RESEARCH ARTICLE

REMOVAL OF HEAVY METALS FROM WASTE WATER BY USING A NATURAL AND BIODEGRADABLE ADSORBENT BASED ON *PRUNUS AVIUM* L. STEMS AS ADSORBENTS

Ali Mcheik, Wassef El Khatib, Akram Hijazi*, Kamal Hariri, Mohamad Reda, Hassan Rammal
Doctoral School of Science and Technology, Research Platform for Environmental Science (PRASE), Lebanese University, Lebanon.

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Manuscript Info	*Abstract*
……………………. *Manuscript History* Received: 20 October 2016 Final Accepted: 22 November 2016 Published: December 2016 *Key words:-* Prunus avium; Copper (II); Adsorption; Langmuir and Freundlich isotherm models.	……………………………………………………………… The objective of this study was to investigate the possibility of using Lebanese *Prunus avium* stems as an alternative adsorbent for the removal of copper ion from aqueous solutions. Different parameters such as the effect of initial metal ion concentration, pH, adsorbent dose, contact time and temperature were studied. Maximum adsorption capacity (89.5%) of copper ion was obtained at pH 10, an initial Copper concentration 150 mg/l after 1 h and at 25 ^{o}C. FT-IR analysis is pointed out the involvement of amine (-NH$_2$) and carboxylic (-COOH) group in the adsorption process. The adsorption isotherm was better described by a Freundlich model rather than by a Langmuir model. Based on these obtained results, it can be concluded that the stems of *Prunus avium* are effective as an alternative adsorbent for toxic copper ions remediation in waste water.

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Introduction:-

Heavy metals are one of the most important wide spread environmental problems in water resources [i]. These metals are toxic since they are non biodegradable [ii], so they must be removed. Copper is one of the top 6 deadliest and toxic materials known, it is most commonly found in 2^+ oxidation state in nature [iii]. It is frequently used in industrial processes such as alloys, painting, electroplating, smelting, batteries and mining industry. When absorbed into the body in quantities greater than ten milligrams, adverse effects are acute and if over a long period of time, can be fatal [iii]. Copper causes damage to kidneys, cardiac tissue, bones and is thought to be a carcinogen [iv]. Symptoms of copper exposure are increased loss of small proteins in the urine, salivation, choking, vomiting, metallic taste, loss of sense of smell, joint pain and others. Different physiochemical techniques are being used to reduce the toxicity of copper from waste water such as ion exchange, chemical precipitation, reverse osmosis, electro dialysis, membrane filtration, flotation and activated carbon adsorption [v], but they have incomplete removal and high material cost.

Several researches are done on natural adsorbent to remove copper from aqueous solutions such as plants material like nut husk [vi], juniper bark and wood [vii], orange peel [viii], orange waste [ix], wheat stem [x], rice husk [xi], agricultural waste biomass [xii], wheat straw [xiii], coconut shell [xiv] and sugar beet pulp [xv]. In the present work, for the first time, the stems of the Lebanese *Prunus avium* has been used as adsorbent to remove Cu (II) from waste water by varying the experimental conditions such as contact time, initial metal ion concentration, temperature and pH, parameters could be applied in the reduction of copper pollution in the environment.

Corresponding Author:-Akram HIJAZI
Address:-Doctoral School of Science and Technology, Research Platform for Environmental Science (PRASE), Lebanese University, Lebanon.

Material and Methods:-

The raw *Prunus avium* (sweet cherry) stems were collected from a local Lebanese plantation. The stems were thoroughly rinsed with water, then, they were dried at room temperature for 10 days. After that, the dried stems were grinded to a fine powder to get a size of 0.25 mm.

Chemicals

The stock solution was prepared by dissolving 0.15 g of $CdCl_2$. H_2O in 1 L deionised water. All the required working solutions were prepared by diluting the stock solution with deionised water. Samples for Fourier transform infrared (FT-IR) were prepared by diluting the adsorbent to 5 % in KBr and cast in disks for analysis. Analysis of standards and simulated samples was done using an AA-140 atomic absorption spectrometer (AAS).

