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# Copper biosorption using local Iraqi natural agents

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## ABSTRACT

Industrial effluents loaded with heavy metals are a cause of hazards to the humans and other forms of life. Conventional approaches, such as electroplating, ion exchange, and membrane processes, are used for removal of copper, cadmium, and lead and are often cost prohibitive with low efficiency at low metal ion concentration. Biosorption can be considered as an option which has been proven as more efficient and economical for removing the mentioned metal ions. Biosorbents used are fungi, yeasts, oil palm shells, coir pith carbon, peanut husks, and olive pulp. Recently, low cost and natural products have also been researched as biosorbent. This paper presents an attempt of the potential use of Iraqi date pits and Al-Khriet (i.e. substances locally available in Iraq and found in the legs of *Typha domingensis*) as basements. The important factors studied which affect the removal of copper ion are solution pH value (4–8), adsorbent dosage (0.5–2 g), contact time [((1/2–4) h) for Al-Khriet and (1/2–24) h for date pits]; and (50–200) ppm copper ion concentration. The results showed that it is possible to remove 96% of $Cu^{+2}$ after 4 h contact time using Al-Khriet, and 84% of $Cu^{+2}$ after 24 h contact time using date pits. The kinetic data agree with a pseudo-second-order equation. Isotherm analysis showed that the adsorption process describes Langmuir better than the Freundlich.

*Keywords:* Biosorption; Date pit; Low-cost adsorbent; Isotherm; Kinetic model; Copper ions

## 1. Introduction

The presence of highly toxic heavy metals and synthetic chemicals in the surrounding water has a great impact on humans and aquatic life [1]. The environmental pollution with heavy metals, e.g. Cu, Pb, Fe, Cd, etc. is mainly caused by industrial wastewater. These metals may be discharged into the wastes from different industries, such as, metal plating, alloy industries, dying, storage batteries, fertilizers, and other chemical industries in Iraq [2]. The World Health Organization recommended 2.0 mg/L as the maximum allowed concentration of copper ion in drinking water [3]. In Iraq, the concentration of copper in the water from the El Eshaki tracer is 38 mg/L, and this water came originally from the Alsomood Company in the steel industry and Alnaser Company for mechanical industries, which is much higher than permissible limits for safe life. Hence, the removal of copper ion from waste water is extremely important and it deserves immediate attention.

The most commonly used methods for heavy metal removing from contaminated water include chemical

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precipitation, electrolytic removal, ion exchange, coagulation, adsorption, solvent extraction, and reverse osmosis, most of these methods are either too expensive to deal with low concentration of metals or generate toxic sludge that present problem for further handling [4].

For these reasons, there is a need to develop low-cost processes for such heavy metal removal. Biosorption presents alternative; potentially cost effective technology, which removes toxic metals and organic compounds from water solutions using dead or live biomass as an adsorbent. Biosorption works very well at low concentrations (i.e. <100 ppm) where other techniques are ineffective or costly [4,5].

Most of the studies show that the heavy metal adsorption by waste material is high (Table 1).

For all the reasons previously described, an attempt in this study had been done to investigate the possibilities of using cheap, wasted material, and locally available in Iraq (namely date pits and Al-Khriet) as potential adsorbents for copper removal. Most of the studies show that heavy metal biosorption by agricultural waste material is high. Table 1 summarizes the work reported in the literature for the removal of the heavy metal by adsorption. This study also aims to gain a fundamental understanding of the chemical and physical phenomena associated with the adsorbent of copper to the two mentioned natural agents.

### 1.1. Material and adsorbent properties

Different types of Iraqi date pits were collected and fresh biomass of Al-Khriet was also collected from the marshes in the south of Iraq. These two raw materials were washed with deionized water to remove surface impurities such as mud and viscous sweet remnants of dates; then, these two substances were air-dried for many days before drying in an oven at 110℃ over night. Next, the date pits were crushed by using electric-agitated mortar. Coffee blender was used to get more powder. The powdered sample was sieved in a sieve series 1-mm mesh size before storing in a desiccator.

