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Removal of Cu(II) Ions from Aqueous Solutions by Adsorption Onto Activated Carbon Derived From Olive Waste Cakes

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ABSTRACT
This paper studied the ability of using local activated carbon (LAC) derived from olive waste cakes as an adsorbent for the removal of *Cu(II)* ions from aqueous solution by batch operation. Various operating parameters such as solution pH, adsorbent dosage, initial metal ions concentration, and equilibrium contact time have been studied. The results indicated that the adsorption of *Cu(II)* increased with the increasing pH, and the optimum solution pH for the adsorption of *Cu(II)* was found to be 5. The adsorption process increases with increasing dosage of LAC, also the amount of *Cu(II)* removed changes with *Cu(II)* initial concentration and contact time. Adsorption was rapid and occurred within 25 min. for *Cu(II)* concentration range from 60 to 120 mg/l isothermally at 30±1 °C. Maximum adsorption occurs at *Cu(II)* initial concentration lesser than 100 mg/l by using adsorbent dosage (1.2 g/l). The equilibrium adsorption data for *Cu(II)* were fitted well with the Langmuir and Freundlich adsorption isotherm models. The maximum adsorption capacity of LAC was found to be 106.383 mg/g. So, the results indicated the suitability use of the activated carbon derived from olive waste cakes (LAC) as low cost and natural material for reliable removal of *Cu(II)* from water and wastewater effluents.

Keywords - Adsorption, Isotherm, Activated Carbon, Copper, Wastewater Treatment.

I. INTRODUCTION

The removal of copper ions *Cu(II)* is gaining wide interest from both environmental and economic viewpoints due to its serious hazardous impacts on humans, animals, and plants. Generally, heavy metal contamination (such as *Cu(II)*) in the environment poses serious health problems due to their accumulation in living tissues throughout the food chain as non-biodegradable pollutants [1, 2]. The major sources of copper ions are products of industries such as metallurgy, wood preservation, plating, electronics plating, tanning, corrosion inhibition, wire drawing and printing operation [2, 3]. Typical concentrations vary from several thousand mg/l from plating bath waste to less than 1 ppm from copper cleaning operations. Copper is a heavy metal that is naturally observed in the environment and in fragmented water resources. The discharge of wastewater including heavy metals increases the environmental pollution and toxic nature of *Cu(II)* ions affects water resources [1].

Conventional methods for heavy metal removal from wastewater include; reduction, precipitation, filtration, membrane technology, ion exchange, evaporation, and electrochemical treatment, all of which may be ineffective or extremely expensive when metals are dissolved in large volumes of solution at relatively low concentrations [4]. Adsorption process is the most frequently applied method in industries for heavy metal removal [5]. Though activated carbon is an ideal adsorbent, due to its organophilic character, its high costs prohibits its use in wastewater treatment. The high cost of active carbon has prompted a search for cheaper substituents [2, 3]. A lot of studies on this process have been carried out [6]. Many studies have recently devoted the usage of different adsorbent materials in processes involving the removal of *Cu(II)* ions from aqueous effluents with the aim of finding cheaper replacements for conventional adsorbent material situations [7] such as activated carbon which is expensive for developing countries [2, 8-10]. Therefore, many investigators have used inexpensive adsorbent materials, such as tree fern [1], anaerobic sludge [11], waste tea [12], fly ash [13], newspaper pulp [14], soil [15], date stones [16], and green waste tea [17]. But till now, the activated carbons have a long history of use in adsorption technology which made from a wide range of natural and synthetic precursors. The use of these inert materials as adsorbents utilizes their large surface area and pore volume size for superior adsorption and avoids complications associated with leachate of plasticizers and other toxins from polymer based systems [18, 19]. So, this work study the possibility of using activated carbon derived from the olive waste cakes, an industrial waste, as an alternative low-cost and natural material adsorbent in the removal of copper from aqueous solution and investigates the effect of pH solution, adsorbent dosage, initial *Cu(II)* concentration, and contact time on the adsorption process of the batch process experiments.

