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Optimization Of Conditions For Enhanced Removal Of Copprer Onto The Granular Tribulus Terreststris Herble

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ABSTRACT

Copper one of the most common toxic environmental pollutants that originate mainly from industrial processes. It is a recalcitrant and hazardous compound, which is toxic at relatively low concentration and hence, the safe level of Cu in drinking water for human is between 1.5 to 2.0 mg / L. The removal of copper pollutant from wastewater was studied. Tribulus terreststris herbal that is easily available in large quantities and feasible economically. Granular Tribulus terreststris herbal was prepared and used for the removal of Cu^{2+} from aqueous solution. The removal of copper pollutant from wastewater was studied. The physical and chemical properties of granular Tribulus terreststris herbal prepared were measured according to standard methods. Batch experiments were carried out as a function of temperature (20, 30, 40 and 50^oC), pH (3, 5 and 7) and different initial concentrations (10, 20 and 30) ppm. The data obtained from the experiments conducted as per the Taguchi design to determine the optimal value of each parameter for the remove. MINITAB 16 software was used to optimize the parameters to remove the copper using the Taguchi method of optimization. pH of the medium effects on removal Cu^{2+} the most as compared to the temperature S/N ratio Larger is better for pH =27.774 in rank =1 while for temperature S/N ratio Larger is better =15.340 in rank =1. The optimum temperature and pH condition for the remove is 30^oC and 5 respectively.

KEYWORDS: *Copper, Granular Tribulus terreststris, Optimization, Taguchi method, Single to Noise Ratio.*

INTRODUCTION:-

Water pollution with heavy metals has become an important environmental threat mainly because of industrial activities and technological development generates effluents containing these and other pollutants (Rosa, et al., 2008). Naturally-occurring copper exists in its elemental state as well as various mineral deposits, primarily as sulfides, carbonates, hydroxides and oxides. With regard to anthropogenic sources, copper is released to the environment primarily through the smelting and refining of copper, as well as municipal incineration Environmental protection agency (EPA, 2006).

These releases may contaminate surface and groundwater sources supplying the distribution system. Copper typically exists in cationic form as either cuprous (Cu^+) or cupric (Cu^{2+}) species, depending on the oxidation-reduction potential. Both species may form mineral precipitates involving carbonate, oxide, hydroxide, or phosphate, though to differing degrees. The solubility of both species is also highly dependent on solution pH, with higher pH levels generally limiting solubility (Trease & Evans, 2002).

Drinking water that contains higher than normal levels of Cu may cause vomiting, diarrhea, stomach cramp and nausea. The chronic effects of consumption of high levels of copper are liver and kidney damage. Hence, removal of copper form water and waste water assumes important
(Najua, *et al.*, 2008, Netzer, *et al.*, 1974 and Nordberg, *et al.*, 2007).

In this study Tribulus terreststris herbal was used as a new biosorbent to remove copper from wastewater. Tribulus terreststris herbal family Zygophyllaceae. Three species, Tribulus cistoides, Tribulus terrestris, and Tribulus alatus, are of common occurrence in India (Duke, et al., 2002**)**. Among them, Tribulus terrestris (TT) is a well patronized medicinal herb by Ayurvedic seers as well as by modern herbalists (Nadkarni, 1927 and the wealth of India,1972). It is small prostrate, 10-60 cm height, hirsute or silky hairy shrub. Leaves are opposite, often unequal, par pinnate; pinnae from five to eight pairs, elliptical or oblong lanceolate Fig. 1. Flowers are yellow in color. Its carpel fruits are of characteristic, stellate shape, somewhat round-shaped, compressed, five cornered, and covered with prickles of very light-yellow color Fig. 2.

There are several seeds in each crocus with transverse partitions between them. It's various parts contain a variety of chemical constitutes which are medicinally important. In this study Tribulus terreststris herbal was used as a new biosorbent to remove copper from wastewater.

The objective of this study is to preparation of granule Tribulus terreststris herbal that is easily available in large quantities and feasible economically for multiple metal ions in solution. Investigation of the potentiality of prepared for granule Tribulus terreststris herbal removing copper. MINITAB 16 - software was used to optimize the parameters to remove the copper using the Taguchi method of optimization.

