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EXPERIMENTAL OPTIMIZATION FOR CU REMOVAL FROM AQUEOUS SOLUTION USING NEEM LEAVES BASED ON TAGUCHI METHOD

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Abstract: This research focuses on understanding biosorption process and developing a cost effective technology for treatement of heavy metals-contaminated domastic water. A new biosorbent has been prepared by crushing of neem leaves. The experiments were designed according to Taguchi's (L16) orthogonal array to optimize experimental runs. In order to assess the biosorption behavior of neem leaves satisfying multiple performance measure, Taguchi approach has been adopted. The biosorption tests were carriedout using Avanta Flame atomic Absorption Spectroscopy (AAS) apparatus with five process parameters, pH values, initial Cu concentration, contact time, leaf particle size and agitation rate. Analysis of variance was applied to determine the significant parameters that effect biosorption. The results indicated thast the % of metal removal was influenced primarily by pH value (80.68%), the initial Cu ion concentration (7.74%), and contact time (5.50 %) and both agitation and particle size have little significant influence on % of material removal rate.
Keywords: Cu ions, AAS, Taguchi, ANOVA, metal removal rate.

1. Introduction

In modern world, man's activities through industrialization, urbanization, technological development and agricultural activities discharge heavy metals into the environment; water, land and air which has become a matter of concern over the past few decades, due to the characteristics of metals to cause objectionable effects by impairing welfare and reducing the quality of life in the environment [1]. The presence of metal ions in the environment is detrimental to many living species [2]. The removal of heavy metals is very important because they are non-biodegradable. In other hand, agricultural residues seem to be preferred [3,4] and the green coconut shell s are a most appropriate example for the bio-sorption removal of dissolved metals [5] and organics [6]. The majority of adsorption studies have been carried out

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in the batch mode [7] but a continuous system should be economically most valuable for waste water treatment [8].

The elucidation of the interaction that governs metal uptake by bio-sorbents (e.g.coconut shells) constituted principally by lignin and cellulose as major constituents and functional groups such as alcohol, ketone and carboxylic groups involve in the ion exchange or complexation reactions with metallic cations. However, much of the attention in bio-sorption studies has concentrated on the removal of heavy metals form the waste water. In any process, the desired testing parameters are either determined based on experience or by the use of handbook. It, however, does not provide optimal test design parameters for a particular situation. Thus several mathematical models based on statistical regression techniques have been constructed to select the proper testing conditions [9-10]. The number of runs required for full factorial design increases geometrically. Fractional factorial design method is an efficient and significantly reduces the time. However, the fractional design might not contain the best design parameters. The Taguchi's design can further simplify by expending the application of the traditional experimental designs to the use of orthogonal array. This method is a simple, efficient and systematic approach to optimize designs for performance, quality and cost. The Taguchi method has led to limited number of applications in a worldwide range of industries [11]. The objective of the present study focused on adsorption of Cu metallic ions in aqueous solution using eucalyptus, neem and mango leaves based on the Taguchi method under various testing conditions. Furthermore, the analysis of variances was employed to investigate the optimum test parameters for better % or removal rate.

2. Experimental Details

2.1 Preparation of adsorbent

In this study the forest wastes such as eucalyptus, neem and magno leaves were selected as adsorbent for removal of Cu ion. Mature leaves were collected and washed thoroughly under running water to remove dust and any adhering particles. The leaves were then dried under sunlight for a few days and then in oven at 80 ºC until it became crisp. The dried leaves were crushed and blended to powder form using a blender. The powdered material was sieved through a different mesh size to obtain fine biomass. The finely sieved biomass was treated with 0.3 M

HNO_3 solution for 24 h, followed by washing with deionizer water until pH of 7.2 was achieved and oven dried at 60°C with constant mixing. The prepared biomass was stored in desiccators.

2.2 Metal salts used and preparation of stock solution of Cu metal ions

Present study was focused cupper ion was used as the adsorbate. A 100 mg/L Cu stock solution was prepared by dissolving accurately weight amount of copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) in double distilled water. Appropriate dilution of the stock solution was carried out in order to obtain the desired concentration of Cu solution used later in the experiment. The solutions were prepared using a standard flask. The range of concentrations used was prepared by serial dilution of the stock solution with deionized water.