Experimental methods

Batch experiments were carried out using a series of Erlenmeyer flask of 50 mL capacity. Batch experiments were prepared to study the effect of initial Cu (II) concentration, pH, contact time, adsorbent dose and temperature on adsorption of the Cu (II) ions from its solution. All the adsorption experiments were carried out at room temperature except where the effect of temperature was being investigated. The initial pH was adjusted with HNO_3 (1 M) or NaOH (1 M) solutions.

Biosorption isotherms

Adsorption isotherms are essential for understanding the mechanism of an adsorption system. Since they represent the amount of compounds adsorbed on a surface as a function of concentration at a constant temperature [xvi]. Two isotherms models were tested:

1.   Freundlich isotherm: is the well-known earliest relationship which describes the adsorption process. It can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption [xvii]. This isotherm is expressed by the following linear equation:

$$\text{Log } qe = \log kF + \frac{1}{n} \log Ce \qquad (3)$$

Where *KF* is the Freundlich constant related to the bonding energy (L/mg), 1/n is the heterogeneity factor and n (g/L) is a measure of the deviation from linearity of adsorption. Freundlich equilibrium constants were determined from the plot of log *qe* versus log *Ce* (Figure 1), basis on the linear of Freundlich equation (3). Where the n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if n=1, the adsorption is linear. If n<1, the adsorption is a chemical process. If n>1, the adsorption is a physical process. The n value in Freundlich equation was found to be 0.983 for *P. avium*. Since n is greater than 1, this indicates the physical biosorption of Cu (II) onto *P. avium*. The values of correlation coefficients R^2 are done as a measure of goodness of fit of the experimental data to the isotherm models [xviii].
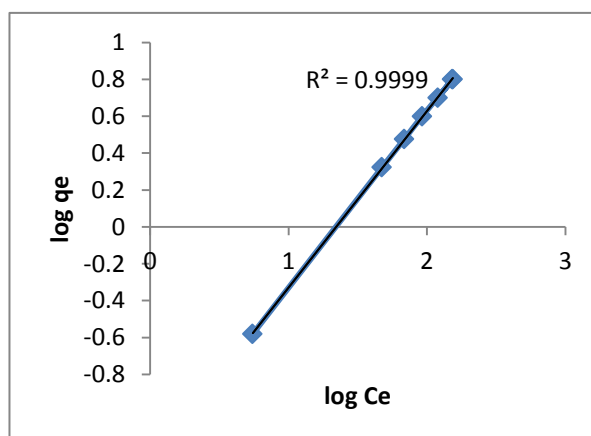

Figure 1:-Freundlich isotherm for Cu (II) biosorption into *Prunus avium* stems

2.   Langmuir isotherm: assumes the formation of an adsorbed solute monolayer on a uniform surface with a finite number of adsorption sites [xix]. When a site is filled, no further sorption can take place at that site. Therefore the surface will reach a saturation point where the maximum

adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} Ce \qquad (4)$$

Where q_{max} is the maximum adsorption capacity (mg/g) and KL is the Langmuir constant related to the energy of adsorption (l/g). Values of Langmuir parameters q_{max} and KL were calculated from the slope and intercept of the linear plot of Ce/qe versus Ce as shown in Figure 2. Values of q_{max}, K_L and correlation coefficient R^2 are listed in Table 1. These values for *P. avium* biosorbent indicated that Langmuir model describes the biosorption phenomena favorable.
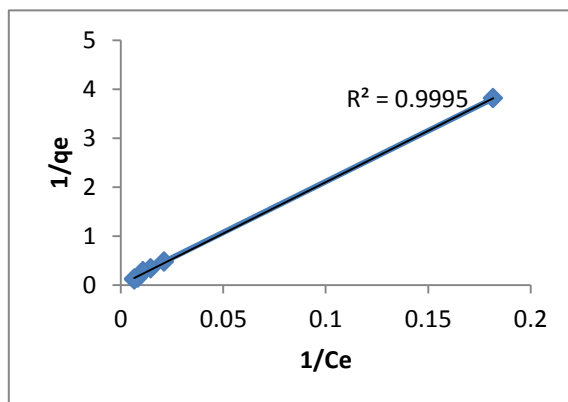

