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RESEARCH ARTICLE

BIOSORPTION OF COPPER FROM SYNTHESIZED WASTEWATER USING AGRICULTURE WASTE (ROASTED DATE PITS)

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ABSTRACT

Bioremediation of heavy metal pollution remains a major challenge in environmental biotechnology. The main objective of this study was to remove Cu^{++} from synthesized wastewater by biosorption using roasted date pits. In order to optimize the biosorption process, the effect of pH, shaking time and $CuCl_2.2H_2O$ with different concentrations were investigated in batch system of adsorption. The results indicated that at pH=7 were favorable for copper removal .Characterization of roasted date pits was analysis through FTIR. The maximum removal efficiency of adsorption of copper ions on roasted date pits was 99.4%. The experimental data were best fitted with pseudo second –order kinetic model. Also, the equilibrium data were analyzed using the Langmuir and Fruendlich adsorption isotherm models and it was observed that the data were fitted very well to Langmuir adsorption isotherm models.

INTRODUCTION

Heavy metals are one of the major factors of environmental contaminations. Physical and chemical methods have been proposed an applied to remove metal ions from effluents, but in general, these methods are commercially impractical, either because of high operating cost or the difficulty in treating. Presently, many techniques such as ion exchange, chemical precipitation, reverse osmosis, extraction, evaporative recovery and flotation. For this purpose is often inefficient and / or very expensive. So there was a need for some alternative method which can overcome all these problems and treat the waste water in an appropriate way attempts have been made in order to find new simple and efficient techniques for dilute concentration. Bio-adsorption process has been an area of extensive research **(**Jaishankar *et al,* 2014 Yilmaz *et al,* 2010 Neran *et al,* 2010 and Deng *et al,* 2013).

Biosorption can be defined as a non-directed physic-chemical interaction that may occur between metal /radionuclide species and microbial cells. It is biological method of environmental control and can be an alternative to conventional contaminated water treatment facilities (Saifuddin and Raziah, 2007). The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution, minimization of chemical and/or biological sludge, no additional nutrient requirement, regeneration of biosorbent and the possibility of metal recovery (Barkhordar and Ghiaassedin, 2005).

The use of biosorbent is economy of environmental remediation dictates that the biomass must come from nature or even has to be a waste material. Microorganisms, including actinomycete, cyanobacteria, and other bacteria, algae, fungi and yeasts, have the ability to accumulate heavy metals. Additionally, agricultural wastes, among other kinds of biomass, have been tested for metal sorption (El-Sherif *et al,* 2008).

Heavy metals have been acknowledged as potential health and environmentally hazardous materials. One of such heavy metal of concern is copper, Cu is a metal that is widely used in industry and is an essential element in human health. However, like all heavy metals, it is potentially toxic (Duffey, 1983) . Many studies have shown that these metals are toxic even at low concentrations. The presence of these metals can cause, in turn, accumulative poisoning, destroy liver, cancer and brain damage when found above the tolerance level. Industrial wastewater containing metal ions such as nickel, lead, copper and zinc are common because their metals are used in a large number of industries (El-Sherif *et al,* 2008 Aljlil, 2010 and OBOH *et al,* 2009).

Copper the metal considered in this project is a widely used material. Copper metal contamination exists in aqueous waste streams from many industries such as electronic and electrical, metal plating, mining, manufacture of computer heat sinks, Cu plumbing, as well as biostatic surface, as a component in ceramic glazing and glass coloring. Unfortunately, Cu is a

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persistent, bioaccumulative and toxic chemical that does not readily break down in the environment and is not easily metabolized (Tumin *et al*, 2008 and Baseri *et al*, 2012). The world health organization in 2006 recommended 2.0 mg/l as the maximum acceptable concentration of copper in drinking water (Muzenda *et al*, 2011).

Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly. Many investigators have evaluated the date pits as low-cost adsorbents (Saifuddin and Raziah, 2007 Aljlil, 2010).

