Optimization Process for Removing of Copper ions from Groundwater of Iraq Using Watermelon Shells as Natural Adsorbent

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Abstract
People are completely dependent on groundwater for drinking and irrigation in distant Iraq. In many places, copper ions are one of the primary pollutants found in extra quantities in groundwater. The current work uses watermelon shell for removing of copper ions from groundwater. An initial concentration of 10 mg / L and an adsorbent particle size of 1 mm were used to examine the working parameters: PH, dosage, and contact time using STATISTICA and WinQSB software. The optimization technique was set to predict the optimum conditions. However, the efficiency of the watermelon shell was more than 80% and the maximum capacity for adsorption was 9.57 mg / g under optimum conditions such as: 8 for PH, 1 g / L for adsorbent dosage and 2.5 hours for contact time. The general findings verified that the shell of watermelon is an outstanding and alternative adsorbent to remove Cu(II) from groundwater of Iraq.

Keywords: Groundwater; Agricultural waste; Adsorption; Copper ions; Removal efficiency.

1. Introduction:
It is essential to remember that the dissolved heavy metal of different activities can pollutes the groundwater, it is harmful to the environment and public health due to its toxicity, food chain accumulation and persistence in the nature.[1]. Groundwater pollution is one of today’s significant environmental concerns in Iraq. This issue was regarded huge, particularly in distant regions of Iraq. There is no safeguard in the drinking water against both natural and man-made contaminants. By conventional treatment and water supply network scheme, most faraway places in Iraqi did not supply clean water. Like many developing nations. However, there is no simple method to supply water disinfectant to these fields. Most individuals live in these places, therefore, mostly rely on the groundwater. In many sectors, heavy metal contamination occurs in aqueous waste such as: metal electroplating, mining, tannery, radiator manufacture, smelting, alloy and battery sectors, etc.) [2]. Copper is one of the contaminations that should be removed from wastewater according to drinking water norms, namely to the toxicity of 100-500 mg per day for humans according to WHO (2017) [3]. Copper is one of the primary contaminants in the electrical, glazing and metal processing sectors. It is often established close to mines, and landfills or
water disposal sites in elevated levels [4, 5]. In 2017, as the highest acceptable copper concentration in drinking water, the World Health Organization proposed 2.0 mg / L [3], while Iraq's normal drinking water specification indicated that 1.0 mg / L was the highest permissible concentration of copper ions. [6]. Copper toxicity would trigger illnesses, cancers and many health effects for humans [7]. It is therefore highly essential to remove copper from wastewater before it discharges into the aquatic system and it deserves instant attention. Several distinct kinds of sorbents were explored in the literature review to be used as adsorptive removal of Cu (II) from its aqueous solutions. Activated carbon, for instance, is the most commonly used extraction sorbent, but its implementation is restricted owing to elevated activation costs and incomplete generation [8, 9]. Agricultural waste and industrial by-product can be cost-effective and have better sorbents compared to activated carbon. Also, many agricultural wastes were reported to be used for removing of heavy metals as potential and low cost adsorbents. For instance, fruit peels were used to remove heavy metals from aqueous solution, such as: banana peel [10], mango peel [11], orange peel [12], lemon peel [13], and jackfruit peel [14]. However, watermelon was used to extract Cu (II) ions from Iraq's natural groundwater, the findings showed an aqueous solution with an adsorption ability of 9.54 mg / g for copper ions [6]. The present work will be devoted to optimizing the parameters that affect the adsorption capacity of the watermelon shell for maximum adsorption capacity of Cu (II) from contaminated groundwater in order to predict the optimum conditions due to the significant application and significant results extracted from previous work [6]. The parameters to be investigated in the optimization technique are the initial Cu (II) concentration, dose, contact time, pH, and particle size. Analyzing the adsorption capacity with Langmuir and Freundlich isotherms are included.

2. Experimental Work:
The experimental method includes collecting of fruit cortex, cutting, washing, drying, and grinding to get a desired particle size. Then the adsorbent particles are used in a batch process for adsorbing copper ions from contaminated groundwater. The details of the experimental procedure are available in the previous work [6]. Adsorption capacity was calculated using the following equation:

\[
\text{Adsorption capacity} = \frac{(c_i - c_f) \times v}{m} \quad \ldots \ldots \ldots \ldots \ldots (1)
\]

\[
\text{Removal efficiency} = \frac{(c_i - c_f)}{c_i} \times 100 \quad \ldots \ldots \ldots \ldots \ldots (2)
\]

Where: \(c_i\) (mg/L), \(c_f\) (mg/L) are initial and final concentrations of copper ions respectively, \(m\) (g) is the mass of adsorbent, and \(v\) (L) is the volume of solution.