II. MATERIALS AND METHODS

2.1. Chemicals

All used chemicals were of analytical grades include phosphoric acid (H_3PO_4), iodine (I_2), Sodium thiosulfate, Hydrochloric acid (HCl), sodium hydroxide ($NaOH$), and copper sulfate ($CuSO_4.5H_2O$).

2.2. Preparation and Properties of LAC

An exhausted olive-waste cakes collected from national olive mills is the raw material it is use to prepare the activated carbon by a chemical activation process as follow stages [3, 20, 21]:

- Olive waste cake was collected then washed and dried in an air oven at 102 °C for 24 hrs then grounded and sieved to obtain desired size fraction (1.2 mm) using a conventional sieve-shaker.
- The selected fraction of dried particle size (precursors) were impregnated with phosphoric acid solution (65% wt.) at 25°C with impregnation ratio 1.75.
- The mixture was kept in stirring at 100°C for 2 hr.
- The impregnated precursor was subjected to carbonization and an activation process in an air programmable electrical furnace at 430 °C for 2 hr.
- After cooling down to room temperature the activated product was washed extensively with hot distilled water to remove free acid.
- The washed activated carbon was dried overnight in an air oven at 100°C, then grind to powder and kept in hermetic bottle for subsequent uses.

The main characteristics of produced LAC are bulk density [22], specific surface area [23], iodine number [24] and ash content [25] were determined as shown in Table.1.

Table.1: Characteristics of LAC

Character	Unit	Value
Bulk density	kg/m^3	570
Surface area	m^2/g	1201
Iodine number	mg I_2/g AC	601
Carbon yield	%	45.4
Ash content	%	0.23

2.3. Adsorption Experiments

A stock solution of $Cu(II)$ (1000 mg/l) was prepared by dissolving ($CuSO_4.5H_2O$) in deionized water. Experimental solutions of copper which have known initial concentrations were prepared by diluting the stock solution in stoppered conical flasks (250 ml). The pH of the experimental solution was adjusted by using 1 N of HCl and $NaOH$ solutions and measured by digital pH meter (HI 8417, HANNA Instrument, accuracy ±0.01).

Sorption experiments were carried out by adding LAC to a conical flask in various amounts containing known concentration of $Cu(II)$ solutions. The temperature of the experiments was maintained at 30 °C ±1. The solutions were shaken in a mechanical rotary shaker at 200 rpm. The effects of adsorption pH solution, adsorbent dosage, initial concentration and contact time were studied. These solutions are filtered using Whatman No. 40 filter paper and the concentrations of residual $Cu(II)$ were measured using a spectrophotometer equipment (UV-Visible spectrophotometer Unicam 8700). All experiments were carried out in duplicate and showed differences less than 1%.

The removal percentage of $Cu(II)$ ions and capacity of LAC were computed using Eqn. (1) [26];

$$Re\ (\%) = \left(\frac{C_o - C_e}{C_o}\right) * 100 \qquad (1)$$

Where C_i and C_e are the initial and equilibrium concentration of $Cu(II)$ ions (mg/l) in solution. Adsorption capacity was calculated by using the mass balance equation for the adsorbent [26];

$$Q = \left(\frac{C_o - C_e}{w}\right) * V \qquad (2)$$

Where Q is the adsorption capacity (mg/g), C_o is the initial and equilibrium concentrations of $Cu(II)$ in solution (mg/l) respectively, V is the volume of $Cu(II)$ ions solution (l) and W is the weight of the adsorbent (g). Also, the adsorption isotherms were studied by using the Langmuir and Freundlich isotherms.

