



### RESEARCH ARTICLE

## POTENTIAL USE OF DATE PALMS AND COTTON STALKS BIOCHARS FOR REMOVING CO (II) AND NI (II) FROM WASTEWATER

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### Abstract

In recent years, removal of heavy metals from contaminated water has become a major topic due to the toxicological problems caused by the toxic metals to the environment and to human health. Among the various removal methods, adsorption has been proven to be an efficient technology, while its large-scale application is limited by the high cost of the adsorbent. Under this situation, some raw agricultural residues materials, as low-cost adsorbents, were tested to evaluate their efficiency in the removal of heavy metals. The main objective of the present study was to investigate the feasibility of biochars, resulted from date palms and cotton stalks slow pyrolysis process, as adsorbents for Co (II) and Ni (II) removal from polluted drainage water. The two biochars (i.e. date palms and cotton stalks) were characterized and investigated for Co (II) and Ni (II) removal from polluted water from a main drain. Similarly, activated carbon (A.C.) from the date palms residues was prepared by thermal analysis as adsorbent and used for comparison with the two biochars. The results indicated that the original product biochars from slow pyrolysis process might be used as inexpensive adsorbents for water purification.

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### Introduction:-

Environmental pollution by toxic heavy metals is a worldwide problem due to increased industrialization. Also, irrigating crops with polluted water from open drainage channels is a common practice in urban agricultural production regions in Egypt. These heavy metals are particularly problematic due to their accumulation in the food chain and their persistence (Bueno *et al.*, 2008). Recently, several researchers indicated that, bio-sorption of heavy metals using biological materials has been identified as a potential technique for remediation of metal bearing effluents (Babarinde *et al.*, 2009; Babarinde and Babalola 2010; Sarma, 2010; Liu *et al.*, 2010; Sari *et al.*, 2007; Zhang and Wang 2010; Vijayaraghavan and Balasubramanian 2010; Fiorentin *et al.*, 2010; Qu and Zhang 2010; and Basu *et al.*, 2010). Also, conventional methods of removing heavy metals from solutions were reported (Sari *et al.*, 2007). There is a need to regulate heavy metals levels in the environment before they accumulate in the food and cause severe health problems. Moreover, El-Haggaret *al.* (2001) reported that there are almost 24 million tons/year of agricultural biomass produced in Egypt. Most of these wastes are being burned in open areas to get rid of them causing the black cloud, polluting the environment, in addition to releasing significant amounts of toxic and greenhouse gases. Agricultural wastes "cotton stalks and date palms" are available in large quantities in several parts

of the world and produced by the farmer in Egypt (Ali *et al.*, 2001). Biomass can be converted by thermo chemical process into valuable products. Currently, there are several thermo chemical technologies such as pyrolysis used for production biochars. Pyrolysis converts organic matters into valuable products namely: solid char (biochars), liquid (bio-oil), a gas and a high carbon. Pyrolysis involves heating of organic materials in absence of oxygen. It is simple and inexpensive process used to produce biochars for thousands of years (Lehmann and Joseph, 2009). Khater and Chandrupa (2006) indicated that, the particular characteristics of biochars depend strongly on their property, which is affected in turn by the pyrolysis conditions, and type of feedstock used in its production. Yield and composition of biochars products depend on pyrolysis conditions. Liang *et al.* (2006) stated that, biochars usually have greater sorption ability than natural soil organic matter due to their greater surface area, negative surface charge, and charge density. These characteristics make biochars an exceptional water amendment for use in sustainable agriculture (Lehmann and Joseph, 2009; and Verheijen *et al.*, 2010).

The first goal of this study was to find a value-added utilization approach for agricultural residues. The second goal was to examine the potential use of biochars, resulted from date palms and cotton stalks slow pyrolysis process, as adsorbents for Co (II) and Ni (II) removal from polluted drainage water compared with A.C. derived from date palms.

## Materials and Methods:-

### Water samples:-

Water samples were collected from El-Qalubia main drain at three locations namely: El-Lemon village (sample 1), El-Gendi village (sample 2), and Belbies drain representing the extension of El-Qalubia main drain (sample 3). The following measurements were done for the collected water samples:

- The pH values were measured by pH-meter (CG710) according to Issam and Antonie (2007).
- The electrical conductivity values ( $\text{mmhos.cm}^{-1}$ ) were measured using a conductivity bridged meter 710 (Issam and Antonie, 2007).
- Total contents of heavy metals (Pb, Co, Ni, Cd, and Cr) were determined by inductively atomic spectroscopy (Issam and Antonie, 2007).