Figure 2:- Langmuir isotherm for Cu (II) biosorption onto *Prunus avium* stems.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using separation factor or dimensionless equilibrium parameter, *RL* expressed as in the following equation:

$$R_L = \frac{1}{(1 + K_L C_o)} \qquad (5)$$

Where Co is the initial concentration of sorbate (mg/l) and KL is the Langmuir constant (L/mg). There are four possible values for R_L: to be irreversible ($R_L=0$), favorable ($0<R_L<1$), linear ($R_L=1$) or unfavorable ($R_L>1$) [xx]. The R_L was found to be 0.9937 for concentration of 25-600 mg/L of Cu (II). They are in the range of 0-1 which indicates the favorable biosorption.

Results and Discussion:-
When *P. avium* stems powder was tested for its ability to adsorb Cu (II) ion from aqueous solution, initial pH 6 was used for most experiments. The effects of the following experimental parameters (pH, initial concentration, contact time, temperature and the adsorbent dosage) on adsorption were studied. The percentage of the uptake or adsorption of Cu (II) was calculated using the following equation:

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

Where Ci = initial concentration (mg/l); Cf = final concentration (mg/l). The adsorption capacity of Cu (II) is the concentration of Cu (II) over the adsorbent mass and it was calculated based on the mass balance principle according to the following equation:

$$q_m \text{ (adsorption capacity)} = \frac{C_0 - C_f}{m} \times V \qquad (2)$$

q_m = amount of Cu (II) per dry weight of *P. avium*; V = volume of the reaction mixture (L); m = mass of adsorbent used (g); C_o = initial concentration (mg/L) and C_f = final concentration (mg/L).

FT-IR and XRF analysis of adsorbent:-
The FT-IR spectrum presented in the figure 3 was used to investigate the functional groups present on the *P. avium* stems that could be responsible for the removal of heavy metal species [xxi]. The spectrum of the adsorbent was measured within the range of 4000-400 cm^{-1} wave number. The comparison of the FT-IR spectra has been done before and after loading with Cu (II). The *P. avium* stems show a number of absorption peaks that reflects its complex nature. Two peaks at 3513 cm^{-1} and 3436 cm^{-1} are due to the presence of N-H bond stretching (primary amine). A broad peak at 3292 cm^{-1} is due to the existence of OH group. The absorption peak at 2924 cm^{-1} could be assigned to C-H stretching vibration, 1736 cm^{-1} to ester carbonyl, 1608 cm-1 to C=C, 1520 cm^{-1} to N-H, 1066 cm^{-1} to C-O.
After adsorption, a broad peak at 3466 cm^{-1} corresponds to the overlapping of OH and NH peak. This phenomenon may be attributed to the water molecule directly interacting with amide.

After Cu (II) binding, a change of peak position occurs (3437-3435 cm^{-1}, 3292-3290 cm^{-1}, 1736-1738 cm^{-1}, 1253-1252 cm^{-1}, 1066-1056 cm^{-1}, 824-811 cm^{-1}, 536-558 cm^{-1}).

The shift in the wave number corresponds to the change in the energy of the functional groups that indicates the existence of Cu binding process done on the surface of *P. avium* stems powder [xxii].