### 1.2. Solution preparation and experimental properties

Stock solutions of $Cu^{+2}$ (50, 100, 150, and 200) "ppm" were prepared by dissolving reagent grade $(CuNO_3).3H_2O$ in deionized water. pH was adjusted in the range from 4 to 8 by adding NaOH and HCl aqueous solutions to $Cu^{+2}$ solution.

Adsorption was performed in a batch experiment at 25℃ for 24 h for date pits and 4 h for Al-Khriet to ensure reaching a state of equilibrium. Each adsorbent of 0.5 g was added to 50 mL of adsorbent solution of concentration range between 50 and 200 mg/L and mixed with rotary shaker of 250 rpm. Sample solution was withdrawn at periods of time and filtered through a filter paper. The concentration of solute in the solution was determined by using atomic absorption spectrophotometer (type Perkin–Eliner-500, USA).

Table 1
Summary of work done by various researches using a variety of waste materials for removing heavy metals

| Adsorbents | Metal | Result | References |
|---|---|---|---|
| Phenol compounds | Activated carbon prepared from date stones | Removal percentage 97.43% | [6] |
| Lead and cadmium ions | Iron-coated sand | 99.99% for Pb and 90% for Cd | [7] |
| Cadmium and mercury ions | Sea shell powder | Adsorption capacity $471.5\times10^{-3}$ mg/kg for Pb ion, and $532\times10^{-3}$ mg/kg for Cd ion | [8] |
| Lead, cadmium and mercury | Baker's yeast biomass | Significant metal uptake | [9] |
| Furfural and phenolic compounds | Activated carbon | Significant metal uptake | [10] |
| Mercury and nickel ions | Baker's yeast | Significant metal uptake | [11] |
| Cadmium ion | Rice husk | Removal percentage 97% | [12] |
| Lead and cadmium ions | Al-khriet | Cd 90% and Pb 96% | [13] |
| Zinc, chromium, and nickel ions | Banana peels | Significant metal uptake | [14] |

## 2. Result and discussion

The results and discussion of the effect of pH (4–8), adsorbent dosage (0.5–2 g), contact time (1/2–4) h for Al-Khriet and (1/2–24) h for date pits, and copper concentration (50–200) ppm, on the removal of copper from synthetic solutions are presented as follows.

### 2.1. Biosorbent characterization

Date pits subjected to elemental analysis showed a composition of calcium, potassium, carbon, and silver with percentages of 30, 20, 36, and 14, respectively. On the other hand, chemical analysis of Al-Khriet showed a composition of silica, carbon, hydrogen, nitrogen, and silver as 43, 40, 12, 3, and 2%, respectively. The Al-Khriet powder was also found to contain 25% hemicelluloses, 36% cellulose, 15% lignin, and other component such as lipids and proteins.

### 2.2. Effect of contact time

The percentage removal was calculated according to the following equation:

$$\text{Percent removal}\,(R) = \frac{C_0 - C_f}{C_0} \times 100 \qquad (1)$$

where $C_0$ and $C_f$ are the initial and final ion concentrations, respectively. Fig. 1 shows the effect of contact time for the biosorption of $Cu^{+2}$ ions by Al-Khriet biosorbent to determine the effect of contact time on $Cu^{+2}$ removal, the contact time was varied from 1/2 to 6 h. It is clear from the figure that significant removal of copper ions took about 4 h. It is evident to state that the initial rapid removal of $Cu^{+2}$ ions is probably due to the availability of active metal binding sites on the biosorbent surface and gradual occupancy of those sites. Fig. 1 also shows that the sorption becomes less efficient in the slower stage [15] as a result of the decrease in competition for available active binding sites and so the metal ions remain in the solution. Similar behavior is shown in Fig. 1, i.e. for the removal of $Cu^{+2}$ ions by the data pits. In this case, the contact time was varied from 1/2 to 30 h, and it's clear that significant removal of copper ions took about 24 h. It can be concluded from the two figures that Al-Khriet as a biosorbent is more efficient to remove $Cu^{+2}$ ions compared with date pits.