## Biochars and A.C. preparation:-

### Biochars preparation:-

The feedstock used for preparation focused on two crop residues, i.e. date palms and cotton stalks. These waste biomass were collected from local sources, where date palms and cotton stalks were obtained from farmers fields at El-Minia governorate, Egypt. The collected samples were left to air dry and subsequently oven-dried over night at 75 °C. Certain weight of samples were added in Teflon-crucible covered with punched alumina paper in closed iron box in presence of  $(\text{NH}_4)_2\text{CO}_3$  as available laboratory mean to generate  $\text{N}_2$  or  $\text{CO}_2$  gas. Then, the samples were placed in muffle, with slow pyrolysis at 250 and 400 °C for 1 h. Finally, the samples were left to cool to room temperature (Wei Zhenget *al.*, 2010).

## Preparation of active carbon (A.C.) from date palms:-

### Materials:-

Prior to carbonization of the raw materials, namely date palms, the sample was left in air for partial dryness, crushed to fragments and then dried at 100 °C for 2 hrs till constant weight. The dried crushed material was subjected to destructive distillation at 625 °C in muffle in presence of excess  $(\text{NH}_4)_2\text{CO}_3$  for 5 hrs to obtain non-activated carbon.

### Preparation of steam A.C.

The steam activated samples of date palms are prepared by gasification of non-activated carbon at 900 °C in presence of excess of  $(\text{NH}_4)_2\text{CO}_3$  for 1/2 h, then left to cool to room temperature. Finally, the samples were kept in a dark bottle (El-Sharkawy, 2001).

### Chemical analysis:-

Chemical properties of biochars types obtained at 250 and 400 °C, and A.C. of date palms including pH, E.C., and carbon and ash contents were measured. Also, the FT-IR spectra was used to investigate the oxygen-surface functional groups. Boehm (2002) titration method was used to determine the concentration of functional groups investigated.

- To measure the pH of biochars types and A.C. of date palms investigated 1% suspensions were prepared by diluting them with double ionized water, then heated to about 90 °C , and stirred for 20 min. to allow the dissolution of the soluble biochars components. Finally, the pH, and E.C.were measured according to Agusalimet *et al.*, (2010).
- Carbon and ash contents of the samples were determined using elemental analysis at 650 °C for 6 hrs in open crucible (ASTM, E1755-01).
- Surface area of the samples were calculated from N<sub>2</sub> adsorption isotherms by BET method using Nova 2000.
- Concentration of oxygen-surface functional groups was determined using the barium titration method (Boehm, 2002).
- Determination of base neutralization capacity (BNC) of A.C. of date palms  
The BNC was determined via the adsorption from aqueous solutions of different bases, namely NaOH, Na<sub>2</sub>CO<sub>3</sub>, and NaHCO<sub>3</sub>, onto A.C. prepared. 0.2 g of the samples in 50 mL (0.2 molL<sup>-1</sup>) base was shaken for 24 h, filtered, then titrating the filtrate using (0.1 molL<sup>-1</sup>)HCl as described by Boehm (2002).
- The main functional groups were identified by the FT-IR spectrum ("IR.Affinity<sup>1</sup>" Fourier transformation IR spectro- photometer, Shimadzu). The spectra investigated the surface carbon-oxygen groups.

#### Batch adsorption experiments:-

100 mL of wastewater solution were taken and adjusted at pH 7, then 1 g /0.2 g of the biochars types obtained at 250 and 400 °C, and A.C., respectively was added. The particle size of the biochars types prepared for this test was 125 µm. The components were put in closed bottles, and shaken for 2½ hrs at room temperature. Finally, the sorbent separated from the samples by filtration and the filtrate was analyzed using atomic spectroscopy technique according to Kilic *et al.*, (2013).

#### Results and Discussion:-

Results of the mean values of pH, E.C., and heavy metals contents in the water samples initially collected from the main drain are presented in Table 1.

##### pH values:-

The measured pH values were 7.15, 7.40, and 7.35 for 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> samples, respectively. Results indicated that, all pH values fall within the normal range according to the guidelines of El-Gendi (2004).