The XRF spectrum has been done to show the metals composition in the stems of *P. avium*. It was consisting of Ca, Fe, Ni, Nb, Mo among others as shown in figure 4.
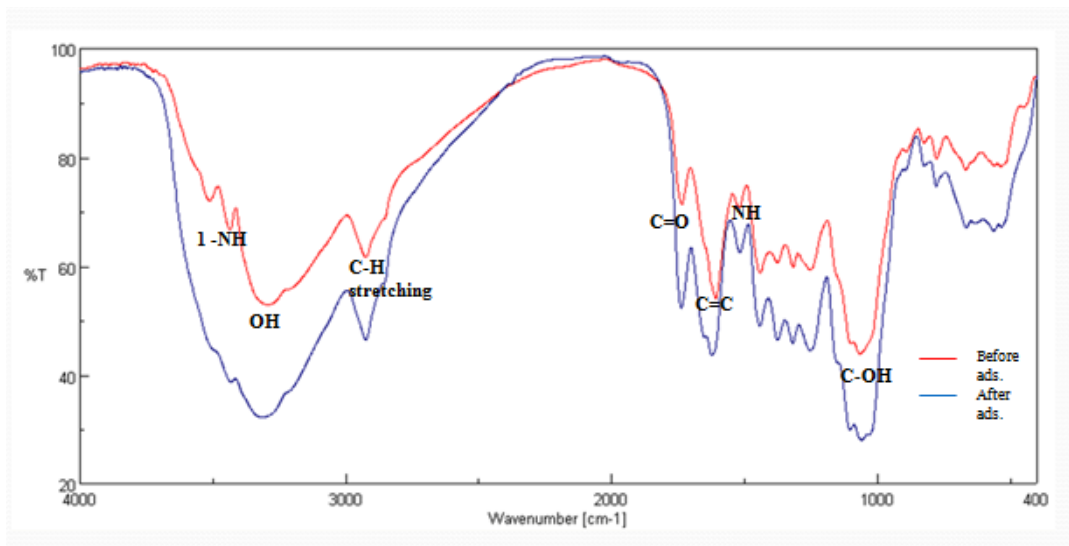

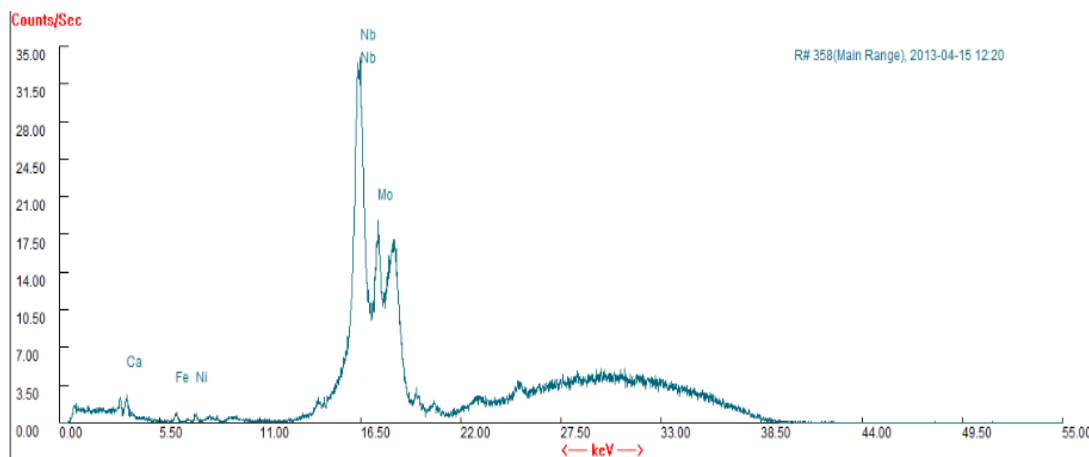**Figure 3:-** FT-IR spectrum of stems of *Prunus avium* before and after adsorption

Figure 4:- XRF spectrum of stems of *Prunus avium* powder before adsorption

The effect of metal ion concentration on adsorption

0.5 g of the adsorbent was shacked with 50 ml of varying concentrations (25, 150, 300, 400 and 600 mg/l) of Cu (II) solution. The mixture was continuously agitated at 25 ± 2 °C with a shaker at 400 rpm. The pH of the solution was adjusted to a pH 6. After the established contact time (1 hour) was reached, the suspension was filtered in 2 steps: first by Buchner filtration then by 0.45 μm filter. After that, the final concentration of Cu (II) in the filtrate was determined using AAS. The adsorbed amount was determined from the difference between the initial and residual concentrations of Cu (II) in the liquid phase.