MATERIALS AND METHODS:-

Preparation Granule Tribulus Terreststris Herbal (GTTH)

Granule Tribulus terreststris herbal was used as a biosorbent. It was supplied from Basrah city. Tribulus terreststris herbal washed several times by distilled water to remove undesired solid materials and dissolved heavy metals. It was dried under sun light and again it dried in oven at 70^0C until having constant weight (24 h) then crushed by jaw crusher and sieved by successive sieves of sizes. The physical and chemical properties will be determined list in Table 1.

Cupric Sulfate Anhydrous ($CuSO_4$)

A standard solution of copper sulfate anhydrous with concentration of (1000 mg/l) was prepared using $CuSO_4$ salt. The specific concentration was measured using atomic absorption spectrophotometer (AAS). The prepared solution was kept at room temperature and used as stock solution to prepare a (10, 20 and 30 mg /l) of Cu^{2+}.

Batch Studies

Batch studies were used to obtain the majority of single, equilibrium data. Solution was prepared containing the desired solute concentration of (10, 20 and 30 mg/l) of copper. A sample of (100 ml) of solution was placed in a beaker of (200 ml) in volume. The solution was agitated at constant temperature 30 ^{O}C at 200 rpm for ten hours which is enough to reach equilibrium, particle size for GTTH (0.380 mm) and dose (1g). pH adjustment at the value of 5 the pH value was adjusted by adding (0.5 N) HCl to each solution and measuring the pH value continuously till reaching the desired value. Then the solution was filtrated using filter paper type (Wattmann no. 4) and a sample of (5 ml) was taken for analysis. The equilibrium concentrations were measured by means of atomic absorption spectrophotometer (modelVGP-210Buck scientific). At this state the concentration was in equilibrium (Sulaymon and Swadi, 2014).

The copper amount was calculated using the following equation (Crittenden, 1987):

$$q_e = \frac{V_L\left(C_o - C_e\right)}{W_o} \qquad (1)$$

The removal percentage of copper was calculated by the difference in the initial and equilibrium concentration of each pollutant using the following (Crittenden ,1987):

$$E = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (2)$$

Design of Experiment (DOE)

The parameter design of the Taguchi method which includes the following steps as summarized by (Trang and Yang Peace, 1993) has been carried out in the present study.

1. The quality characteristics and process parameters to be evaluated were identified.
2. The number of levels for the process parameters and possible interactions between the process parameters were determined.
3. The appropriate orthogonal array was selected using the Minitab-16 software and the process parameters were assigned to the orthogonal array.
4. The experiments based on the arrangement of the orthogonal array were carried out.
5. The experimental results were analyzed using the signal-to-noise ratio.

Orthogonal array (OA), L27 each with mixed levels, was chosen (temperature and pH of at various initial concentration of Cu^{2+} (Lochner & Matar, 1990).

The selection of parameters and their level was an important step to design an Orthogonal array (OA). Orthogonal array (OA), L27 each with mixed levels, was chosen (temperature and pH of the media at various initial concentration of copper) (Fowlkes & Creveling ,1995, Park, 1996). Table 2. represents the selected orthogonal array for this study.

The value of the loss functions is further transformed into a signal-to-noise (S/N) ratio. There are four categories of performance characteristics in the analysis of the S/N ratio depending on the goal of design (Phadke, 1989, Taguchi& Konishi, 1987, Takeo, et.al., 1995).

- **Larger is better**

$$S/N = -10*\log(\Sigma (1/Y^2) / n) \qquad (3)$$

When the goal is to maximize the response and data Positive.

- **Nominal is best**

$$S/N = -10*\log(\sigma^2) \qquad (4)$$

When the goal is to target the response and want to base the S/N ratio on standard deviations only and data positive, zero, or negative.

- **Nominal is best (default)**

$$S/N = 10*\log((Y^2) / \sigma^2) \qquad (5)$$

The adjusted formula is:

$$S/N = 10*\log((Y^2 - s^2 / n)/ s^2) \qquad (6)$$

When the goal is targeting the response and want to base the S/N ratio on means and standard deviations.

- **Smaller is better**

$$S/N = -10*\log(\Sigma (Y^2)/n) \qquad (7)$$

When the goal is minimizing the response non-negative with a target value of zero.

Where n the number of observations, and Y the observed data.