Therefore the aim of the present work is to study the possibility roasted date pits as adsorbent for adsorption of heavy metal such as copper from wastewater .The effect of time, pH and the metal concentration on removal efficiency were investigated and modeling of the experimental results has been carried out.

MATERIAL AND METHODS

Preparation of Date Pits

In order to prepare the waste, it was powdered with the help of a grinder and passed through sieve analysis apparatus.

Sieve Analysis

The size analysis of **(DP)** was carried out by sieve with mesh size number of (200-1180 micron) and data shown in Table **1** give 332.7 particles (Number frequency in range **dN**) in five class intervals which are in geometric progression. The data in Table (1) showed the maximum number frequency (dN) is (87.1) within the range of (600-1000) µm and maximum percentage per micron (dQ/dx) =0.05 within the range (500-600) µm.

Table 1 Sieve Analysis

Particle size (µm), X2 to X1	Interval (dX)	Average size (X)	Number frequency in range	Percentage in range (dQ)	Percentage per micron
0-200	200	150	18	1.8	0.009
200-500	300	350	40	4	0.013
500-600	100	550	47	4.7	0.05
600-1000	500	800	87.1	8.71	0.022
1000-1180	180	1090	11.3	1.13	0.006

Collection of Adsorbents

The date pits were collected from Baghdad city, were dried, and roasted in an oven at 130°C for 4 hrs. **(**Fredrick and Jan, 1995**)** and ground in Willy mill to obtain powder for experimentation using 1000µm.

Batch biosorption studies were carried out using amount of powdered date pits 1.0 gm according to experiments was conducted with samples having different concentration of date pits in order to determine the effect amount on sorption, that obtained at 1 gm of DP increase of sorption, similar results are showed in removal heavy metals from industrial effluent using (Baker' s yeast) (Siafuddin and Raziah, 2007).

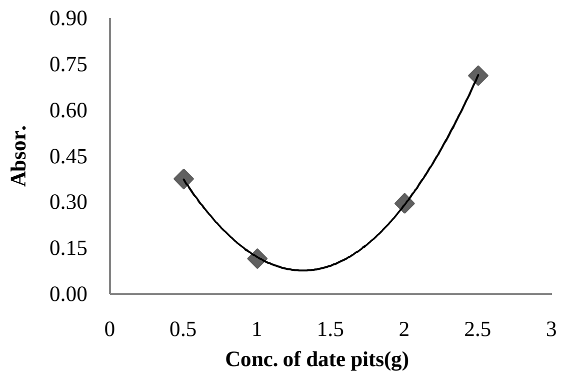

Fig. 1 Absorption of biomass

Preparation of the metal solution

All the reagents were analytical reagent grade and were prepared in laboratory; an aqueous stock solution (1000mg/l) of Cu ions was prepared by using copper chloride [$CuCl_2.H_2o$] salt [Mal.Gew.170, 48 Germany] dissolved in distilled water. This was used as a source of Cu ions in the synthetic wastewater; fresh dilutions were used for each study.

Experimental Procedure

Batch experiments were performed in 500 ml Erlenmeyer flasks, containing 500ml of metal solution the initial concentration of copper($CuCl_2.2H_2O$) were (10, 30, 50, and 100mg /L). Samples were taken from solution after (3, 6, 9, 12, 15min) to determine optimal shaking time. The separation of the biomass from experimental solution was achieved by membrane filtration in all cases. pH of the solution was adjusted by using 0.1*N* HCL and 0.1*N* NaOH. The flasks were agitated on a shaker at rate 150 rpm (Yilmaz *et al*, 2010) under ambient temperature 25°C (Aljlil, 2010) . All the glasses were washed to be free from precontamination.

Analytical Method

The sample (10 ml) were removed at experiment, filtered and analyzed for heavy metal by atomic absorption. An atomic absorption spectrophotometer (AA-6300) (Shimadzu) was used for analyses of the concentration of Cu ions. The percentage of Cu removal due to biosorption was calculated as (Saifuddin and Raziah, 2007).

$$\% \text{ Cu Removal} = (C_o - C_L)/C_o * 100\% \quad \text{---------------- (1)}$$

Where C_o and C_L is the initial and equilibrium concentration of Cu solution mg/L respectively.