2.3 Batch sorption experiment

Batch experiments were carried out at room temperature using a conical flask by shaking a mixture of 0.1 g of prepared leaves powder and 20 mL of Cu solution in a centrifuge tube, at agitation rate of 150 rpm for allowing sufficient time for adsorption equilibrium. All samples were carried out in duplicate under the same conditions and the average results were taken. After agitation, the powder was removed by filtration using filter paper. The concentration of Cu in the filtrates as well as in the control samples were determined by using GBC Avanta Flame atomic Absorption Spectroscopy (AAS). Percentage removal of metal ions can also be computed using the following equation:

$$\%R = \frac{c_o - c_e}{c_o} X100 \qquad \text{Eq. 1}$$

Where Co =Initial concentration of Cu (mg/L), Ce = Concentration of Cu at equilibrium state (mg/L) The selected experimental design parameters are as given in Table1.

Table 1: Selected experimental parameters and their assigned levels

Symbol	Factors	Unit	Levels			
			1	2	3	4
A	pH		3	5	7	9
B	Initial Cu concentration	Mg/L	5	10	15	20
C	Contact time	Min	10	20	40	80

D	Particle size	μm	75	175	375	750
E	Agitation rate	Rpm	50	100	150	200

Table 1 shows five factors and four levels used in the experiment. If four levels were assigned to each of these factors and a factorial experimental design was employed using each of these values, number of permutations would be 625. The fractional factorial design reduced the number of experiments to sixteen. The pH value (A), initial Cu concentration (B), contact time (C), particle size (D) and Agitation rate (E) were assigned to the 1st, 2nd, 3rd 4th and 5th column of L16 array respectively. The orthogonal array of L16 type was used and is represented in Table 2. This design requires sixteen experiments with four parameters at each of these four levels. The interaction between main factors was neglected. The S/N ratios were computed for wear rate in each of the 16 trial conditions and their values are as given in Table 2.

Table 2: Experimental data and sample statistics for Neem leaves

Ex. No.	Main factors					% of Removal of Cu ions			Average wear rate	Standard Deviation	S/N ratio (db)
	A	B	C	D	E	1	2	3			
1	1	1	1	1	1	84.85	80.84	82.53	82.74	2.013	32.28
2	1	2	2	2	2	80.39	79.58	80.45	80.14	0.486	44.35
3	1	3	3	3	3	77.62	76.56	77.86	77.34	0.692	40.97
4	1	4	4	4	4	62.22	61.01	62.05	61.76	0.655	39.49
5	2	1	2	3	4	97.38	96.4	97.03	96.93	0.497	45.81
6	2	2	1	4	3	96.90	95.2	96.22	96.11	0.856	41.01
7	2	3	4	1	2	91.88	90.52	91.74	91.38	0.748	41.74
8	2	4	3	2	1	91.08	89.52	90.44	90.35	0.784	41.23
9	3	1	3	4	2	98.74	97.47	98.52	98.24	0.679	43.21
10	3	2	4	3	1	99.11	98.04	98.93	98.69	0.573	44.72
11	3	3	1	2	4	97.3	95.76	96.56	96.54	0.770	41.96
12	3	4	2	1	3	99.14	98.59	99.10	98.94	0.307	50.17

13	4	1	4	2	3	98.06	96.89	97.47	97.47	0.585	44.43
14	4	2	3	1	4	96.55	95.35	95.75	95.88	0.611	43.91
15	4	3	2	4	1	98.11	97.38	97.87	97.79	0.372	48.39
16	4	4	1	3	2	94.64	93.78	94.56	94.33	0.475	45.96

3. Results and discussion

3.1 Fourier Transform Infrared (FTIR) Analysis

FTIR analysis was carried out in order to identify the different functional groups present in different leaves which were responsible for adsorption process. The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wave numbers as reported in literatures. Fig 1(a) shows the FTIR spectrum of leaves before adsorption. The broad and intense peak at 3448 cm^{-1} was attributed to the stretching of O-H group due to inter- and intramolecular hydrogen bonding of polymeric compounds such as alcohols or phenols as in pectin, hemicelluloses, cellulose and lignin. The peak observed at 2925 cm^{-1} was associated with the stretching vibrations of C-H bond of methyl, methylene and methoxy groups. The peaks around 1654 cm^{-1} corresponded to the C=C stretching which might be attributed to the presence of lignin aromatic bond. The intense peak at 1057 cm^{-1} corresponded to the C-O stretching of alcohol or carboxylic acid. The FTIR spectrum of neem leaves loaded with Cu ions was presented in Fig 1(b). It was observed that the peaks at 3438, 2925, 1654, and 1057 cm^{-1}.