RESULTS AND DISCUSSION:-

Effect of Temperature

Effect of temperature on remove of $Cu^{2+}$was studied by conducting different sets of experiments at different temperatures (20, 30, 40 and 50ºC), while the other operational parameters were kept constant at initial concentration (20 ppm for Cu^{2+}), pH (5), agitation speed (200 rpm), particle size for GTTH (0. 380 mm), dose GTTH (1g) and contact time (10h). Fig. 3 shows that the uptake capacity decrease with temperature increase that be attributed to the possible damage to active sites in the GTTH at higher temperatures. This agree with (Pankaj, P., et al.,2009 and Emine, Y.,2008).

Effect of pH

The experimental were done under the conditions of constant temperature (30 ^{0}C), constant time (10h), GTTH amount (1g), particle size (0. 380 mm), agitation speed (200 rpm) and initial concentrations were kept at 20 ppm for Cu^{2+}.While different pH (3, 5 and 7). The experimental data are presented in Fig. 4. It was found that the uptake capacity decrease with the increase in pH.

This phenomenon can be demonstrated as follows: granule Tribulus terreststris herbal GTTH has active sites with negative charge while the copper ion has active sites with a positive charge at low pH. The increase in pH causes increase in the concentration of hydroxyl ion (OH^-) negative charge which increases the hindrance for diffusion of copper and GTTH charge and thus reduces the removal percent of Cu^{2+}. Therefore, the initial pH= 5 is the best value and will be selected as for the next experiments to removal Cu^{2+} ions from wastewater by using GTTH. This agree with (Sulaymon, et al.,2008).

Effect of Initial Concentration

Effect of initial concentration on Cu^{2+} was investigated by conducting different sets of experiments at different initial concentrations (10, 20 and 30) ppm . Other parameters were kept constant, such as, temperature, pH (5) agitation speed (200 rpm), particle size for GTTH (0. 380 mm) and dose (1g). The uptake versus time were ploted Fig. 5. It was found that the uptake capacity increased with the increase in initial concentration. This result improves the fact that the removal percent of copper is strongly dependent on the initial concentration of copper. This agree with (Sulaymon, et al.,2008 and Teixeria, et al.,2004).

Analysis of Taguchi Design of Experiment

Experimental work has been designed in a sequence of steps to ensure that data was obtained in a way that its analysis will lead immediately to valid statistical inferences. This research methodology is termed as DOE that attempts to extract maximum information with minimum number of experiments.

The data were analyzed by Minitab16 software. Two basic factors have been opted for studying their effect on the optimal remove of copper. The factors were temperature and pH of the media at different initial concentration of copper. To use the S/N ratio for the maximum for the response performances S/N calculation was performed and calculated from Eq.3.Table 3. Response table for single to noise ratio value for different experiment parameters using Taguchi design Larger is better. The optimal level of a process parameter is the level with the highest S/N ratio. Fig. 6 shown main effect plots of process parameter vs S/N ratio and Fig. 7 shown the interaction plot for S/N ratios for different parameters responsible for copper remove.

From Table 3. and Figs. 6 & 7 pH of the medium effects on removal Cu^{2+} the most as compared to the temperature S/N ratio Larger is better for pH =27.774 in rank 1 while for temperature S/N ratio Larger is better =15.340 in rank 2.

Percentage Remove Versus Temperature, pH and Initial Concentration of The Medium

The interaction between different parameters was also studied by the contour plot obtained between various parameters. These plots were drawn using the Minitab 16 software and these plots will suggest the best possible range of parameters for the study. Fig. 8 represents the contour plot for removal Cu^{2+} % vs temperature and PH. From the figure it can be inferred that with increasing the temperature the remove of the copper percentage decreases. It exemplifies that the optimum pH range of the copper remove is from (5-5.5) and the optimal temperature is around 30ºC.

Fig. 9 shows the percentage of copper remove % corresponding to the change in temperature with change in the initial concentration of copper. The figure delineates that temperature have a less effect on the remove of the substrate as compared to the concentration of the substrate present initially in the medium.

Fig. (10) indicates the contour plot between percentage removal vs pH at various initial concentration of copper in the media. From the Fig. 10, it can deduce that the percentage of copper remove shown the highest when the pH of the medium ranges from 5 to 5.5 which is the optimum pH condition for the remove. It is observed that with increase in the initial copper concentration the percentage of copper remove decreases. At both end of the extreme pH conditions, the percentage of copper is below 10%.