The effect of pH on adsorption of Cu (II) ions

The pH of the aqueous solution is an important parameter which controls the Cu (II) adsorption process, as it affects the surface charge of the adsorbents and the degree of ionization [xxiii]. Figure 5 shows clearly that *P. avium* stems exhibit maximum Cu (II) removal at pH 4, which were rather acidic. At low pH (below 3), the increased number of protons in solution on this biosorbent often refuses the formation of links between Cu (II) ions and the active site. At moderate pH values (3 to 6) the number of H^+ becomes fewer, allowing more Cu (II) ions to be adsorbed to the active sites [xxiv]. At pH lower than 8, the dominant forms of Cu was Cu (II); while $Cu(OH)_2$ was present as precipitate at pH greater than 8. Based on these results, the Cu was bound to active surface by O^{2-} ions and released H^+ into the solution, thereby decreasing the pH [xxv].
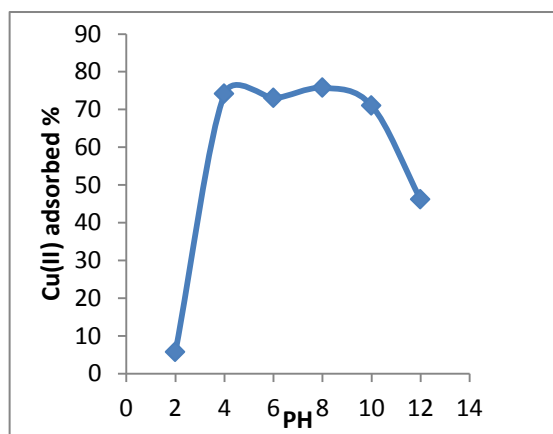

Figure 5:- Effect of pH on adsorption

The effect of contact time on the Cu (II) adsorption

The effect of contact time on the adsorption of Cu (II) from its solution is shown in figure 6. There is a general increase in the % adsorption of Cu (II) with time. However, the adsorption slowed down after 2 hours, where the maximum removal efficiency is 67.9%. This could possibly be the time required for the equilibrium to be established.
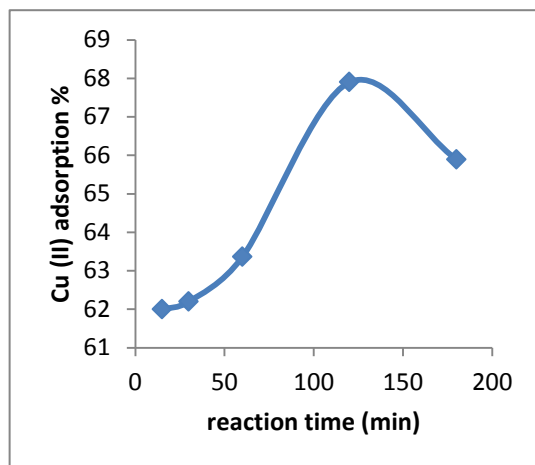
Figure 6:- Effect of contact time on the adsorption of Cu (II)

The effect of temperature on the metal adsorption

The adsorption of Cu (II) from aqueous solutions at different temperatures was investigated. Samples were subjected to temperatures ranged from 0 to 66 ℃. Figure 7 shows that the adsorption capacity reached a maximum at 25 ℃ and thereafter it decreased gradually. The maximum adsorption efficiency of 3.0855 mg/g (65.1 %) occurred at 25 ℃. However, overheating might result in desorption kinetics dominating.
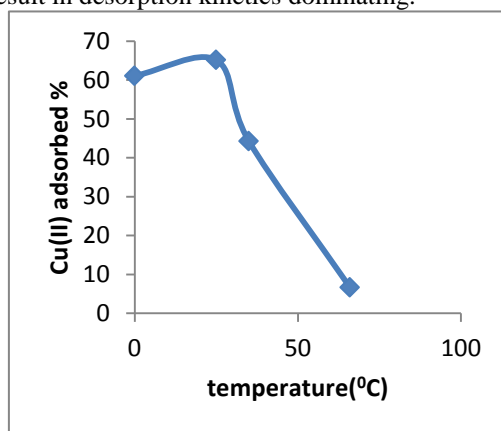