And the amount of Cu adsorbed per unit of DP was calculated according to mass balance of copper concentration Known as adsorption capacity (Sirilamduan *et al*, 2011).

$$q_e = (C_i - C_e) * V/M \quad \text{-----------------(2)}$$

Where q_e is the amount of copper adsorbed at equilibrium, C_i and C_e (mg/L) the initial and equilibrium concentration of Cu in solution, V (L) volume of solution and M (g) is the mass of dry adsorbent used.

RESULTS AND DISCUSSION

Effect of pH

The initial solution pH was considered is an important parameter for adsorption of metal ions from aqueous solution because it effects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during the reaction (Naomi *et al*, 1993). In this study the pH of the synthesis wastewater was varied in the range of (3 to 9) at ambient temperature and 10ppm of $CuCl_2.2H_2O$ to determine the optimum pH for biosorption of Cu^{++} by date pits .The results represented in Fig. 4 shows that the biosorption of Cu^{++} uptake reaches a maximum at pH =7.when the pH increased that was from 7 to 9 the alkalinity increased there was further decrease in the rate of adsorption by date pits. The roasted date pits where have chemical functional groups such as carboxylic (COOH) groups, because pH of solution affects the charge on the functional groups, therefore with increase of pH of solution, deprotonation of the functional groups might have occurred which allowed metal ion binding. And the metal ion has attraction with negative charge on the function groups of the date pits. Similar results agree with those of (Aluyor, *et al*,), and (Aljalil, 2010), who studied the biosorption heavy metals from industrial wastewater by using agriculture waste. They reported that the percent adsorption increased with increase of pH reach at maximum at pH=7. (Have good positional to remove heavy metal ion from industrial wastewater).

Effect of the shaking Time

The Effect of shaking time at different concentration of copper chloride on biosorption is represented in Fig 5. It was studied by varying concentration of $CuCl_2.2H_2O$ (10,30and 50mg/L) at pH =7 and 25°C, from this figure observed that the concentration of the $CuCl_2.2H_2O$ is increases with increasing of the shaking time up to equilibrium state which is an achieved at time of 15 min. The availability of surface functional group that presented in the date pits are required for interaction with the Cu^{++} ions in order to improve the binding capacity between them, and to increase the process rapidly, Saifuddin and Raziah, 2007. [4]. As seen at lower concentration of Cu^{++} 10 ppm biosorption was complete in 15 min, at lower concentration the metal ions present in the solution would interact with the binding sits and thus facilitated 100% adsorption. At higher concentrations of metal ions are left unadsorbed in solution due to the saturation of binding sites (Tumin *et al*, 2008). Therefore equilibrium time is very important parameter in waste water treatment economical.

Shaking time was varied from 3 minute to 20 minute. As can be seen in Fig 6, the percentage removal of copper increased with increase of shaking time, and attained an optimum at time 15 min, was obtained 0.994% removal of heavy metal at 10 ppm of Cu^{++}, because the metal ions present in the solution would interact with the binding sites and thus facilitated 100% adsorption.

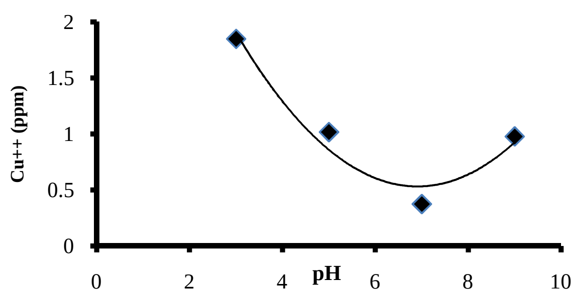

Fig .2 The Effect of pH on biosoption of CuCL2.2H2O at 10ppm of biosorbent and 25oC

