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Assessment of Heavy Metals Removal from Irrigation Water by Charcoal Using Laser Induced Breakdown Spectroscopy (LIBS)

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Abstract: Charcoal filters were prepared from PVC pipes of D_{out} 90 mm, D_{in} 84 mm, L 100 cm provided with groove near bottom. Constant gravel depth of 20, 40, 60 and 80 cm was used as bed below the charcoal. Water containing heavy metals Cu^{+2}, Fe^{+2}, Cd^{+2} and Pb^{+2} of different concentrations 100, 200, 300 and 400 mg/L were used. In Combinations of charcoal with depths indicated above for charcoal and contact times 20, 40, 60, 80, 100 and 120 min were applied. Removal efficiency of the heavy metals were determined using laser Induced Breakdown Spectroscopy (LIBS), Q-switched Nd:YAG, Max. Energy 450 mJ, pulse duration 6ns, Rate 1-20 Hz. With respect to the effect of the contact time on the removal efficiency % the results illustrated that the more contact time produced more removal efficiency until reaching certain value Rmax, for each heavy metal after that a constant graph obtained this is due to an equilibrium condition which was reached at different times as following: the contact time needed to reach such equilibrium conditions for Fe, Cu, Pb were 40 min whereas for Cd was 20 min at 100 mg/L and 20 cm depth of charcoal. The filter combinations (FC) can be arranged in the following order FC_1 (400 mg/L, 80 cm and 120 min) > FC_2 (300 mg/L, 60 cm and 100 min > FC_3 (100 mg/L, 40 cm and 60 min) the removal efficiency values were 92.73, 86.70 and 79.20, respectively.

Key Words: Adsorption, Charcoal, Heavy metals, Irrigation water, Removal efficiency.

1. Introduction:

LIBS was studied in the last decades as a new technique deal with the study of spectral distribution of line intensities and line shapes where it is based on optical emission of plasma spectra (Wu X *et al*., 2008). Considerable attention has been paid to methods for heavy metal removal and those commonly used include electrochemical methods, reverse osmosis, chemical precipitation, ion exchange, biological processes, flotation and membrane process (Park D. *et al*., 2010). Adsorption by activated carbon becomes a preferred choice than other physico-chemical techniques of heavy metal remediation due to its simplicity, cheap, easy to scale-up and most importantly able to remove low concentration substance even at mg/L levels with high efficiency and it has been widely applied for removal of heavy metals at trace levels (Huang C.P. and Blankenship D.W., 1984). The removal efficiency (RE%) of adsorbent was defined in equation (1) as:

$$RE\ (\%) = \frac{C_0 - C_1}{C_0} \quad x \quad 100 \qquad (1)$$

Where C_0 and C_1 is the initial and equilibrium concentration (mg/L), respectively (Bernard E. *et al.*, 2013).

1.1. Effect of Contact time on removal efficiency:

The relationship between contact time and the removal % of heavy metals from wastewater with activated carbon produced from coconut shell. The effect of contact time was studied at a temperature 32°C, at time of 20 min (Nomanbhay S. M. and Palanisamy K., 2005).

The present study was dedicated to assign depth of charcoal: 20, 40, 60 and 80 cm and contact time 20, 40, 60, 80, 100 and 120 min, as potential filter materials for removal of heavy metals (Cd, Cu, Pb, and Fe) from synthetic aqua solution containing individual metal contaminants at different concentrations and surface irrigation water using LIBS.

2. Materials and Methods:

Filter column consists of three PVC pipes of Outer diameter of 90 mm, inner diameter 84 mm, length 100 cm provided with groove near bottom, Charcoal column depth 20, 40, 60 and 80 cm depth were used. Underdrain collector Screen net connected to the bottom of the filter (120 mesh) was used to prevent any particles greater than 133 micron from passing through the bottom of the filter. Water samples concentrations were ranged from 100, 200, 300 and 400 mg/L respectively, preparation of heavy metals solutions, A stock solution of Cadmium (II), copper (II), iron (II) and lead (II) ions concentration 1,000mg/L was prepared by dissolving an

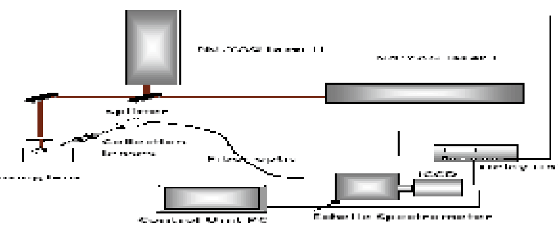

Fig. 1. Laser Induced Breakdown Spectroscopy (LIBS) setup.