Figure 7:- Effect of temperature on Cu (II) adsorption

The effect of the adsorbent dose on the removal of Cu (II) ions:-

The adsorbent dosage is another important parameter because it influences the extent of metal uptake from the solution and thus the effect as shown in figure 8. The percentage removal efficiency of Cu (II) decreased from 71.08% to 46.64% when the adsorbent dosage increased from 0.2 to 1 g. The adsorption capacity decreased sharply with the increasing of adsorbent dosage. These results may due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles. Moreover, the high adsorbent dosage could impose a screening effect of the dense outer layer of the cells, thereby shielding the binding sites from metal.
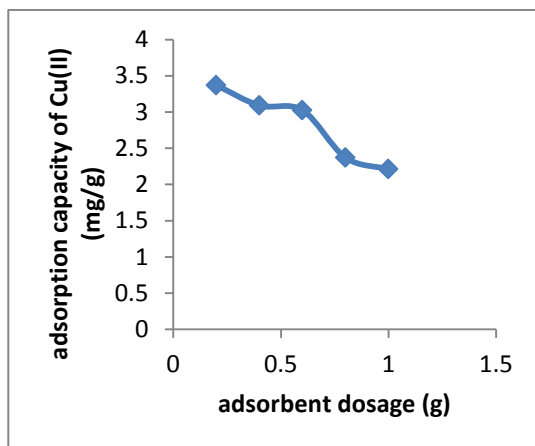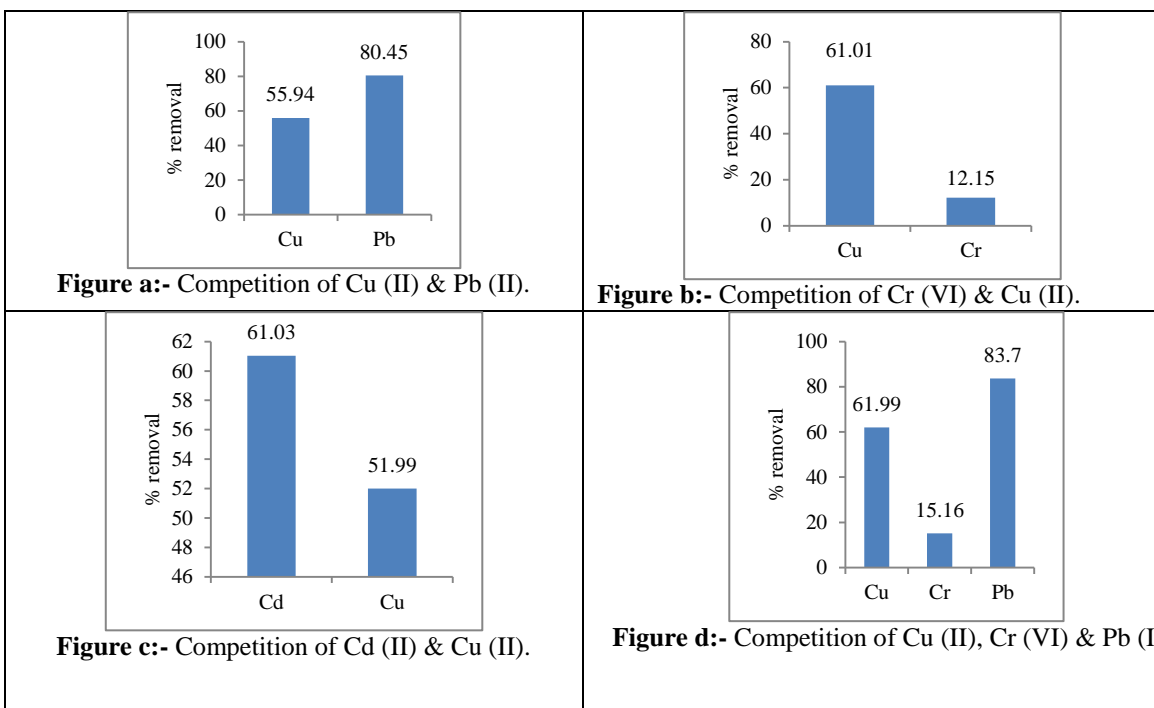
Figure 8:- Effect of adsorbent dose on adsorption capacity