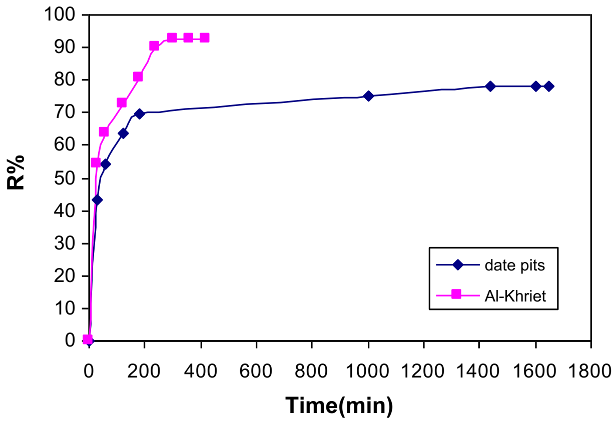

Fig. 1. Effect of time on removal efficiency using Al-Khriet and date pits as adsorbents, biomass dosage 0.5 g, pH 6, 250 rpm, and $Cu^{+2}$ concentration 50 ppm.

### 2.3. Effect of solution pH

The effect of acidity in the medium (pH) is the important variable in adsorption studies because it controls the metal ion sorption process. In synthetic solutions, the effect of pH on percent removal of $Cu^{+2}$ ions on both Al-Khriet and date pits was studied by varying in pH ranges from 4 to 8 as shown in Fig. 2. The $Cu^{+2}$ ion uptake was observed to have an optimum value of pH 6 for both biosorbents. The effect of pH on the percent removal of $Cu^{+2}$ ions can be attributed to interaction between $Cu^{+2}$ ions in solution and complexes formed at the adsorbent surface. Fig. 3 very clearly shows that Al-Khriet has a higher removal percentage (96%) compared to date pits (84%) at pH 6, and this may be due to the interaction of $Cu^{+2}$, Cu(OH), and $Cu(OH)_2$ with the surface functional groups present in the medium. The second reason behind this difference in removal percentage could be

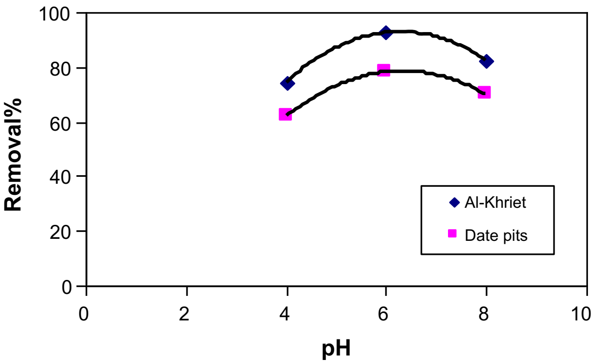

Fig. 2. Effect of solution pH on copper ions adsorption biomass dosage 0.5 g, agitation 250 rpm, and $Cu^{+2}$ concentration 50 ppm.

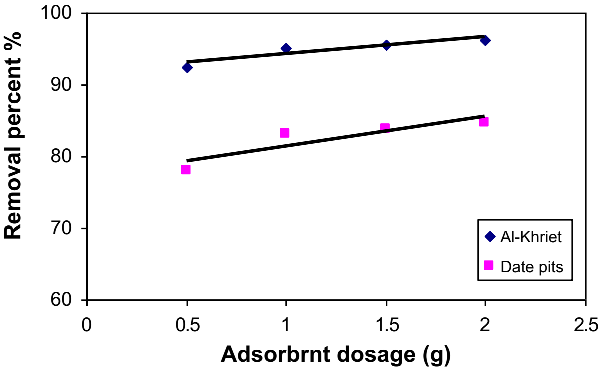

Fig. 3. Effect of adsorbent dosage on percent removal of $Cu^{+2}$, $Cu^{+2}$ concentration 50 ppm, pH 6, and agitation 250 rpm.

the electrostatic attraction between the negative sites of Al-Khriet and the positive metal ion, and this is due to the presence of silica [16]. The various components, from which Al-Khriet is comprised, may have a significant effect on the adsorption process, and it is due to these components that the selected characteristics of heavy metals are different. These components are cellulose, hemicelluloses, and lignin which contain a variety of functional groups such as acetamido groups, carbonyl, structural polysaccharides, phenolic, amino, amide, sulphydryl carboxyl groups alcohols, and esters [17]. These functional groups decide the activity of bioabsorbents. Similar results have been reported by several earlier works for metal sorption on different adsorbents [16,18].