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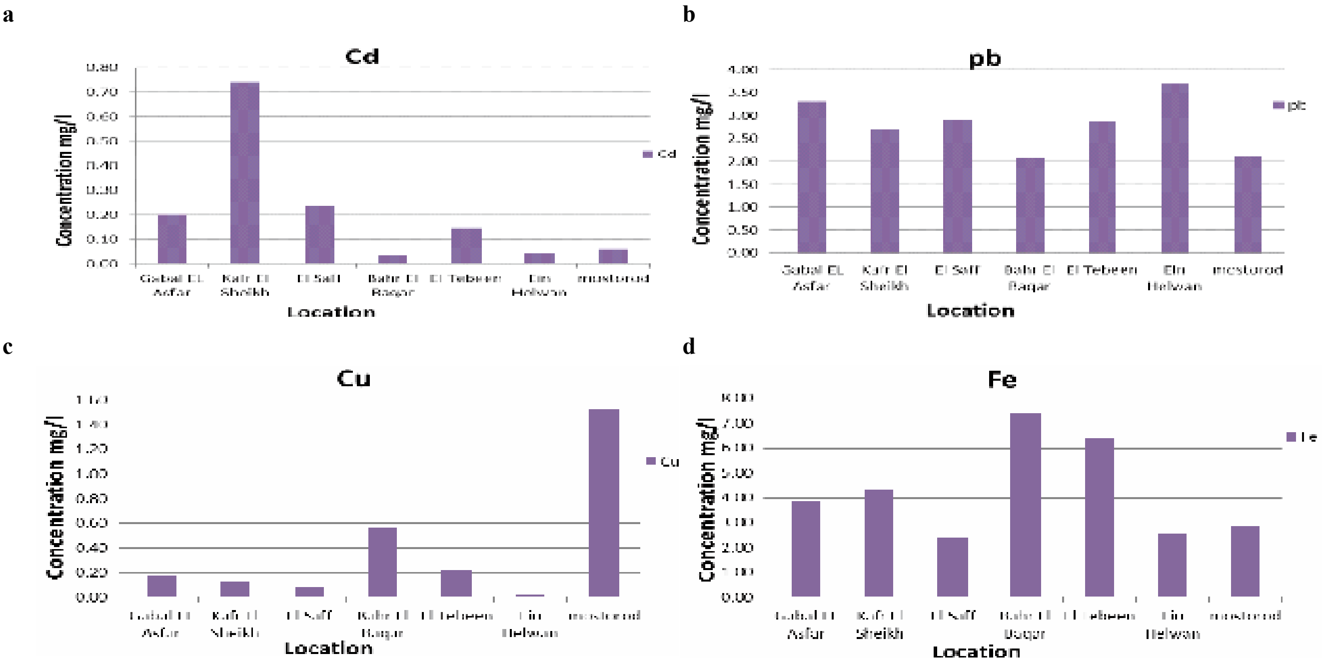

Fig. 2. Concentration for heavy metals for different locations.

accurate quantity of 2.75 gm Cd $(NO_3)_2$, $4H_2O$ (Merck), 4.40 gm $Cu(NO_3)_2{\cdot}5H_2O$ reagents from J.T. Baker, 5.0 gm $FeSO_4{\cdot}7H_2O$ reagents from J.T. Baker and 1.60 gm $Pb(NO_3)_2$ (Merck) in deionized water. Other concentrations prepared from stock solution by dilution varied between 100 and 400 mg/L. The charcoal was collected from El Safa company (private company for water purification) with mass 47.1 gm and bulk density 0.471 gm/cm^3 and particle size 2-4 mm.