Also, surface plot provides a three-dimensional view that may provide a clearer picture of the response surface. Fig. 11 surface plot of conc. Cu^{2+} (ppm) vs Temp. (^{O}C) and pH. It can deduce that the percentage of copper remove shown the highest when the pH of the medium 5, temperature 30 ^{O}C and initial concentration 20 ppm the optimum conditions for the remove.

CONCLUSION:-

The salient features of the findings were outlined

- GTTH had proved to be an efficient for the removal of Cu^{2+} from aqueous solution with low concentration.
- Effect of pH on copper remove onto (GTTH) shows the rate of copper remove was maximum at pH 5.
- The rate of copper remove was maximum at an optimum temperature 30^{0}C.
- 20 ppm initial copper concentration, GTTH has been found to have better removal efficiency, while increase in the concentration of the copper in the medium, the decreases which owes to the toxic GTTH.
- MINITAB 16 - software was used to optimize the parameters to remove the copper using the Taguchi method of optimization.

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NOMENCLATURE

Symbol	**Description**	**Units**
C_e	Equilibrium concentration	mg/g
C_o	Initial solute concentration	mg/l
E	Removal percentage of copper	

HCL	Hydrochloric Acid	
n	Number of experiments	
N	Error	
PPM	Parts Per Million	
q_e	Uptake capacity	mg/g
S	Mean standard deviations	
S/N	Signal-To-Noise Ratio	
σ	Standard deviations	
V_L	Initial Volume of solution	ml
W_o	Mass of granule	g
Y	Observed data	

Figure 1. Whole plant of Tribulus terrestris Chhatre, et al., 2014.

Figure 2. Flowers of Tribulus terrestris plant.

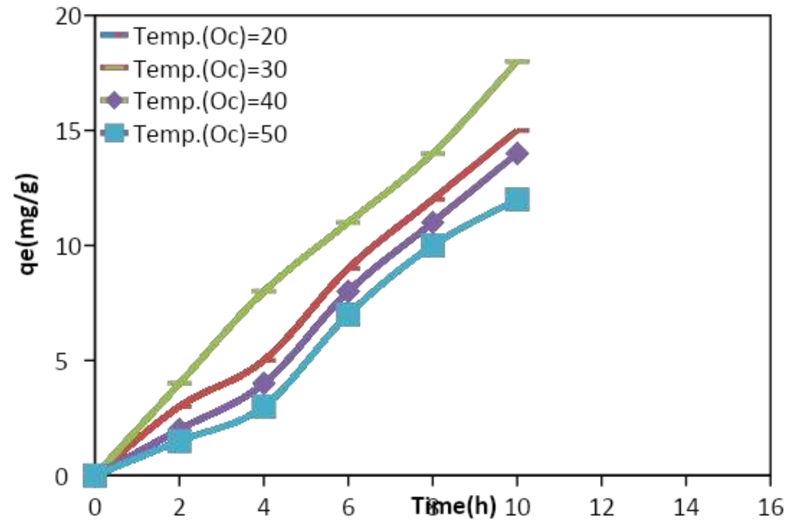

Figure 3. Effect of temperature on Cu $^{2+}$ uptake capacity(GTTH)

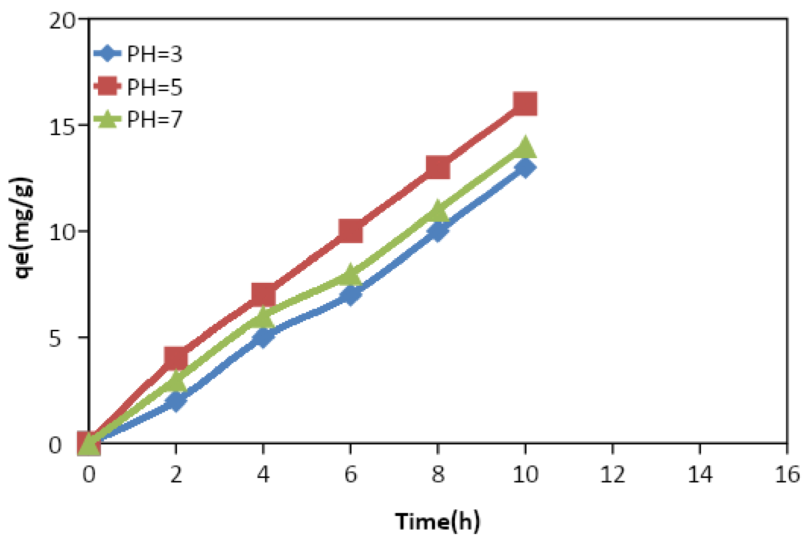

Figure 4. Effect of pH on Cu $^{2+}$ uptake capacity(GTTH).