III. RESULTS AND DISCUSSION

3.1. Effect of pH on Copper Adsorption

Initially batch adsorption studies performed to study the influence of pH on the adsorption of $Cu(II)$ ions onto LAC from aqueous solutions. The copper adsorption was conducted using an initial concentration of 60 mg/l over a pH range of 2-7 at 30 °C±1, agitation rate 200 rpm, adsorbent dose 1.2 g/l and 60 min. as a contact time. Fig.1 shows that the increase of pH leading to increases the amount of copper adsorption to pH 5 whereas the maximum removal of copper is 96% (48 mg/g). In the case of LAC a pH range of 4.5-6 is more suited for the quantitative removal of copper from aqueous solution. The variation in the amount of adsorption clearly indicated the influence of pH on adsorption process. At lower values, the metal ions uptake was limited in this acidic medium, and this can be attributed to the presence of H^+ ions which compete with the $Cu(II)$ ions for the adsorption sites. Contrarily, the metal ion was prone to $Cu(OH)_2$ deposition through hydrolysis at higher values of pH, (pH>7 as mentioned by literatures [3, 27-29]. Therefore pH 5 was selected as optimum value for conducting further adsorption experiments.

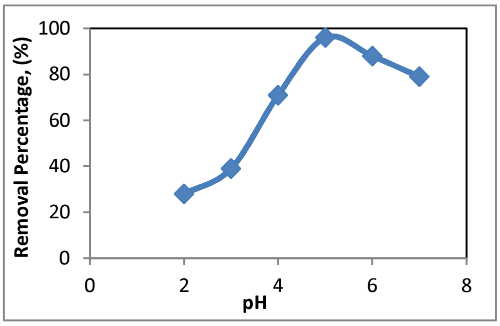

Fig.1: Removal percentage of *Cu(II)* versus pH for batch process, (30 °C temperature, agitation rate 200 rpm, adsorbent dose =1.2 g/l, contact time= 60 min. and initial conc.=60 mg/l).

3.2. Effect of adsorbent dosage

The adsorption studies of *Cu(II)* ions on LAC were done at 30 °C±1 temperature by varying the quantity of adsorbent from 0.1 to 0.5 g while keeping volume of the metal solution constant (250 ml) at agitation rate 200 rpm, contact time= 60 min., pH 5, and initial concentration=60mg/l. The influence of adsorbent dosage in removal percentage of *Cu(II)* ions is shown in Fig.(2).

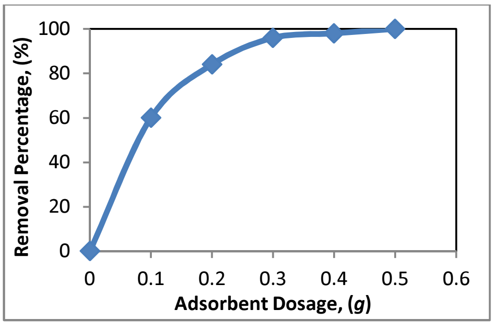

Fig.2: Removal percentage of *Cu(II)* versus adsorbent dosage for (30 °C temperature, agitation rate 200 rpm, contact time= 60 min., pH 5, and initial concentration=60 mg/l).

Fig. (2) indicates to that the removal percent increased with increase in the dose of adsorbent, due to increase the active sites on the adsorbent and thus making easier penetration of the metal ions to the adsorption sites [5, 30, 31].

3.3. Effect of Contact Time and Initial Concn.

Adsorption of *Cu(II)* ions was carried out by LAC at (30 °C±1, 200 rpm and pH 5) with various initial concentrations are shown in Fig.3. The adsorbed amount of *Cu(II)* by LAC increased with the increase of contact time and the attained equilibrium at 25 min. for initial concentrations ranged between 60-120 mg/l.

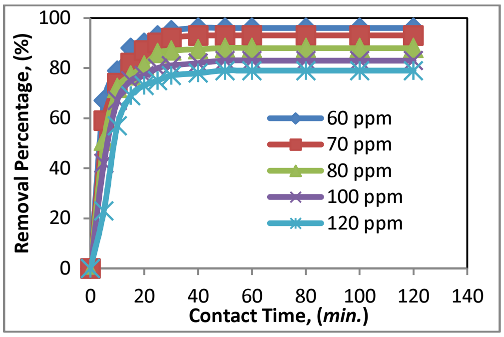

Fig.3: Variation of *Cu(II)* Removal percentage versus contact time at (30 °C, agitation rate 200 rpm, pH 5, and adsorbent dose=1.2 g/l).