##### Electrical conductivity (E.C.):-

Results in Table 1 showed that the E.C. values of the initial water samples were 1.14, 0.90, and 1.44 mmhos.cm<sup>-1</sup> for 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> samples, respectively. All E.C. values fall in the acceptable range according to the guidelines of El-Gendi *et al.*, (2004). According to Ayers and Westcott (1985) who classified the quantity of saline water with respect to its total salinity (E.C.), the three samples collected from the three locations may cause increasing salinity problem for soil for continuous irrigation uses.

##### Heavy metals contents:-

The values of total Ni, Co, Cr, Pb, and Cd contents of the three samples of wastewater under investigation are presented in Table 1. Results indicated that, total Ni values were 0.76, 0.86, and 0.51 mmolL<sup>-1</sup> for 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> samples, respectively. Total Co values were 0.85, 0.11, and 0.61 mmolL<sup>-1</sup> for 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> samples, respectively. Results showed also that, Cd values were 0.021, 0.025, and 0.028 mmolL<sup>-1</sup> for 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> samples, while Pb values were 0.47, 0.28, and 0.26 mmolL<sup>-1</sup> for 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup> samples, respectively. As for Cr contents, the measured values were zero for 1<sup>st</sup> and 3<sup>rd</sup> sample; while for the 2<sup>nd</sup> sample it was 0.03 mmolL<sup>-1</sup>. The obtained results showed that, the values of Pb, Cd, Ni, Co, and Cd are higher than that reported by El-Gendi *et al.*, (2004). The heavy metals contents can be arranged in descending order as follow:

Co > Ni > Pb > Cd	for 1 <sup>st</sup> sample
Ni > Pb > Co > Cr ≈ Cd	for 2 <sup>nd</sup> sample
Co > Ni > Pb > Cd	for 3 <sup>rd</sup> sample

Also, it is concluded that there was no contamination or hazard effect for Pb, and Cr and not for Cd, Ni, and Co heavy metals. On the other hand, the obtained values were within the save range according to Kabata-Pendias and Pendias (1992) and Bowen (1979).

**Table 1:-**The pH, E.C. values and concentration of heavy metals of the investigated wastewater of El-Qalubia main drain

Sample	pH	E.C.	Heavy metals (mmolL <sup>-1</sup> )					
		<i>mmoScm<sup>-1</sup></i>		Pb	Ni	Co	Cr	Cd
1	7.15	1.14		0.47	0.76	0.85	-	0.02
2	7.40	0.90		0.28	0.86	0.11	0.03	0.03
3	7.35	1.44		0.26	0.51	0.61	-	0.03

**Table 2:-** Recommended values of heavy metals in water according to Bowen (1979)

Heavy metals contents (mmol L <sup>-1</sup> )					
Metal	Cd	Pb	Ni	Co	Cr
Limits	0.01	0.50	0.20	0.05	0.10

**Characterization of the prepared biochars types and active carbon (A.C.):-**

Generally, Chen *et al.*, (2016) showed that there were number of parameters affecting properties of products. These include the biomass type, biomass pretreatment (physical, chemical, and biological), reaction atmosphere, temperature, heating rate, and vapor residence time. This manuscript gives a general summary of the properties of the pyrolytic products and their analysis methods.

**pH values:-**

Results in Table 3 represent the measured pH values of the biochars types obtained at 250 and 400 °C prepared from the biomass of date palms and cotton stalks. The average pH values of biochars obtained at 250 °C were 7.10 for date palms and 7.60 for cotton stalks. Also, average pH values of biochars types obtained at 400 °C were 7.55 for date palms and 7.70 for cotton stalks. The obtained results indicate that pH of biochars increased with the pyrolysis temperature. From the obtained results it could be concluded that the two biochars types obtained at 400 °C have net negative surface charge more than those obtained at 250 °C. Results presented in Table 3 showed also that, active carbon (A.C.) prepared from date palms at 900 °C has higher pH value 8.95 than biochars types obtained at 250 and 400 °C. The results agreed with that reported by Zainabet *al.* (2015), who indicated that the A.C. prepared from date palms had a highly porous structure and thus it is expected to be a suitable adsorbent for heavy metals ions removal from wastewater systems.