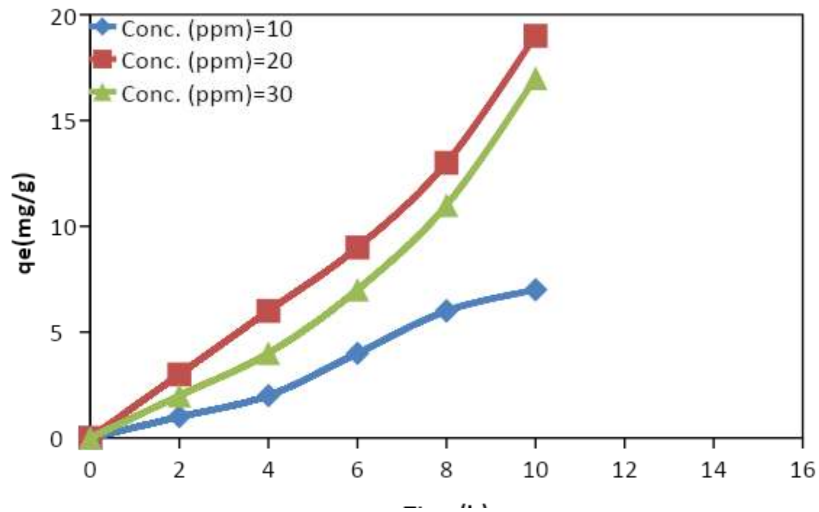

Figure 5. Effect of initial concentration on Cu^{2+} uptake capacity(GTTH).

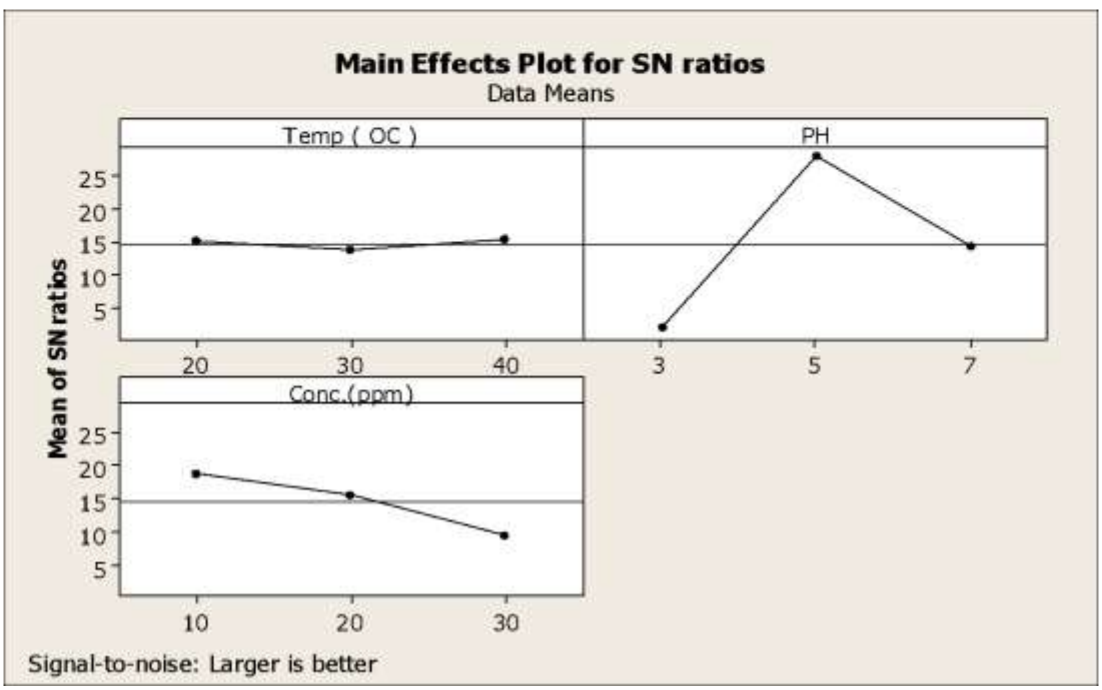

Figure 6. Main effect plots of process parameters vs S/N ratio.