## 2.4. Effect of adsorbents dosage

The influence of adsorbent dosage of both Al-Khriet and date pits on the percentage of copper removal is shown in Fig. 3. It was observed that the percent removal of copper increases for both adsorbents when dosage increases, but this increase was more pronounced for Al-Khriet compared with date pits (i.e. 96% removal observed for 2 g of Al-Khriet compared to 85% percent removal for 2 g of date pits). It is evident that adsorption increases with the increase in the mass of sorbent. This is because at high dosage of sorbent, due to a larger surface area, more adsorption sites are available causing higher removal of copper ions. A similar trend was reported by Madhava et al. [19].

## 2.5. Effect of copper ions

Fig. 4 shows the effect of initial concentration on $Cu^{+2}$ removal by both biosorbents. It was studied by carrying out the experiments at different initial concentrations varying from 50 to 200 ppm of $Cu^{+2}$ at pH 6 and 0.5 g of both adsorbents. It can be concluded that at low $Cu^{+2}$ concentration, the ratio of available surface to the initial $Cu^{+2}$ concentration is larger, so the removal is higher. However, in the case of high concentration this ratio is low; hence, the percent removal is also less. It is evident that since, at high metal ion concentration, high adsorption capacity was not found (i.e. there is no increase in percent removal). This can be attributed to say, that the rate of mass transfer is negligible (i.e. there is no increase in driving force due to the concentration difference [20]).

## 2.6. Adsorption kinetics

In order to examine the adsorption mechanism, the pseudo-first-order and pseudo-second-order equations were used to test experimental data.

The equation below by Langergren [9], is described by the following equation:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \tag{2}$$

whereas the pseudo-second-order [21] is described by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

where $q_e$ and $q_t$ are the amount of each solution (mg/g) adsorbed onto the adsorbent at equilibrium and time $t$, respectively.

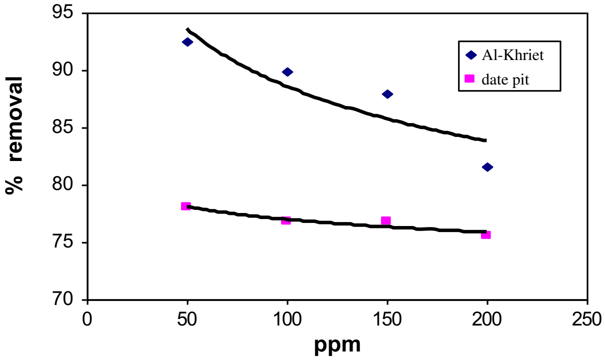

Fig. 4. Removal of copper ion using different concentration of copper 50–200 ppm, pH 6, and 0.5 g of both adsorbents.

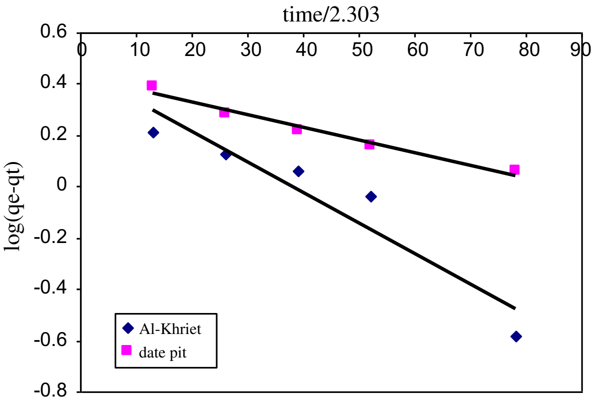

Fig. 5. Pseudo-first-order kinetics for copper ion adsorption, pH 6, 0.5 g of both adsorbents, and 50 ppm of $Cu^{+2}$.