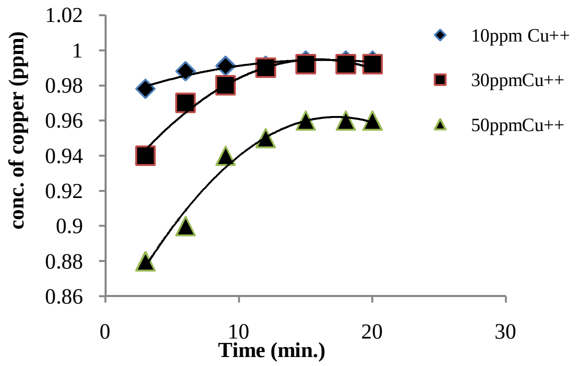

Fig.3 The effect of shaking time with different concentration of Cu++ at pH=7 and temp,25oC

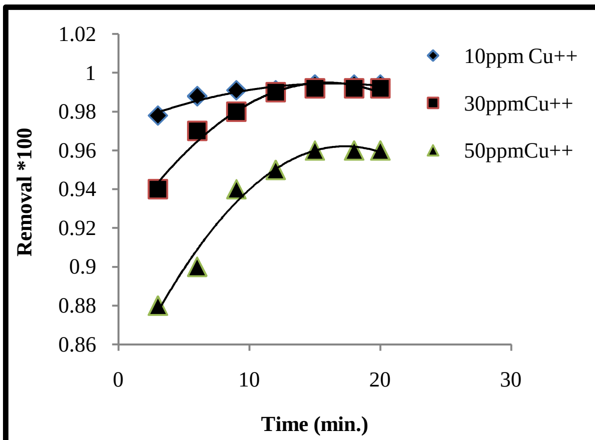

Fig. 4 Removel of Cu++ verses Time at pH=7 and 25 oC

Equilibrium Isotherm Results

The present work was used Langmuir and Fruendlich isotherm models to investigate which it represent the experimental data of removal copper ions from wastewater.

Langmuir model is presented by the following equation(Baseri *et al*, 2012). :-

$q_{eq} = q_{max}*b*C/1+b*C_{eq}$ ---------------(3)

Where q_{eq} is equilibirium adsorption capacity, q_{max} is maximum adsorption capacity, b is adsorption efficiency and C_{eq} is equilibrium concentration.

The Freundlich isotherm can be represented as (Saeed and *et al,* 2005).

Log q_e= log K +(1/n)*log Ce -----------------(4)

Where K is Fruendlich constant and n is another that informs about the heterogeneity degree of the surface sites, both isotherm show the relationship between C_{eq} and q_{eq}. Figs. 7, 8 show the adsorption isotherm curves for copper ion onto DP. It can be seen from Figs 7, 8 that the experimental data follow the Langmuir isotherm model better than the Fruendlich isotherm model and R^2=0.993.