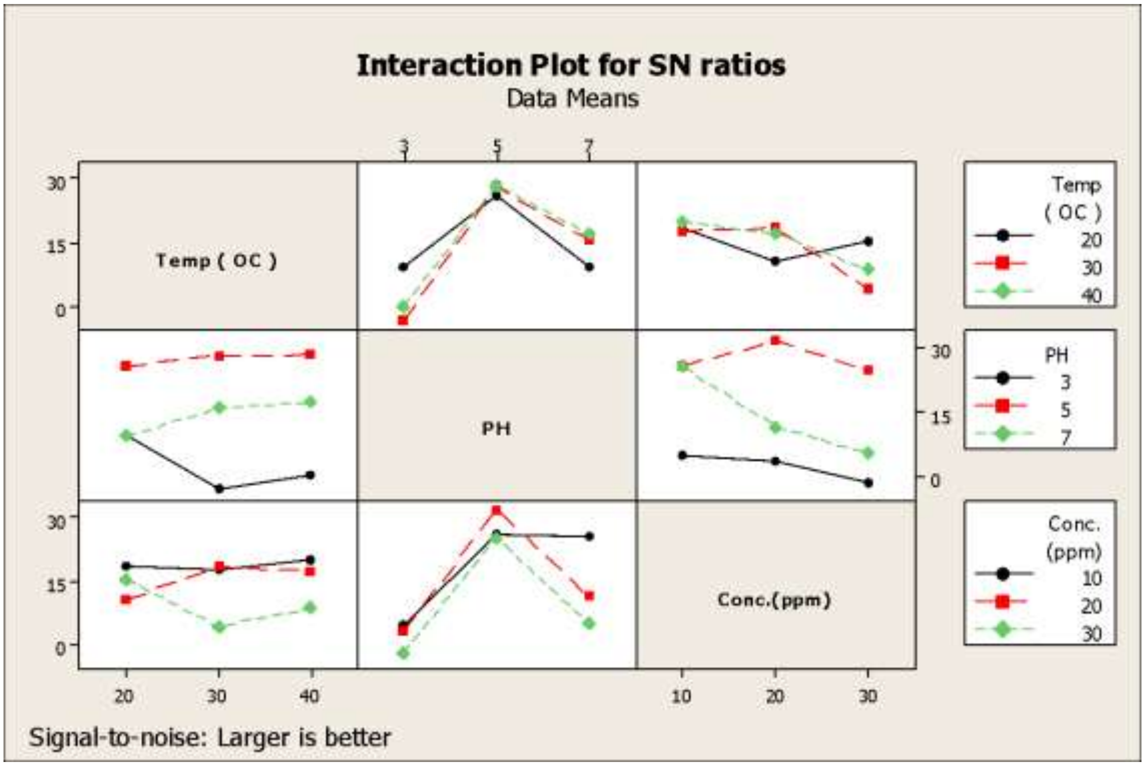

Figure 7. Interaction plots for SN ratio vs different parameters responsible.