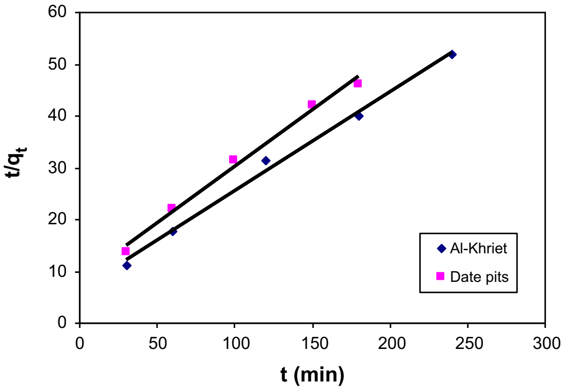

Fig. 6. Pseudo-second-order kinetics plot for copper ion adsorption, pH 6, 0.5 g of both adsorbents, and 50 ppm of $Cu^{+2}$.

The experimental amount of metal ion biosorption $q_t$(mg/g) at time $t$ was calculated by the following equation:

$$q_t = \frac{v(C_0 - C_t)}{ms} \tag{4}$$

while, the amount of adsorption at equilibrium $q_e$ (mg/g), was calculated by:

$$q_e = \frac{v(C_0 - C_e)}{ms} \tag{5}$$

where $C_t$(mg/g) is concentration of copper ion at time $t$; $C_0$ and $C_e$(mg/L) are the initial and equilibrium concentrations of copper ion, respectively; $v$ (L) is the volume of the solution, and $ms$ (g) is the mass of adsorbent used; $k_1$ (min$^{-1}$), the rate constant using pseudo-first-order rate expression, was obtained from the slope of linear plots of log ($q_e - q_t$) against ($t$) using Eq. (2), as shown in Fig. 5, while $k_2$ (mg g$^{-1}$ min$^{-1}$) the rate constant for copper ion using pseudo second order were obtained from slope and intercept of the plot $\frac{t}{q_t}$ against t using Eq. (3), as shown in Fig. 6.

The values of the rate constant and corresponding correlation coefficient are present in Table 2 for both kinetic models.

It can be concluded that the correlation coefficient for the second-order kinetic model is greater than that obtained from the first-order for both adsorbents.

These suggest the sorption system is the second-order model.

### 2.7. Equilibrium modeling

Langmuir isotherm and Freundlich isotherm were tested to describe the experimental results. The linear expression of the Langmuir model [22] is given by Eq. (6):

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \tag{6}$$

where $q_e$(mg/g) and $C_e$(mg/L) are the amount of adsorbed copper ion per unit mass of adsorbent and copper ion concentration at equilibrium.

The Langmuir constant $Q_0$, and b were determined from the slope and intercept of the plot $C_e/q_e$ against $C_e$ as shown in Fig. 7. There is a good matching between the predicted and the experimental Langmuir isotherm plots, as shown in Fig. 7.

The Freundlich isotherm [22] is given by Eq. (10).

Table 2
The rate constant and correlation coefficient for pseudo-first and second-order for both adsorbents

| | $K_1$ for first order × 10 (1/min) | $K_2$ for second order × 10 (mg g$^{-1}$ min$^{-1}$) | $R^2$ for first order | $R^2$ for second order |
|---|---|---|---|---|
| Al-Khriet | 0.05 | 0.06 | 0.90 | 0.99 |
| Date pits | 0.12 | 0.05 | 0.97 | 0.99 |

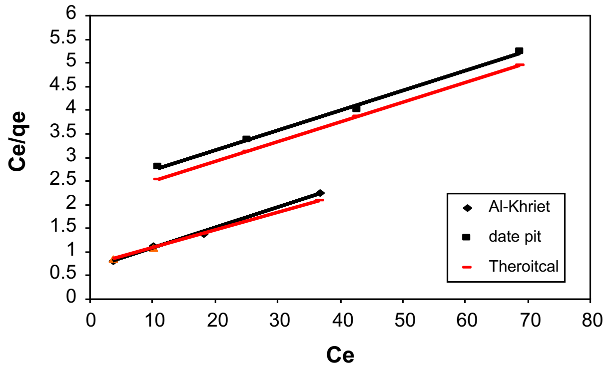

Fig. 7. Langmuir isotherm plots for copper ion adsorption, pH 6, 0.5 g of both adsorbents, and 50 ppm of $Cu^{+2}$.