3. Optimization technique:
The optimization process was achieved by STATISTICA program version 8.0 to predict the coefficients of polynomial correlation that represents the adsorption capacity as the objective function. Eq. 1 shows the polynomial correlation.
Where $y$ is the objective function (adsorption capacity), $x_1$, $x_2$, and $x_3$ are design parameters as PH, dosage, and contact time respectively. ANOVA analysis was achieved through STATISTICA to prove the confidence level of the objective function with the experimental results of adsorption capacity. Also, the standard deviation and correlation coefficient were estimated and the predicted and observed values are involved. The objective of the optimization is to predicate the optimum conditions to produce maximum removal percentages. The optimum conditions were estimated through maximizing the objective function (adsorption capacity) using WinQSB software version 1.0.

4. Results and discussion:
The results are divided into experimental results of the adsorption process and the optimization results for optimum condition predications.

4.1 Adsorption process

4.1.1 Impact of pH

Fig.1 shows the impact of pH on Cu(II) removal. With raising pH from 2 to 8, Cu adsorption by watermelon shells (WS) improves vividly. The optimal pH for WS adsorption with Cu(II) was 8. Due to rivalry for metal binding locations between strongly loaded Cu(II) ions and hydrogen ions, lower metal removal at extremely acidic pH could result. The adsorbent surface was also loaded more favorably at low pH, decreasing the attraction between WS and metal ions. An additional rise in pH (beyond pH 8) can be ascribed as [6] to Cu(II) rainfall. This reduces Cu(II) concentration in the solution and therefore reduces WS ’ extraction effectiveness. Similar findings are in excellent agreement with Ho et al.[15].

![Figure 1 PH effect on the percentage of removal (initial conc.=10 mg / L, dosage=1g / L, contact time=2 hr, particle size 1 mm).](image)

4.1.2 Effect of adsorbent dose
Cu(II) adsorption on WS was explored by altering the adsorbent amount in the test solution while maintaining the original Cu(II) concentration at (10 mg / L). Increased adsorbent dose enhanced the removing of Cu(II), as shown in Fig.2, because of an
improvement in the adsorbent surface area. But the change in effectiveness of removal is much less after a specific dose. This is due to elevated concentration of adsorbents; on the adsorption surface there is a very quick superficial adsorption that generates a reduced amount of solute in the solution than when the amount of adsorbents is small. Thus, with an increase in the adsorbent dose, the amount of copper ions that have been adsorbed per unit mass is reduced, resulting in lowering the equilibrium uptake[6]. The peak removal at 1 gm / L dose was discovered to be 90 percent. The findings showed excellent support for Banerjee et al.,[16].

Figure 2 Dose effect on the percentage of removal (initial conc.=10 mg / L, pH=8, contact time=2 hr, particle size of 1 mm).

4.1.3. Effect of contact time
The contact time had an impact on the extent of Cu(II) ion adsorption. Fig.3 shows the variation in the quantity of Cu(II) adsorption on WS for constant metal concentration. As can be shown from Fig.3, the quantity of the adsorbed Cu(II) on the adsorbent rises rapidly with time in the initial stage (1 to 2 hr) and at the same time (2 hr) it reaches a fixed amount beyond which the solution is no longer extracted, i.e. no further rise in contact time has any important impact on the quantity taken. At this point, the amount of the adsorbent Cu(II) is in a dynamic balance with the adsorbent metal being adsorbed. Bello et al. achieved similar results [17 ].

Figure 3 Contact time effect on the percentage of removal (initial conc.=10 mg / L, dose=1g / L, pH=8, particle size 1 mm).
4.2 Optimization results

The results of adsorption capacity were represented in a polynomial (Eq. 1), the coefficients of the polynomial were found in Table 1. The correlation coefficient value (R) was 0.953.

Table 1 Polynomial coefficients values.

|  \(a_0\) |  \(a_1\) |  \(a_2\) |  \(a_3\) |  \(a_4\) |  \(a_5\) |  \(a_6\) |  \(a_7\) |  \(a_8\) |  \(a_9\) |
|------|------|------|------|------|------|------|------|------|------|
|  1.333 |  13.521 |  1.367 |  -0.986 |  13.766 |  -1.355 |  -0.904 |  -1.206 |  -38.217 |  1.043 |

The observed values that represents the experimental values of adsorption capacity with predicated values that represents the values obtained from model equation are shown in Figure 4. It can be observed that the model values are best fit to experimental results.