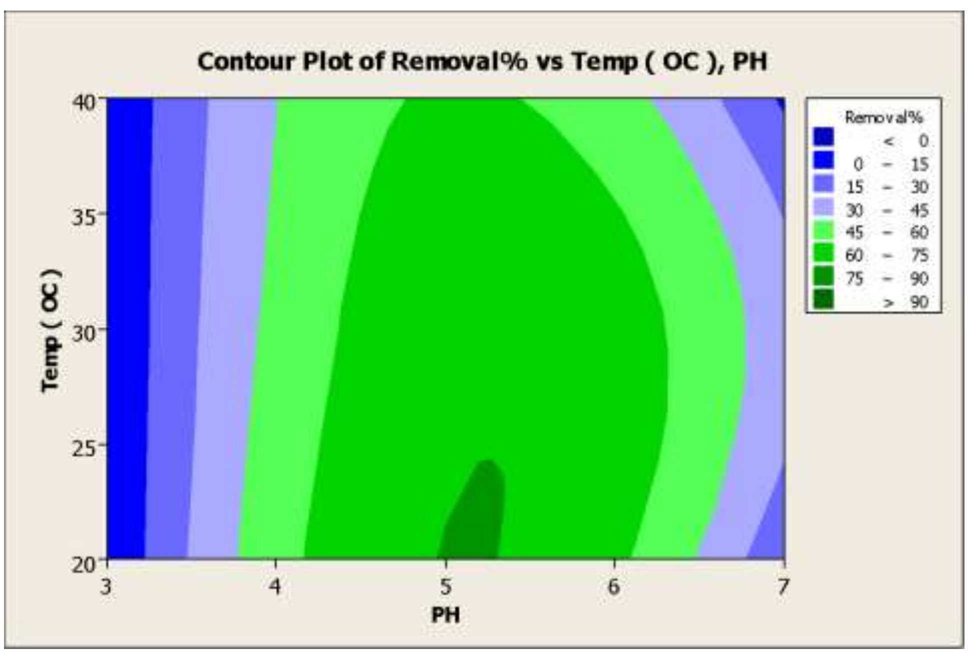

Figure 8. Counter plots between removal Cu^{2+} % vs temperature and pH.

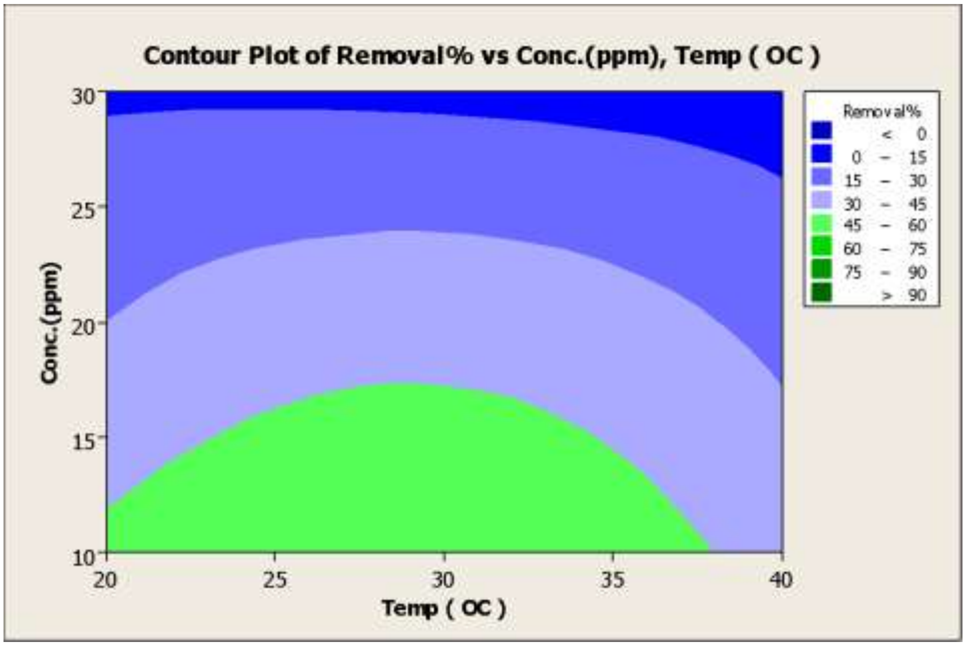

Figure 9. Counter plots between removal Cu^{2+} % vs concentration and temperature.