**Electrical conductivity values:-**

In general, E.C. values of both biochars types obtained at 250 and 400 °C, and the active carbon were found less than 1 (Table 3). The average E.C. values of biochars types obtained at 250 °C were 0.21 mmol.cm<sup>-1</sup> for date palms and 0.23 mmol.cm<sup>-1</sup> for cotton stalks. While, average E.C. values of biochars types obtained at 400 °C were 0.12 mmol.cm<sup>-1</sup> for date palms and 0.38 mmol.cm<sup>-1</sup> for cotton stalks. Also, results indicated that the E.C. value was 0.38 mmol.cm<sup>-1</sup> for the A.C. prepared from the date palms. For the biochars obtained from date palms, the E.C. values decreased with increasing temperature, while the E.C. values decreased for the biochars prepared from cotton stalks. According to the classification reported by Logan *et al.* (1997) and Al-Wableet *al.* (1998), biochars types obtained at 250 and 400 °C, and A.C. of date palms did not cause increasing in the water salinity. Zahra *et al.* (2015) showed that liquid-phase E.C. was very high, indicating that soluble ions were mainly separated by the effluent from the solid phase (biochars obtained at 700 °C) used. This led to a low concentration of soluble ions in the biochars suspension compared to sewage sludge.

**Carbon and ash contents:-**

Results listed in Table 3 showed that the average carbon and ash contents of both biochars types obtained at 250 °C were 71, 29, 75, and 25 % for date palms and cotton stalks biochars, respectively. The values obtained at 400 °C were 75.5, 24.5, 77, and 23 %. For the A.C. of date palms, the respective values were 85 and 15 %. Results indicate that, carbon contents generated from the two biochars types and A.C. type increased with temperature increase. Conley *et al.*, (2009) reported that carboxylic and lactone groups decompose "carbonize" in the range from 200 to 700-800 °C, the guanine, phenol and ether groups decompose in the range from 500-1000 °C, and the phenolic groups decompose in the range from 200-300 °C to 400-500 °C.

**Surface area measurements ( $S_{\text{BET}}$ ):-**

Surface areas generally increased with increasing temperature. Average surface area values measured for both biochars types obtained at 250, and 400°C as well as the A.C. of date palms are presented in Table 3. Results showed that, average surface area values of biochars types obtained at 250 °C were 1.60 m<sup>2</sup>g<sup>-1</sup> for date palms and 1.67 m<sup>2</sup>g<sup>-1</sup> for cotton stalks. While, the same respective surface area values of biochars types obtained at 400°C were 3.95 m<sup>2</sup>g<sup>-1</sup> and 3.99 m<sup>2</sup>g<sup>-1</sup>. Results indicated that, increasing the temperature increases the surface area of the raw materials used. For the A.C. of the date palms, average surface areas was 8.87 m<sup>2</sup>g<sup>-1</sup>. The obtained value was the highest as compared with biochars types obtained at 250 and 400, which reflect the formation of fine-pore structure generated through a well-controlled activation process. The obtained results agreed with that of Chen *et al.* (2008), who indicated that the increased surface area of biochars and A.C. produced at higher pyrolysis temperature is attributable to the removal of -OH, aliphatic C-O, and ester C=O groups from outer surfaces of the feedstock.

**Table 3:-** Some characteristics of derived biochars at 250, 400 °C & A.C

Raw materials	pH	E.C mScm <sup>-1</sup>	$S_{\text{BET}}$ m <sup>2</sup> g <sup>-1</sup>	C%	Ash%
D.P 250	7.10	0.21	1.60	71	29
C.S 250	7.60	0.23	1.67	75	25
D.P 400	7.55	0.12	3.95	75.5	24.5
C.S 400	7.70	0.38	3.99	77	23
A.C of D.P	8.95	0.38	8.87	85	15

**Functional groups concentration:-**

The concentration of the oxygen-surface functional groups of biochars types obtained at 250 and 400 °C are represented in Table 4. At 250 °C average surface functional groups concentration values varied from 0.270 to 0.320 mmole.g<sup>-1</sup> for date palms, and from 0.172 to 0.219 mmole.g<sup>-1</sup> for cotton stalks. While, biochars types obtained at 400°C, average values varied from 0.982 to 0.983 mmole.g<sup>-1</sup>, and from 0.257 to 0.357 mmole.g<sup>-1</sup> for date palms, and cotton stalks, respectively. Results indicated that, increasing the temperature, increases the concentration of the functional groups. Results indicated also that, with increasing pyrolysis temperature the concentration of functional groups increases.