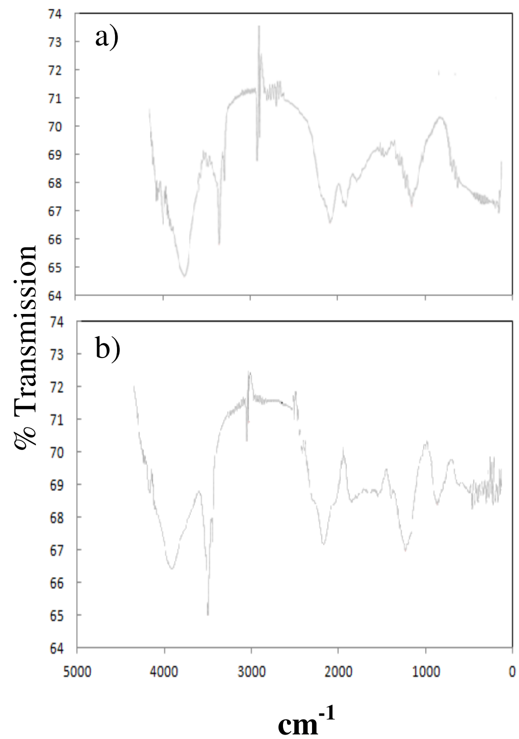

Fig 1: FTIR spectrum of Neem leaves a) without loaded and b) loaded with Cu ions

3.2 Taguchi's analysis of % of metal removal

Sixteen different set of experiments were performed using the design parameter combinations in the specified orthogonal array table. Three specimens were fabricated for each of the parameter combinations. The completed response table for these data appears in Table 2. In order to estimate the effect of factor A (pH of the solution) on the average value of response variable, were average together three observed response at level 1 of factor A. Then the sum was divided by 4 to obtain the average response at level 1 of factor A. The average responses at level 2, 3 and 4 were obtained in the similar manner. The estimated effects are presented graphically in Fig. 1 and shown in Table 3.

Table 3: Estimated individual factors effect on % of removal of Cu ions from aqueous solution by Neem leaves

	1	2	3	4	Optimum level
pH value (A)	75.78	93.69	98.16	97.96	pH = 7
Initial Cu Concentration (B)	93.93	92.72	90.89	86.61	Initial con. = 5 mg/L
Contact time (C)	93.28	93.57	90.44	87.50	Contact time = 20 min
Particle size (D)	92.37	91.14	92.01	88.64	Particle size = 75 µm
Agitation rate (E)	92.50	91.25	92.60	87.74	Agitation rate=150 rpm

The estimated individual factors effect on % of removal of Cu ions form aqueous solution is shown in Fig. 1. The range of average responses at Table 2, over the four levels of each experimental factor, is: for pH value (A), 7, for initial Cu concentration (B), 5 mg/L, for contact time (C), 20 min, for particle average size (D), 75 µm and for agitation rate (E), 150 rpm. In particular, factor A (3), factor B (1), factor C(2), factor D(1) and factor E (3) for maximize the % of metal removal combinations.

Table 3 suggests that the optimum condition for the maximum % of Cu removal is the combination of A3B1C2D1E3 levels of the respective control factors. It is evident from Fig. 1 that pH (factor a) has the greatest increasing effect on the % of removal rate.