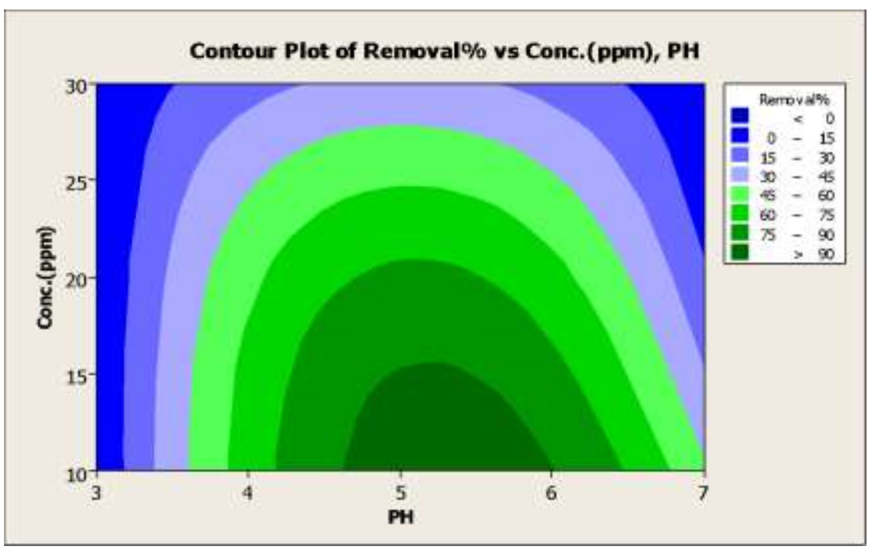

Figure 10. Counter plots between removal Cu^{2+} % vs concentration and pH.

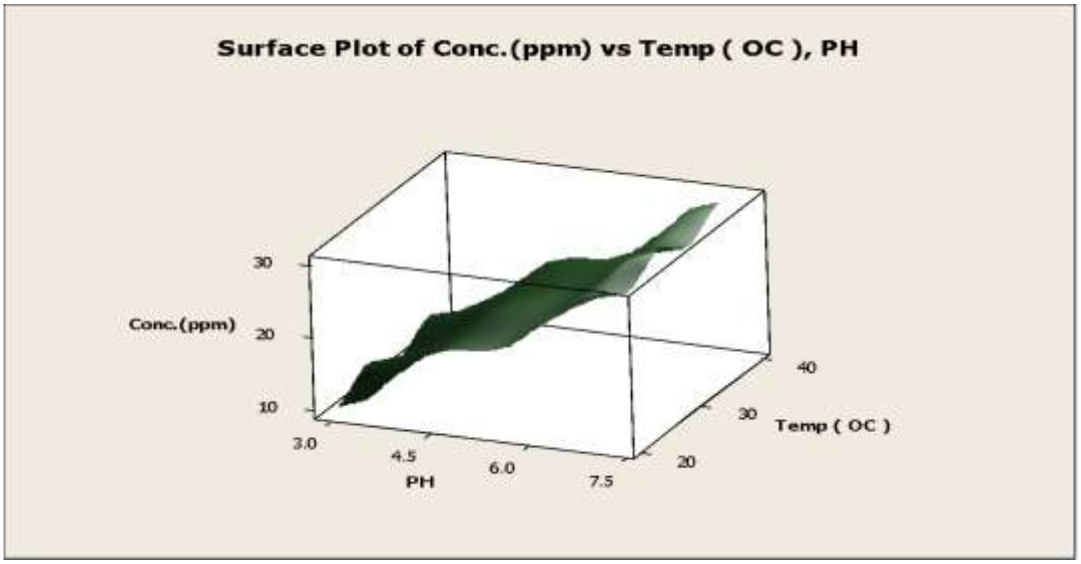

Figure 11. Surface plot of concentration vs temperature and pH.

TABLE 1: **Physical and chemical properties of GTTH.**

Physical properties	**GTTH**
Actual density, kg/m^3	1531
Apparent density, kg/m^3	625
Particle porosity	0.47
Bed porosity	0.45
Average particle diameter, mm	0. 380
Pore volume, cm^3/g	0.44
Chemical properties	
pH	7.85
Ash content, (%)	12

TABLE 2: Orthogonal array for the L_{27} Taguchi design.

Temp.(^{0}C)	**pH**	**Conc. (ppm)**
20	**3**	**10**
20	**3**	**20**
20	**3**	**30**
20	**5**	**10**
20	**5**	**20**
20	**5**	**30**
20	**7**	**10**
20	**7**	**20**
20	**7**	**30**

30	**3**	**10**
30	**3**	**20**
30	**3**	**30**
30	**5**	**10**
30	**5**	**20**
30	**5**	**30**
30	**7**	**10**
30	**7**	**20**
30	**7**	**30**
40	**3**	**10**
40	**3**	**20**
40	**3**	**30**
40	**5**	**10**
40	**5**	**20**
40	**5**	**30**
40	**7**	**10**
40	**7**	**20**
40	**7**	**30**

Table 3. Response table for single to noise ratio value for different experiment parameters using Taguchi design (Larger is better)

Level	**Temp. (^{O}C)**	**pH**
1	14.977	1.945
2	13.607	27.774
3	15.340	14.205
Delta	1.733	25.830
Rank	2	1