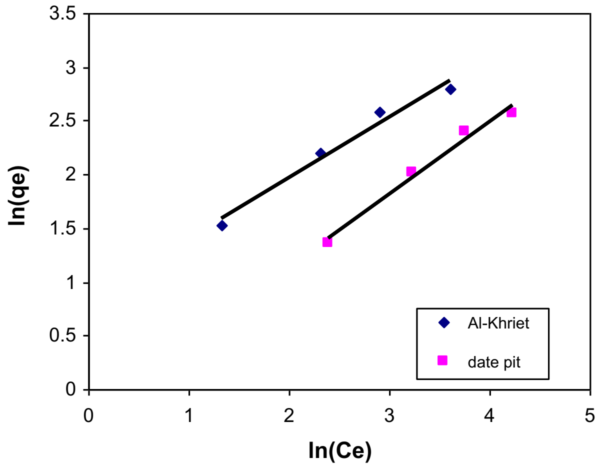

Fig. 8. Freundlich isotherm plots for copper ion adsorption.

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \tag{7}$$

where $k_f$ (mg/g $(\text{L/mg})^{1/n}$) and $n$ are Freundlich constants, value of $k_f$ and n are calculated from the intercept and slope of the plot ln $q_e$ against ln $C_e$ as shown in Fig. 8.

Table 3
Parameters of isotherms and correlation coefficients for $Cu^{+2}$ on both adsorbents for Freundlich and Langmuir

| Kinetic model | Parameters | Al-Khriet | Date-pits |
|---|---|---|---|
| Langmuir | $Q_0$ (mg/g) | 26.67 | 23.87 |
| | $B$ (L/mg) | 0.05 | 0.02 |
| | $R^2$ | 0.99 | 0.99 |
| Freundlich | $k_f \left( \frac{mg}{g} \left( \frac{L}{mg} \right)^{\frac{1}{n}} \right)$ | 2.31 | 0.81 |
| | $n$ | 1.76 | 1.49 |
| | $R^2$ | 0.98 | 0.98 |

Table 4
Different values of $R_L$ for different concentrations of $Cu^{+2}$

| $Cu^{+2}$ concentration (mg/L) | $R_L$ for Al-Khriet | $R_L$ for date pits |
|---|---|---|
| 50 | 0.38 | 0.99 |
| 100 | 0.19 | 0.49 |
| 150 | 0.13 | 0.33 |
| 200 | 0.09 | 0.25 |

The equilibrium isotherm shows a nonlinear dependence on the concentration of equilibrium. The accounted coefficients are observed in Table 3, which point out that the Langmuir model gives the best fit as judged by its correlation coefficient for the absorbents. To establish the favorability of an adsorption process to Langmuir isotherm, the extremely important features of the isotherm can be represented in a term of dimensionless constant separation factor $R_{L.}$ $R_L$ is defined as:

$$R_L = \frac{1}{1 + BC_0} \tag{8}$$

value of $R_L$ point out whether the isotherm is irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) [23,24].

Values of $R_L$ for $Cu^{+2}$ on both adsorbents are given in Table 4. In all cases, the $R_L$ values for the present experimental data fall between 0 and 1, showing that the Langmuir isotherm is favorable [25].

## 3. Conclusion

It was found that both Al-Khriet and date pits can be used to eliminate copper from aqueous waste water. However, Al-Khriet is more preferable than copper, and this is because of its higher effectiveness as well as its being more cost effective due to its natural abundance compared to date pits, which need relatively more money and efforts to collect them before turning them into powder. The biosorption efficiency is affected by many variables, i.e. pH, contact time, bioadsorbent dosage, and initial $Cu^{+2}$ ion concentration. This study proved that Al-Khriet gave higher adsorption capacity than raw date pits. It had observed that the removal process increased with contact time, and attained equilibrium in about 4 and 24 h for both Al-Khriet and date pits, respectively. The adsorption equilibrium had better described by Langmuir isotherm model than the Freundlich model.

Kinetic examination showed that adsorption on both adsorbents followed well the pseudo-second-order kinetics model.

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