The initial rapid adsorption is due to the availability of the positively charged surface of the adsorbents for adsorption of anionic Cu^{+2} species present in the solution. The later slow adsorption is probably due to the electrostatic hindrances between adsorbed negatively charged adsorbate species into the surface of adsorbents and the available anionic adsorbate species in solution, the slow pore diffusion of the solute ions into the bulk of the adsorbent [32]. The curves shown in Fig.3 present the initial portion of the curve rises linearly and they are changed into a curve and levels of 25 min. of contact time in the case of LAC, after which there is no clear change in adsorption. This attributed to an increase in the driving force of the concentration gradient with the increase in the initial concentration of *Cu(II)* in order to overcome all mass transfer resistance of *Cu(II)* ions between the aqueous and solid phase [31].

3.4. Adsorption Isotherms

3.4.1. Langmuir Isotherm

Langmuir proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has found successful applications in many other real adsorption processes of monolayer adsorption. Langmuir's model of adsorption depends on the assumption that intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation further assumes that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a *Cu(II)* molecule occupies a site, no further adsorption can take place at that site. Moreover, the Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all adsorption sites are identical and energetically equivalent. Theoretically, the adsorbent has a finite capacity for the adsorbate. Therefore, a saturation value is reached beyond which no further adsorption can take place [4, 30].

The experimental data was fitted to the linear form of Langmuir equation [30] as shown in Fig.(4):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o b} \qquad (3)$$

Where C_e (mg/l) is the equilibrium concentration of metal ions, q_e (mg/g) is the adsorption capacity in equilibrium state, Q_o is the maximum adsorption capacity, and b is the Langmuir constant (equilibrium constant (l/mg)) which reflects quantitatively the affinity between LAC and *Cu(II)* ions. The affinity between *Cu(II)* and LAC adsorbent can be predicted using the Langmuir parameter b from the dimensionless separation factor R_L [33];

$$R_L = \frac{1}{1+bC_o} \qquad (4)$$

Where C_o is the initial *Cu(II)* concentration, and b is Langmuir isotherm constant. The adsorption process as a function of R_L must be laying $0 < R_L < 1$ to be the adsorption process acceptable.

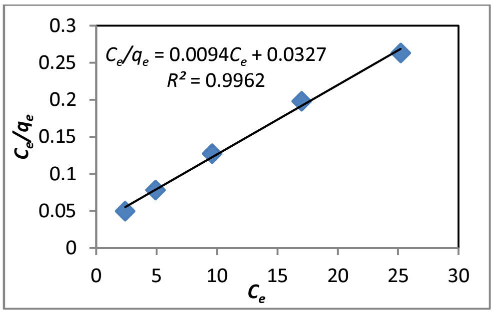

Fig.4: The Langmuir adsorption isotherm for *Cu (II)* adsorption onto LAC.

The high value of correlation coefficient R^2 shown in Fig.(4) indicates that the adsorption of *Cu(II)* ions by LAC follows Langmuir isotherm model. Table 2 gives information about the adsorption capacity (Q_o) and energy of adsorption b of LAC. The maximum adsorption capacity for *Cu(II)* ions from aqueous solution by LAC is 106.383 mg/g (Langmuir model).

Table.2: Equilibrium model parameters of *Cu(II)* adsorption onto LAC

Isotherm	Parameter	Value
Langmuir	Q_o (mg/g)	106.383
	b (l/mg)	0.2875
	R^2	0.9962
	RMS (%)	1.884
Freundlich	K_F (mg/g).(l.mg)$^{1/n}$	38.452
	$1/n$	0.287
	R^2	0.9909
	RMS (%)	2.169

The calculated R_L value for the adsorption of *Cu(II)* onto LAC were (0.0548, 0.0473, 0.0416, 0.0336 and 0.0282) for initial used concentrations (60, 70, 80, 100 and 120 mg/l), which indicates a highly favorable adsorption of *Cu(II)* onto LAC within concentration range (60-120 ppm).