**Base neutralization capacities:-**

It is the most simplest and convenient technique for the qualitative and quantitative identification of surface acidic groups on the surface of A.C. type. It was found that the titration with Na<sub>2</sub>CO<sub>3</sub> can neutralize carboxylic and lactonic groups, NaHCO<sub>3</sub> neutralize the carboxylic groups, while NaOH neutralize all acidic groups on the surface. The base neutralization capacities of the investigated samples expressed in meq.g<sup>-1</sup> are shown in Table 5. Results showed that the sum of functional groups concentration related to negative surface charge of active carbon (A.C.) was higher than each biochars types obtained at 250 and 400 °C. The concentration of the functional groups were 0.708 meq.g<sup>-1</sup> for the carboxylic and lactonic groups neutralized by Na<sub>2</sub>CO<sub>3</sub>, 0.475 meq.g<sup>-1</sup> for the carboxylic groups neutralized by NaHCO<sub>3</sub>, and 0.125 meq.g<sup>-1</sup> for all acidic groups neutralized by NaOH.

**Table 4:-** Functional groups concentrations of lignocellulosic biochars 250 & 400 °C determined using the Barium titration method

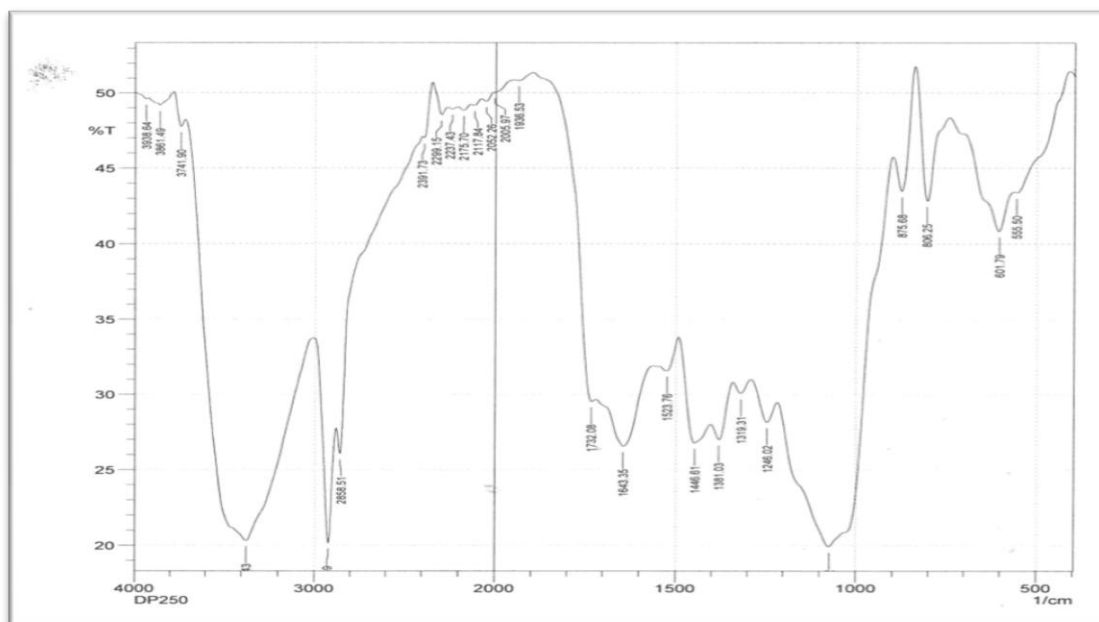
Types of biochars	Functional groups concentration mmol g <sup>-1</sup>
D.P 250	0.270 – 0.320
C.S 250	0.172 – 0.219
D.P 400	0.982 – 0.983
C.S 400	0.257 – 0.357

**Table 5:-** Functional groups concentrations of the A.C. of D.P.

A.C type	NaOH	Na <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>
	meq.g <sup>-1</sup>	meq.g <sup>-1</sup>	meq.g <sup>-1</sup>
A.C of D.P	0.708	0.475	0.125