![Figure 4 Observed and predicated values of adsorption capacity.](image)

A statistical analysis of the model for mean and standard deviations for polynomial model is shown in Table 2.

Table 2 Mean and Standard Deviations.

| Variable | Mean     | Standard Deviation | Minimum | Maximum  |
|----------|----------|--------------------|---------|----------|
| X1       | 7.41176  | 1.83912            | 2.00000 | 10.00000 |
| X2       | 1.00000  | 0.39528            | 0.00000 | 2.00000  |
| X3       | 2.9706   | 1.891              | 1.00000 | 10.00000 |
| WS       | 68.35294 | 26.53050           | 3.00000 | 96.00000 |

Analysis of variance which represent the significant of each parameter on the objective function is shown in Table 3.
Table 3 ANOVA analysis of the objective function.

| Effect            | sum of squares | df   | mean squares | F value | P value |
|-------------------|----------------|------|--------------|---------|---------|
| Regression        | 89650.93       | 10.000 | 8965.093     | 60.512  | 0.000008 |
| Residual          | 1037.07        | 7.0000 | 148.154      |         |         |
| Total             | 90688.00       | 17.000 |              |         |         |
| Corrected Total   | 11261.88       | 16.000 |              |         |         |
| Regression vs. Corrected Total | 89650.93 | 10.000 | 8965.093 | 12.736 | 0.000008 |

4.3 Interaction effect:
The interaction effect between two parameters on removal percentage are presented in Figures (5-7). The interaction impact is one of the advantage of optimization technique to protend the optimum operating conditions accurately. Figure 5 displays the impact of $x_1$ (PH) and $x_2$ (dosing) on $Y$ (removal efficiency of WS), from the results it can be shown that the higher adsorption capacity is available when $x_1$ is greater than 7.0 and $x_2$ is above 0.65 gives higher removal efficiency of more than 80%.
Figure 5 Effect of PH and dosing on removal efficiency.

Figure 6 shows the impact of $x_1$ (PH) and $x_3$ (contact time) on $Y$ (removal efficiency of watermelon). It can be shown that maximum adsorption can be achieved by lowering $x_2$ (from 5 to 6) and at $x_1$ of 8 gives maximum removal efficiency of more than 80%.
Figure 6 PH effect and contact time on removal efficiency.

Figure 7 shows the impact of $x_2$ (dosing) and $x_3$ (contact time) on $Y$ (removal efficiency of watermelon). It can be shown that maximum adsorption can be achieved by lowering $x_2$ (1.0 g/L) and at $x_3$ (from 1 to 1.5 hr) to give the maximum removal efficiency of more than 80%.
4.4 Optimum conditions
The optimum conditions were predicated using the available computer program to obtain the maximum removal efficiency of more than 90% and the maximum adsorption capacity was 9.57 mg/g at the optimum conditions. Table 5 shows the optimum conditions results.

| x₁ (PH) | x₂ (dosing) | x₃ (contact time) | y (adsorption capacity) |
|---------|-------------|------------------|------------------------|
| 8 (-)   | 1 (g/L)     | 2.5 (hr)         | 9.57 (mg/g)            |

4.5 Adsorption models
WS adsorption capability results were evaluated at separate temperatures using the Freundlich and Langmuir equation. In the meantime, the feature parameters were predicted for each isothermal adsorption. The results are available in the previous work [6].

5. Conclusions
Clearly, the current research indicates that using watermelon shells (WS) as adsorbents is much more cost-effective, effective, and feasible. The predicted study from the present job showed that WS cortex can be utilized effectively to remove copper ions from groundwater with no dangerous impact on water quality. During the investigation phase, the distinct
operation parameters observed in batch studies reveal that the pH, dosage, and contact time govern the process. The optimization method demonstrated that peak adsorption capability could be disclosed as 9.57 mg / g and removal proportion of more than 90 percent at optimum circumstances (PH= 8, 1 g / L dosage and 2.5 hr contact time). Therefore, WS is demonstrated to a significant and environmental friendly adsorption material for removing of Cu(II) ions from polluted groundwater in Iraq.

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