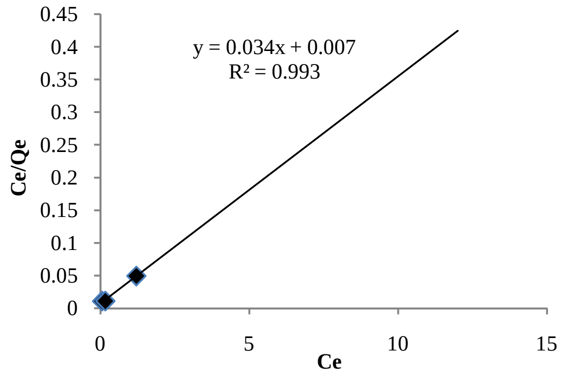

Fig.5 Langmiur isotherm plot of copper adsorption on DP

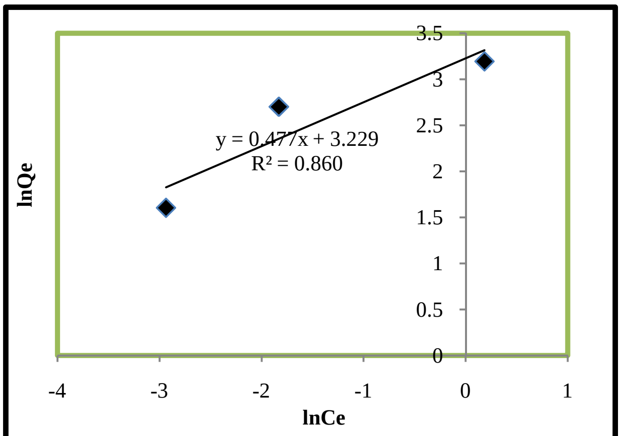

Fig.6 Fruendlich isotherm plot of copper adsorption on DP

Kinetic Studies

In this study, the adsorption of Cu^{++} onto different concentration of copper chloride and different shaking time was analyzed using pseudo –first order and second order kinetic models. Pseudo first order model assumes that the rate of change of solute uptake with time is directly proportional to difference in solution concentration and the amount of the solid uptake.

The pseudo-first order rate equation is (Baseri. *et al,* 2012).

$(dq/dt)=k_1(q_e-q_t)$ b ---------------(5)

Where, q_e and q_t are the amount of copper chloride (mg/g) at equilibrium and time t (min) and $k_1$is the pseudo-first rate constant (min^{-1}). The integrated linear from of pseudo first order equation is

Log $(q_e-q_t)=log q_e-(k_1/2.303)t$. --------------- (6)

The plot of log(q_e-q_t) versus t should give a straight line with slope of $-k_1/2.303$ and intercept log q_e (figure not shown).
The pseudo-second order kinetic equation is expressed as

$t/q_t=(1/k_2q_e^2)+t/q_t$ -------------(7)

Where, *K2* is the rate constant (g/mg min) and q_e is the equilibrium adsorption capacity (mg/g) (Baseri. *et al,* 2012)
The initial adsorption rate, h, (mg/g min) is expressed as:

$h=k_2*q_e^2$ ---------------- (8)

Figure 9 show the pseudo-second order plots for the adsorption of copper at different time and different concentrations of the Cu^{++} and 25°C. The value of k_2 and *qe* determined from the intercept and slope of the plot. K_2 decreasing with increase in initial Cu^{++} concentration. The values of the parameters and correlation coefficients are also presented in Table 2. the adsorption of Cu^{++} at different time and different concentration best fits well to the pseudo second order kinetic model than the pseudo first order kinetic model with high correlation coefficient The correlation coefficients of examined data were found very high (R^2 > 0.9). This shows that the model can be applied for the entire adsorption process.

Table 2 Kinetic parameters for the adsorption of Cu^{++} with different concentration of $Cucl_2.(H_2O)$ and different shaking time at 25°C and pH=7.

Adsorbent	Date Pits		
Parameter	Initial copper chloride concentration ,mg/L		
	10	30	50
q_e exp.(mg/g)	1	2.89	4.88
	Pseudo first order kinetic		
K_1 (min^{-1})	1.32	1.26	1.39
q_e cal (mg/g)	3.75	1.15	1.09
R^2	0.305	0.834	0.845
	Pseudo second order kinetic		
K_2 (g/mg min)	4.92	3.29	1.36
h	1.33	4.24	6.89
q_e cal (mg/g)	0.52	1.134	2.25
R^2	0.929	0.912	0.929