**FT-IR Spectrum analysis:-**

The FT-IR analysis investigates the surface C-O groups. It is the main tool to identify these groups as some of important functional groups that lead to negative surface charge are responsible for the interaction. Results in Figs1-4 showed that the spectra of biochars types obtained at 250 and 400 °C were relatively similar in shape and their intensities. This is due to the fact that the lignocellulosic materials were charred at relatively low temperature, and only partial ionization occurred. The FT-IR spectrum as illustrated in Figs.1 and 2 for date palms and cotton stalks biochars obtained at 250°C, had a band at 3200  $\text{cm}^{-1}$  stretching indicating the presence of both free alcohol-OH, H-bonding. A band at 1064  $\text{cm}^{-1}$  stretching of date palms, and a band at 1049  $\text{cm}^{-1}$  of cotton stalks indicates the possibility of C-O stretching, or alcohol-OH, or carboxylic acid. There was a sharp band at 2924  $\text{cm}^{-1}$  of date palms that is related to C-C of alkenes. While in the FT-IR spectra of date palms and cotton stalks biochars obtained at 400°C (Figs 3 and 4), there was a band at 1589  $\text{cm}^{-1}$  of the two biochars types which is related to C-C alkenes and aromatic rings. In addition, there are other secondary bands of both of biochars types obtained at 250 and 400°C related to more substituted C=N,  $\text{NO}_2$ , ---- etc. Results of the FT-IR analysis indicate the similarity in the main functional groups and the properties of date palms and cotton stalks biochars prepared at 250 and 400°C. The FT-IR spectrum of the A.C. from date palms type showed a band at 1100  $\text{cm}^{-1}$  which is related to the possibility of the presence of C-O stretching. This band is a predominant band that is considered as an important functional group and the responsible for interactions that may be occurred. Also, there were other bands of the A.C.type related to other secondary groups. The obtained results agree with those of Chen (2008) and Chun *et al.* (2004), who reported that the absence of significant adsorption bands in the spectrum of A.C. suggests that the graphic structure is symmetrical and little change in dipole moment occurs during vibration.



**Fig.1.** FT-IR spectrum of D.P 250

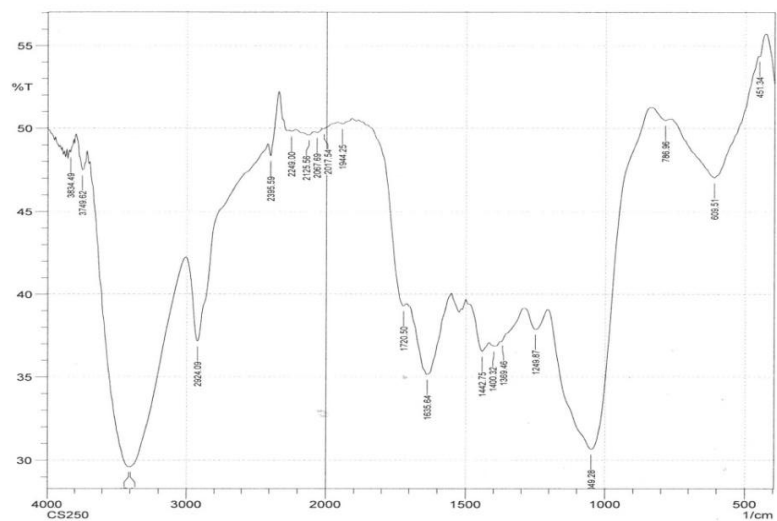


Fig. 2:- FT-IR spectrum of C.S 250.