2.1. Detailed descriptions of the components used in present LIBS experiment

Laser system, digital Delay/Pulse generator Q-switched Nd:YAG Max. Energy 450 mJ, pulse duration 6ns, Rate 1-20 Hz, Q-switched Nd:YAG Max. Energy 350mJ, pulse duration 10ns, Rate 1-0 Hz. Stanford Research (Model DG535). focusing System, Two Plano-convex Lens of 5cm focal length Spectroscopic detection system, wavelength range, 190-1100 nm, Focal length: 20 cm, f number: 10 spectral resolution, ICCD camera (Princeton, PI-MAX), Data acquisition, GRAMS version 8.0 Spectroscopic Data Analysis software, Energy meter, Nova, Ophir Optronics Ltd., USA, Light collection optical system, Two Focused Lens of 5 cm focal length as shown in **Figure 1**. Subsequent adsorption experiments were carried out with only optimized parameters. Adsorption isotherm tests were also carried out in the reaction mixture consisting the concentration. The change in heavy metals concentration due to adsorption was determined by LIBS (Vieira RHSF and Volesky B., 2000).

Seven different locations were selected to collect water samples used for irrigation and heavy metals Cd, Pb, Cu and Fe were determined using LIBS, results shown in **Figure 2**.

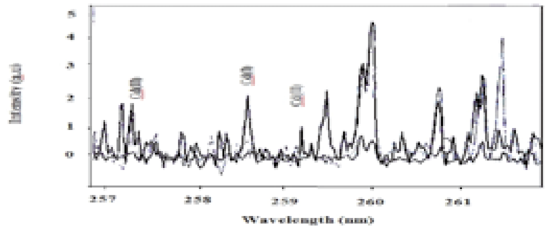

Fig. 3. Emission spectra of Cd filtrate through charcoal.

Fe concentration ranged from 7.44 and 2.36 mg/L for Bahr El Baqar and El Saff respectively. Cu concentration ranged from 1.53 and 0.03 mg/L for Mostorod and Ein Helwan respectively. Pb concentration ranged from 3.70 and 2.08 mg/L for Ein Helwan and Bahr El Baqar respectively. Cd concentration ranged from 0.74 and 0.03 mg/L for Kafr El Sheikh and Bahr El Baqar respectively.

3. Results and Discussion

3.1. Effect of charcoal depth on removal efficiency of different studied heavy metals

Figure 3 shows the Emission spectra of Cadmium (I) and (II) ions filtrate through charcoal by LIBS technique, Data presented in **Figure 4** show the effect of charcoal column depth on the maximum removal efficiency Rmax % at 20 min for different heavy metals, the data reveal that the relationship between depth and Rmax is third order polynomial equation were Y is the depth of charcoal cm and X is the Rmax %. Also it indicated that the average of the Rmax values for Fe, Pb, Cu and Cd respectively in the column of 20, 40, 60 and 80 cm depth receiving 100 mg/L at 20 min are 65.33, 67, 67.33, 68%,39.67, 40.20, 43.67 and 44%, 69.67, 70, 70.33 and 71%,