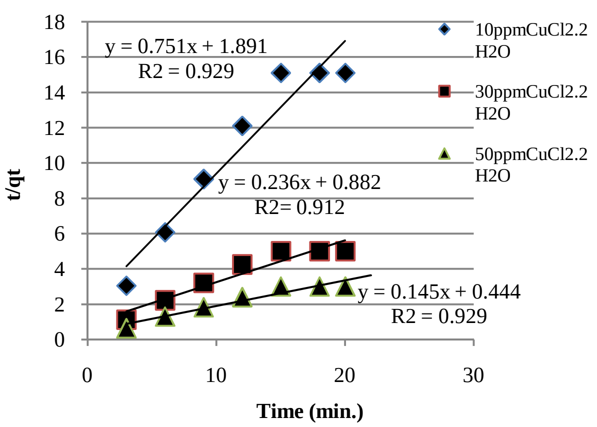

Fig. 7 t/qt versus time for pseudo-second order

Biosorbents Characterization

FTIR spectra for date pits (Fig 10) show a number of absorption peaks, suggesting complex properties of the biosorbent .The bands observed at 2922 and 2852 cm^{-1} are assigned to asymmetric C-H present to alkyl groups .The peak 1728 cm^{-1} is assigned to carbonyl C=O due to the acetyl and ester groups of hemicelluloses .The peak at 1014and 1011cm^{-1} may represent C-O stretching vibrations. The FTIR spectra of date pits are in a good agreement with the result of (Zohra *et al*, 2011).This results is in accordance with the composition of lignocelluloses materials such as date pits which are essentially composed of cellulose, hemicelluloses and lignin (Zohra *et al*, 2011) .The FTIR results indicated that the biosorbents presented different functional groups such as carboxyl and carbonyl which may be potential biosorption sites for copper ions (Pavan and Lina, 2008).

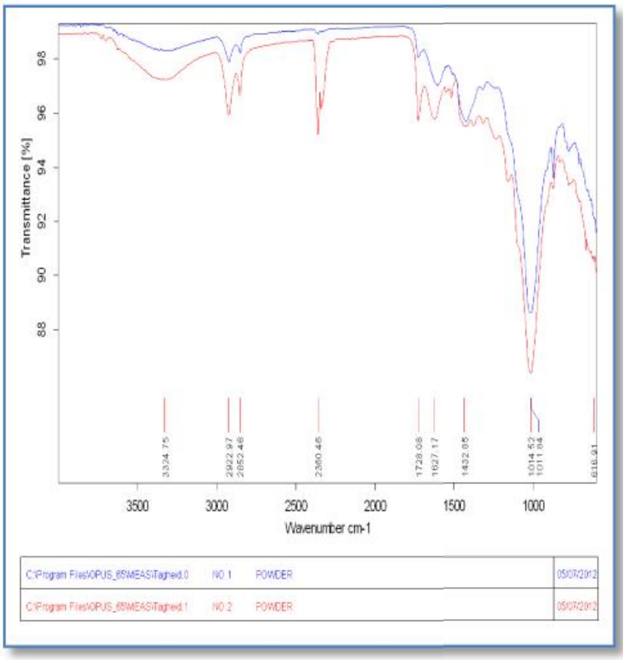

Fig.8 FTIR spectra of biosorbents.

CONCLUSIONS

Making use of bio-adsorbents is an effective method to adsorb toxic heavy metals from effluents not polluting the ground water and at the same time utilizing the discarded open agricultural wastes in the environment for a useful purpose of waste water treatment. This method not only requires minimal energy input, less labor and low investment, but also proves to be very economical. Experiments were performed by varying the pH, initial metal ion concentration, contact time and were founded the best conditions as 15 min which it give higher efficiency removal copper from wastewater. For the biosorption process, the results indicated that the adsorption equilibrium data fitted with the Langmuir isotherm model. The biosorption process was found to conform to a pseudo-second-order kinetic equation. From results Can be concluded that the roasted date pits, has a potential to be used as an alternative biosorbent material for the removal of Cu^{++} ions from aqueous solution.

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Symbols

b Initial concentration of Cu solution mg/l.
C_{eq} Equilibrium concentration mg/l
C_L Equilibrium concentration of Cu solution mg/L
C_o Initial concentration of Cu solution mg/L
K Fruendlich constant.
M Mass of dry adsorbent (g).
n Heterogeneity degree of the surface sites
q_e Amount of copper adsorbed at equilibrium
q_{eq} Equilibirium adsorption capacity
q_{max} Maximum adsorption capacity.
V volume of solution ml.

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