Competition among heavy metals in waste waters:-
The metals of interest are usually found with a number of other metals. *Prunus avium* stems can effectively bind a number of heavy metal ions but it would be doubtful that all ions have been equality bound. Figures (a-e) show the percentage of adsorption of each ion in the presence of other. The general binding affinity of the *P. avium* for the metals studied, in order decreasing affinity is Cu (II) > Cd (II) ≈ Pb (II) > Cr (VI) (fig. e). While it is clear that some of the metal ions compete with one another for bark binding sites, it is of interest to note that the binding of Pb (II) is relatively unaffected by other metals [xxvi]. The difference in the adsorption behavior of Pb (II) and Cd (II) compared Cr (VI) and Cu (II) may also be explained by the different affinity of metal ions for the donor atoms present in the structure of *P. avium* stems.
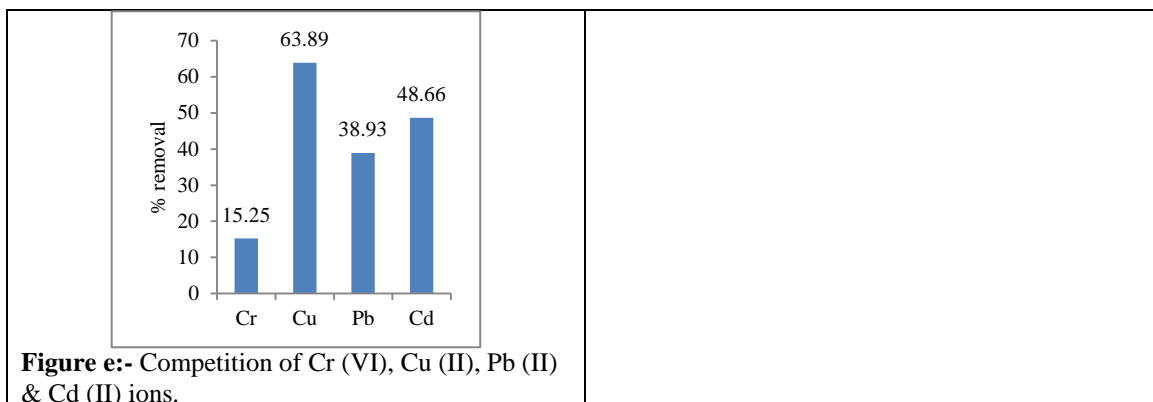

Figure a:- Competition of Cu (II) & Pb (II).

Figure b:- Competition of Cr (VI) & Cu (II).

Figure c:- Competition of Cd (II) & Cu (II).

Figure d:- Competition of Cu (II), Cr (VI) & Pb (II

Figure e:- Competition of Cr (VI), Cu (II), Pb (II) & Cd (II) ions.

Figures a-e: Percentage of adsorption of each ion in the presence of other

The values of correlation coefficient R^2 are regarded as a measure of goodness of fit of experimental data to isotherm model. Therefore, from table 1 for Cr (IV) and Pb (II) we can see that Langmuir gave a better fit than Freundlich isotherm, while for Cu (II) and Cd (II) Freundlich gave a better fit than Langmuir isotherm.

Table 1:- Langmuir constants for studied heavy metals ion biosorption by *P. avium* stems

	K_L	q_{max}	R_L	R^2	Type of adsorption
Cr (VI)	0.000542	100	0.996	0.9997	**Favorable**
Pb (II)	0.05223	9.572718	0.561	0.9999	**Favorable**
Cu (II)	0.00482	10	0.974	0.9995	**Favorable**
Cd (II)	0.00505	10	0.983	0.9937	**Favorable**

Conclusion:-

This study investigated the adsorption of Cu (II) ions from aqueous solutions onto dried *Prunus avium* stems that is dependent on biosorption process such as initial metal ions concentration, pH, adsorbent dose, and temperature and contact time. To provide best correlation for biosorption of Cu (II) ions onto *P. avium* stems, Freundlich and Langmuir biosorption isotherm were demonstrated. From this study, it was observed that stems of *P. avium* stems can be used as an alternative low cost, eco-friendly and effective adsorbent for treatment of waste water containing Cu (II) ions. Other heavy metals adsorbed by stems of *P. avium* are under study.

Acknowledgement:-

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