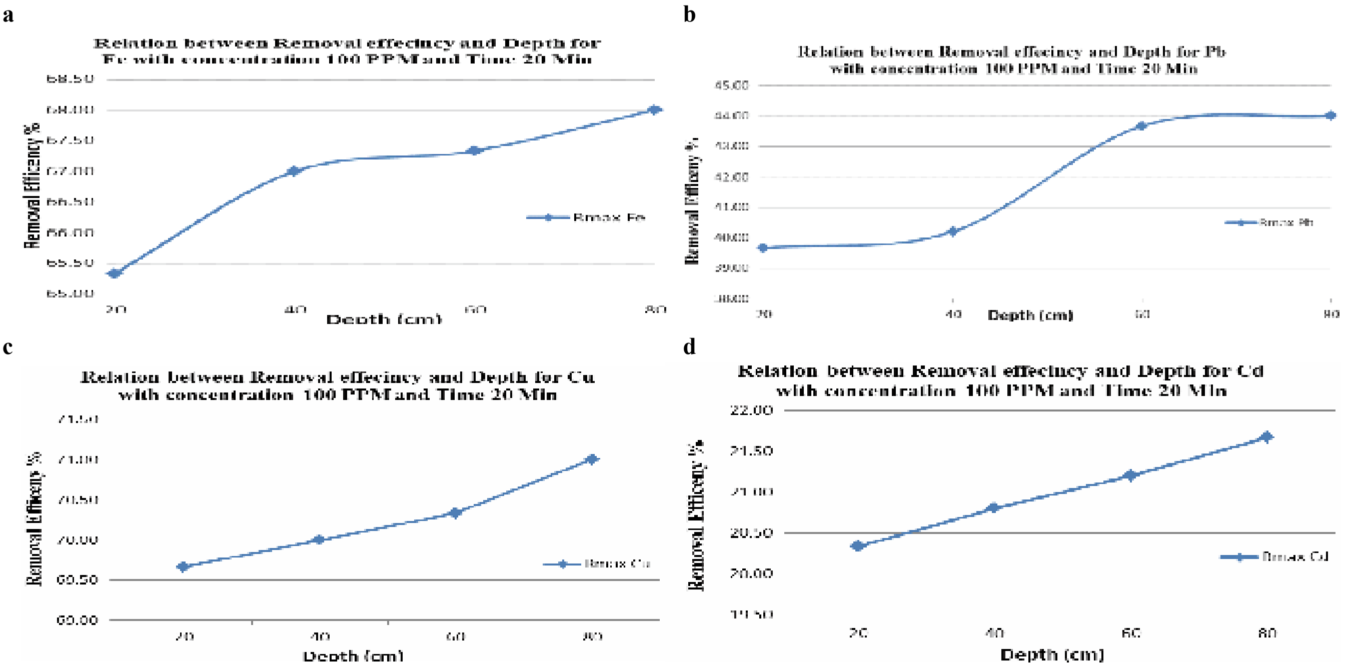

Fig. 4. Relationship between depth of charcoal and Rmax at 100 mg/L and 20 min.

20.33, 2.80, 21.20 and 21.67% respectively.

3.2. Contact time

With respect to the effect of the contact time on the removal efficiency % results generally show that the more contact time produced more removal efficiency until reaching certain value, (maximum removal efficiency Rmax), for each heavy metal, after that a constant graph obtained this is due to the equilibrium condition which reached at different time as following: The contact time needed to reach such equilibrium conditions for Fe, Cu, Pb were 40 min whereas for Cd was 20 min at 400 mg/L and 80 cm depth of charcoal. The effect of contact time was studied at intervals of 20, 40, 60, 80, 100 and 120 min. Relationship between Contact Time and removal efficiency of heavy metals for 100 and 400 mg/L at 80 cm depth are shown in **Figures 5** and **6** respectively.

4. Conclusion

The present study demonstrated that the charcoal as an efficient and cost effective adsorbent for heavy metals present in wastewater by LIBS. The Depth of charcoal showed the best efficiency in metals removal within time interval ranging between 20 to 120 Min. Finally it could be concluded that the contact time needed to reach such equilibrium conditions for Fe, Cu, Pb were 40 min whereas for Cd was 20 min at 400 mg/L and 80 cm depth of charcoal. Statistical analysis with ANOVA (F test) reveals that the date presented not only reveals that all treatments have significant difference for all studied concentrations 100, 200, 300 and 400 mg/L between removal efficiency means but also for all depths and times.

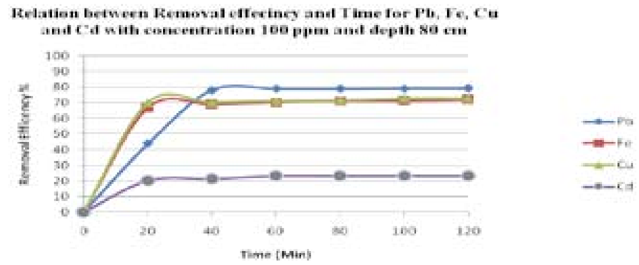

Fig. 5. Effect of contact time on removal efficiency for Pb, Fe, Cu and Cd with concentration 100 mg/L and depth 80 cm.

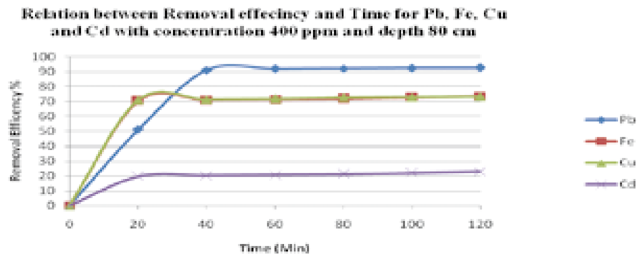

Fig. 6. Effect of contact time on removal efficiency for Pb, Fe, Cu and Cd with concentration 400 mg/L and depth 80 cm.

Where P-value < 0.01. Equilibrium time is one of the important parameters for an economical wastewater treatment system. It is indicated that the depth of charcoal are responsible for the increasing of the Removal efficiency. The studied heavy metals can be arranged due to their removal efficiency on the following descending order Pb > Fe > Cu > Cd.

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