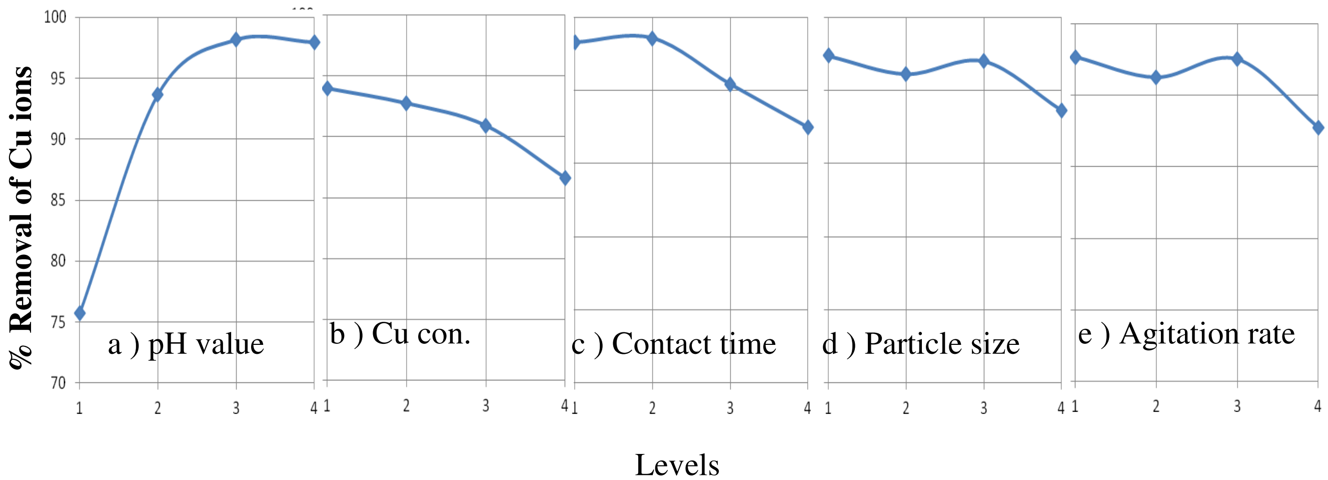

Fig. 1: Estimated individual factors effect on % of removal of Cu ions from aqueous solution by neem leaves

Fig. 1(a) shows the effects of pH on the adsorption of Cu by neem leaves. The pH of the aqueous solution is an important operational parameter governing the adsorption process of metal ions in solution. This is because it affects the solubility of the metal ions concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of adsorbate during reaction [12]. At the range of pH 7 to 9 the % removal became consistent, ranging between 95 to 98.7 %. The low adsorption of metal ions for lower pH was due to high concentration and high mobility of H+ ions, which competed with metal ions for the adsorption sites, hindering the adsorption of metal ions by adsorbent. Protonated adsorption sites were incapable of binding metal ions due to electrostatic repulsion between positively charged metal ions and positive charged sites. Hence, only low percentage of Cu ions was adsorbed at pH value 3. As the pH increased, there were fewer H+ ions present in the solution and consequently more negatively charged sites were made available and this facilitated greater metal ions removed by electrostatic attraction.

The impact of adsorbent dose on the adsorption of Cu in shown is Fig. 1(b). The results showed that the % of removal Cu ions decreased from 94.36% to 82 % with the increment of initial Cu ions concentration from 5 mg/L to 20 mg/L for neem leaves. According to SenthilKumar *et al.*[13], at lower metal ions concentration, the percentage removal was higher due to larger surface area of adsorbent being available for adsorption. When the concentration of Cu ions became higher, the percentage removal decreased since the available sites for adsorption became less due to saturation of adsorption sites.

The Fig. 1 (c) shows the effect of contact time on sorption of Cu ions by neem. This result revealed that adsorption of Cu was fast and the equilibrium was achieved after 20 min of contact time. The fast initial % removal occurred in the early stage of adsorption was due to the fact that most of the binding sites on leaves were free which allowed quick binding of Cu ions on the biomass [14]. As the binding sites became exhausted, the uptake rate slowed down due to competition for decreasing availability of actives sites by metal ions. According to the test results, agitation time was fixed at 20 minutes for the rest of the batch experiment to ensure equilibrium was achieved. The plots of metal removal as a function of time are single, smooth, and continuous, suggesting the possibility of the formation of monolayer coverage of Cu ions at the outer surface of adsorbent.

The particle size of adsorbents is one of important factors affecting the adsorption capacity as it influences the surface area of adsorbent. The lower the particle size higher the surface area hence it absorbs more metal ions. Fig. 1(d) shows the variation of Cu removal rate as a function of particle size. The results indicated that the metal ions uptake increased with decreasing particle size. The higher % of removal with decreasing particle size was attributed to the fact that smaller particles had larger external surface area compared to larger particles, hence more binding sites were exposed on the surface and thus, leading to higher adsorption capacity since adsorption is a surface process. Apart from that, particles with smaller size also moved faster in the solution compared to larger particles, consequently, the adsorption rate was faster.

Fig. 1(d) shows the variation of Cu ions % of removal with agitation rate for different leaves. It was observed that the percentage uptake increased when the agitation rate was increased while after 150 rpm it decreased. This was because increasing the agitation rate reduced the boundary layer resistance to mass transfer surrounding the sorbent particles, resulting in higher sorption rate. In addition to that, higher agitation rate also spread the Cu ions in the solution, providing better access to the active sites on adsorbent surface.

3.3 Implementation of ANOVA

Table 4 shows the process parameters (factors) that were chosen for the % of metal ion removal from aqueous solution by neem leaves. Four levels were specified for each parameter. Table 4 shows the ANOVA for % of metal ion removal rate.