Table.3: Comparison for adsorption capacity of *Cu(II)* ions by activated carbon obtained by previous studies

Activated Carbon Source	**Capacity (mg/g)**	**Ref.**
Apricot stone	22.85	[34]
Soybean hulls	39.37	[35]
Olive waste cakes	12	[36]
Kraft lignin	136	[37]
Rice husk	29	[38]
Phoenix dactyliera stone	37.3	[39]
Palm shell	22	[40]
Nipa palm nut	166.67	[41]
Palmyra palm nut	200	[41]
Oil palm fiber	333.3	[41]
Oil palm empty bunch	333.3	[41]
Oil palm shell	250	[41]
Rice husk	112.43	[31]
Olive waste cakes	65.5	[32]
Date stone	31.25	[16]
Hazelnut shell	195	[42]
Olive waste cakes	106.38	This Work

Values of the adsorption capacity of other low-cost activated carbons from the literature are given in Table 3 for comparison. The value for *Cu(II)* ions sorption observed in this work is in good agreement with values found by other researchers. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area. While the higher value for the adsorption capacity obtained in this study can be attributed to the greater specific surface area and pore volume of the LAC due to a chemical activation done by phosphoric acid.

3.4.2. Freundlich Isotherm

The Freundlich adsorption equation has the following linear form [30];

$$ln(q_e) = ln(K_F) + \frac{1}{n} ln(C_e) \qquad (5)$$

Where K_F and n are the isotherm parameters to be determined. The Freundlich adsorption isotherm represents the relationship between the correspond-ing adsorption capacity q_e (mg/g) and the concentration of the metal in the solution at equilibrium C_e (mg/l) (Fig. 5).

From the Table 2, the Freundlich constant, *1/n* denoting the intensity of adsorption indicates a favorable adsorption since $1/n < 1$ [31, 43] the adsorptions of *Cu(II)* ions onto LAC studied had been more favorable. The adsorption capacity (K_F) obtained for LAC shows highest value of adsorption capacity.

The values of R^2 and *RMS*, % for the adsorption of *Cu(II)* ions on LAC are presented in

Table 2, show that the data fits Langmuir isotherm well compared to Freundlich isotherm. It shows the homogeneity of the material as well the possibility of monolayer adsorption of *Cu(II)*. The values of *n* greater than one indicate that the adsorption is favorable [31].

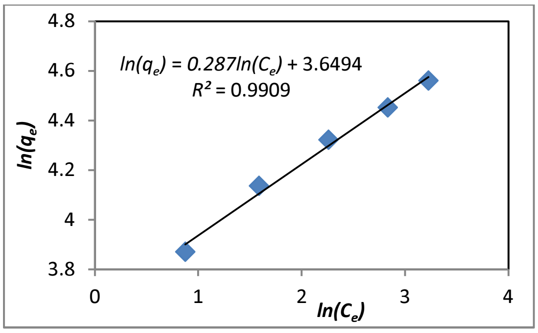

Fig.5: The Freundlich adsorption isotherm for *Cu(II)* adsorption onto LAC.

IV. CONCLUSION

The adsorption behavior of copper onto the activated carbon derived from olive waste cakes (LAC) from aqueous solution has been investigated in this study. The present study indicates to the amount of *Cu(II)* ions adsorbed onto the LAC increased with an increase in pH. The optimum pH was found as pH 5 for the removal of *Cu(II)* ions by LAC at 30 °C±1. On increasing the adsorbent dosage, the adsorption percentage also increases. The optimum contact time for efficient removal was 60 min. The Langmuir and Freundlich isotherms used to describe the adsorption equilibria of *Cu(II)* onto LAC. It was found that the equilibrium in the solid-solution interface was best explained by Langmuir adsorption isotherm and the adsorption capacity of LAC for the removal of *Cu(II)* was found to be 106.383 mg/g at 30 °C±1. So, the present study shows the feasibility of the practical use of LAC as a low cost, and natural material adsorbent for the effectively removal of *Cu(II)* from aqueous solutions.

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