and Ni-(WB), KYCV-(WB) and GPC-(WB) respectively due to loading of heavy metals.

The N-H band in secondary amine was also shifted in from 1640cm-^{1}to 1629cm-^{1}to 1640 cm-^{1} to 1611cm-^{1} and 1629cm-^{1}for Co, Ni, KYCV and GPC respectively, the carbonyl peak C=O at 1707cm-^{1} was shifted to 1719cm-^{1} in KYCV and GPC spectra and disappeared in Co-(WB) and Ni(WB) spectra due bio-sorption process, the C-O band at 1242cm-^{1}was disappear in Co-(WB) and shifted to 1236cm-^{1}, 1229cm-^{1} and 1324cm-^{1}, in Ni-(WB), KYCV-(WB) and GPC(WB) respectively, the C=C stretching band at 1022cm-^{1} stretching band were not significantly shifted. As shown in Figure 7. The rest of stretching and bending infrared bands e.g. C=C and C-O etc., were not significantly shifted. There was significant shift in the infrared of O-H, C=O, C-O, C-H after bio-sorption process. The shifting and appearance of new infrared band suggest that bio-sorption of metal ions on to (CC, WB and SB) bio-sorbents has taken place (Baby *et al.*, 2019).Figure 7 shows the bands of (WB) before and after the bio-sorption.

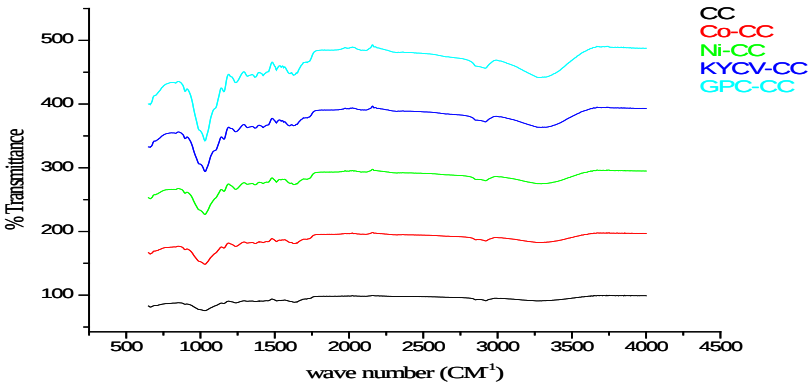

Figure 6: Shows the spectra of raw-(CC) before and after bio-sorption with Co- (CC), Ni-(CC), (KYCV-CC) and (GPC-CC)

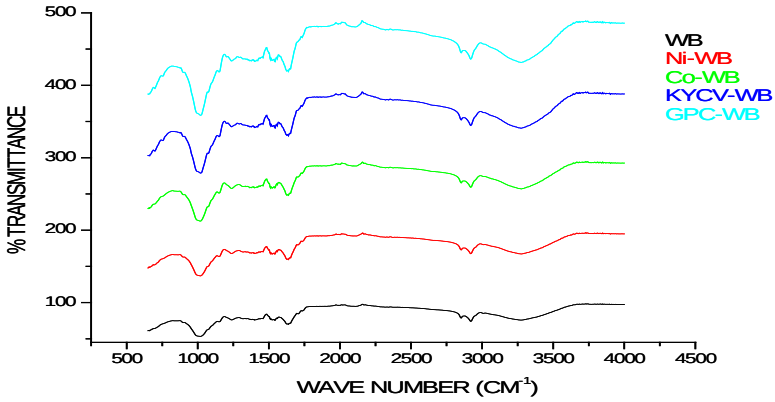

Figure 7: FTIR spectra of raw-(WB) before and after biosorption with Co-(WB), Ni-(WB), (KYCV-WB) and (GPC-WB).

Table 1: Assignments of FTIR spectra of raw-(CC) before and after biosorption with Co-(CC), Ni-(CC), (KYCV-CC) and (GPC-CC)

Bio sorbents	(O-H) (cm^{-1})	(C-H) (cm^{-1})	N-H (cm^{-1})	C=O(cm^{-1})
Raw-(CC)	3398	2921	1637	1715
Co-(CC)	3301	2948	1637	1652
Ni-(CC)	3312	2899	1607	1722
KYCV-(CC)	3335	2918	1592	-
GPC-(CC)	3286	2903	1629	1722

Table 2: Assignments of FTIR spectra of raw-(WB) before and after bio-sorption with (Co-WB), (Ni-WB), (KYCV-WB) and (GPC-WB)

Bio sorbents	O-H (cm^{-1})	C-H (cm^{-1})	N-H (cm^{-1})	C=O (cm^{-1})
Raw-(WB)	3875	2899	1640	1707
Co-(WB)	3279	2921	1629	-
Ni-(WB)	3276	2918	1640	-
KYCV-(WB)	3275	2921	1611	1719
GPC-(WB)	3275	2921	1629	1719

CONCLUSION

This study was conducted for the development of natural, cheap, easy to prepare and effective technology for the removal of heavy metals from contaminated water , the selected agricultural waste (CC, WB) bio-sorbents have successfully remove Co(II) and Ni(II) from contaminated water. The result demonstrated that both (CC and WB) effectively removed Co(II) and Ni(II) with (97%) removal efficiency and (77.6 mg/g) bio-sorption capacity in metal solution,(92% and 29.4 mg/g) and (80% and 3.2 mg/g) removal efficiency and bio-sorption capacity from (KYCV and GPC) contaminated wastewater. Among the selected bio-sorbents (WB) possess higher sorption efficiency.

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