Table 4: Summary ANOVA Table for % of Cu metal removal rate by neem leaves

Factors		**A**	**B**	**C**	**D**	**E**	**Total**
	1	303.1	375.7	370.6	369.5	370.0	
	2	374.8	370.9	374.3	364.5	365.0	1456.6
Sum at factor level	3	392.6	363.6	361.7	368.0	370.7	
	4	386.1	346.5	350.0	354.6	351.0	
Sum of squares of differences	SS	20532	1970	1398	542	1005	25447
Degree of freedom	3	3	3	3	3	3	15
% contribution	% C	80.68	7.74	5.50	2.13	3.95	
	Level	03	01	02	01	03	
	Factors	A3	B1	C2	D1	E3	
Optimum level	Value	07	5 mg/L	20 min	75µm	150 rpm	

From Table 2 the values of sum at factor level, sum of squares of differences and % contribution are found as shown in Table 4, and it can be seen that the third level of factor (A) give the highest summation (i.e. A3, which is 7 pH value solution). The highest summation for factor (B) is at the first level (i.e. B1, which is initial concentration of Cu ions of 5 mg/L), the highest summation for factor (C) is at the second level (i.e. C2, which is 20 min contact time, the highest factor for factor (D) is one first level, which is 75 µm particle size of neem leaf powder, and the highest summation for factor (E) is at the third level (i.e. E3, which is 150 rpm of agitation rate. These results have proved the success of Taguchi method in the prediction of the optimum parameters for higher % of Cu ion removal rate. Examination of the calculated contribution for all control factors also shows a very high influence of factor A and low influence of factor D on the % of Cu ion removal rate shown in Table 4. The optimum test conditions were estimated from the significant factors. Thus, based on the level of % of contribution only A (80.68 %) were significant while the factors followed by B (7.74%), C (5.50 %), E (3.95%) and D (2.13%) were less confidence as shown in Fig. 2.

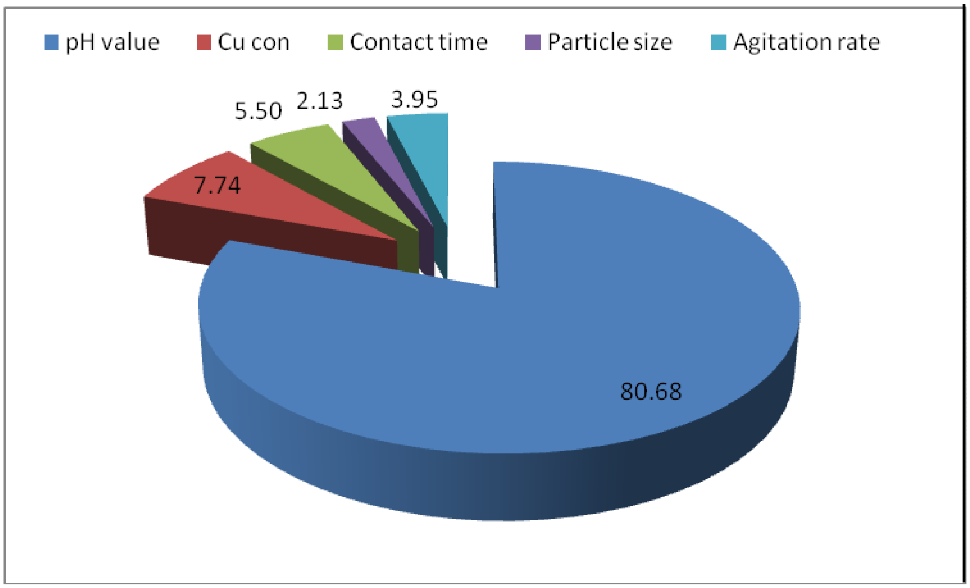

Fig. 2: Shows the contribution of parameters on % of Cu ion removal from aqueous solution by neem leaves.

4. Conclusion

The Taguchi and ANOVA methods were applied to investigate the effects of pH value of aqueous solution, initial Cu ion concentration, contact time, neem leaf powder particle size and agitation rate on % of Cu metal ion removal by neem leaf powder. The conclusions drawn from this work

- The pH value of aqueous solution is the major parameter for % of Cu ion metal removal rate, its contribution 80.68 %. The neutral aqueous solution is most suitable for higher efficiency of metal ion removal from water.
- The % of metal removal was influenced primarily by pH value (80.68%), the initial Cu ion concentration (7.74%), and contact time (5.50 %) and both agitation and particle size have little significant influence on % of material removal rate.
- The optimum test condition, at which the lowest rate is obtained, has been determined to be A3B1C2D1E3 levels

- Finally it was observed that neem leaves can be used as an alternative low const adsorbent for Cu ion remediation for polluted water / waste water.

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