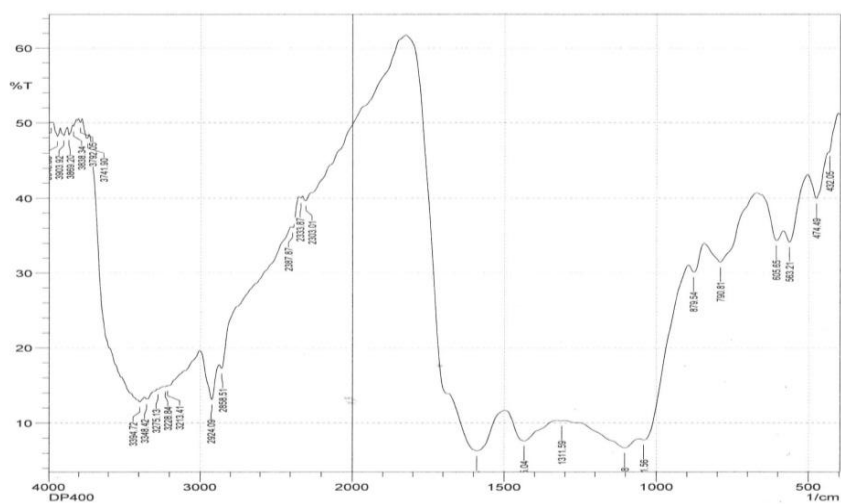


Fig.3:- FT-IR spectrum of D.P 400

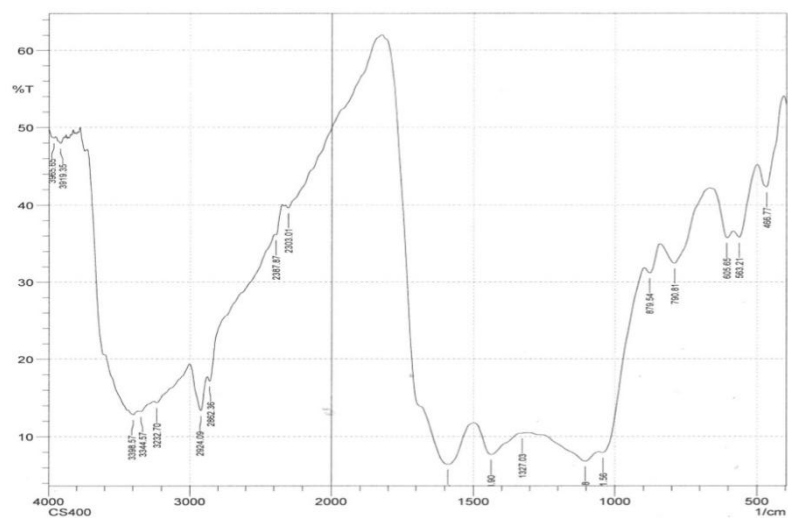
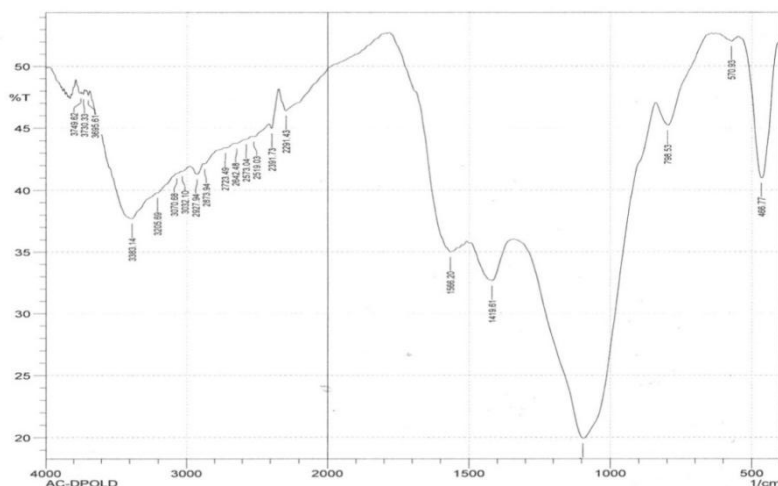


Fig.4:- FT-IR spectrum of C.S 400



**Fig.5.** FT-IR spectrum of A.C of D.P

### Wastewater remediation using biochars types and A.C of date palms:-

Results indicated that both date palms and cotton stalks biochars obtained at 250 and 400 °C, and A.C. of date palms affected the physical properties of the wastewater samples under study by removing their color, odor, and suspended matters. The obtained results are due to the development of surface basic groups of the used biochars and the more basic character of the active carbon. The results were agree well with those reported by Nancharaiah (2011), Namasivayam (2006), Yin (2007), and Demiral (2010), who reported that biochars and active carbon materials are widely used in the removal of several different organic and inorganic pollutants from wastewater.

**Ni (II), and Co (II) adsorption:-**

Results in Table 6 showed Ni (II) and Co (II) adsorption at pH 7 and their removal percentage as compared to the initial conditions. It was noticed that both biochars types obtained at 250 and 400 °C had the same efficiency of Co (II) removal, but results were different for Ni (II). The removal reached 100 % for Co (II) for both biochars obtained at 250 and 400°C. For the biochars prepared from date palms, Ni (II) concentrations and the removal values were 0.113 mmolL<sup>-1</sup> (84.9 %) and 0.12 mmolL<sup>-1</sup> (84 %) at 250 and 400°C, respectively. While, for the biochars prepared from cotton stalks, Ni (II) adsorption increased with increasing temperature. Ni (II) concentrations and the removal values were 0.197 mmolL<sup>-1</sup> (73.7 %) and 0.09 mmolL<sup>-1</sup> (88 %) at 250 and 400 °C, respectively.

There are two mechanisms, specific (inner-sphere complexation) and nonspecific (outer-sphere complexation) between anionic ligand adsorbed onto metal oxides. Outer-sphere complexation will form a neutralized surface as an anion coordinates to a protonated hydroxyl on the adsorbent surface. Anions complexed in the outer-sphere of a metal oxide are readily exchangeable and free to move in solution and no complex is formed with surface functional groups. Hydroxyl ligand exchange can occur after surface pretention, which is known as inner-sphere complexation (Tor and Cengelöglu.2006). All such interactions can be occurred between metal ions and biochars as adsorption mechanism (Mohan *et al.* 2014). The adsorption capability of the biocharspyrolyzed at 200 °C exceeded that of pyrolyzed samples at higher temperatures (Li., (2016).

There are several interpretations of the variation of Ni (II), and Co (II) adsorption ratios. The first is that may be due to Co (II) prefers reaction with basic groups "as predominant groups" of Alcohol-OH and C-O or COO groups of date palms, and cotton stalks biochars obtained at 250°C rather as well as than that of C-C "alkenes" as predominant groups" of the corresponding biochars obtained at 400°C forming stable complex with respect to Ni (II) as mentioned previously in FT-IR analysis. The second interpretation may be attributed to the high affinity, and selectivity of Co (II) with respect to Ni (II). This behavior is explained according to hard-soft acid-base rule (Pulls and Boehn, 1988; Prada's *et al.*,1994). The third onemay be due to the basic character of biochars related to the functional groups ;the mean responsible of interactions, leads to preferring combination with Co (II) as central atom with biochars type as ligand rather than Ni (II) forming stable complex.

Also, results in Table 6 showed that the active carbon type had the same efficiency of Co (II) removal compared with Ni (II) removal. Adsorption ratio at pH 7 reached maximum of 100 % for Co (II), while it reached 84 % for Ni



(II). Maximum adsorption occurred at pH 7 because overall surface charge of A.C. type prepared have highly net negatively charged correlated to its active sites. pH affects the adsorption as well as that related to the ionization degree of the acidic or basic compound (El-Zayat and Edwards, 2009). This ability to chelate the different molecules is mainly due to its higher specific surface area (Saudi Embassy, 1997). The mixed heavy metals compete with each other during the adsorption process on A.C. prepared (Mohamed and Edwards, 2015).

**Table 6:-Ni (II) and Co (II) concentrations in the remediated wastewater of El-Qalubia main drain by the biochars types and the A.C determined at pH 7**

Biomass type	Ni(II)		Co(II)	
	Conc. (mmolL <sup>-1</sup> )	Removal (%)	Conc. (mmolL <sup>-1</sup> )	Removal (%)
D.P 250	0.113	84.9	-	100
C.S 250	0.197	73.7	-	100
D.P 400	0.120	84.0	-	100
C.S 400	0.090	88.0	-	100
A.C of D.P	0.120	84.0	-	100

#### pH effect on Co (II), and Ni (II) adsorption:-

Since pH is one of the main variable affecting the sorption process, beside the adsorbent dosage, contact time, particle size, room temperature, it has influence not only on the metal ions speciation, but also the surface charge of the sorbent and ionization degree of the adsorbateduring the reaction (Yu *et al.*, 2013). Ni (II) and Co (II) adsorption was carried out at pH 7 and the results given in table 6.

#### Conclusion:-

In this study biochars, an original product of pyrolysis process prepared at 250 and 400 °C, were evaluated as an alternative low-cost adsorbent for Ni (II) and Co (II) ions removal from wastewater solutions besides A.C of date palms for comparison. Optimum adsorption conditions were determined as a function of pH 7, adsorbent dosage 1/0.2 gL<sup>-1</sup> ofbiochars types and A.C type, respectively. The particle size of the biochars types was 125 µm, and contact time 2½h at room temperature for Ni (II) and Co (II) removal. Maximum adsorption reached 100 % for Co (II) and 84.9 % for Ni (II).

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