Taguchi's Optimizing Technology for Removal of As(III) from Aqueous Solution by Khangar

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Khangar has been used for the removal of As(III) ions from aqueous solution by adsorption process. Taguchi optimization method was used for optimization of process parameters like pH, adsorbent dose, metal ion concentration and contact time. L_{16} orthogonal array was used in designing the experiments. Statistical tools *viz.* signal to noise ratio and analysis of variance have been used at 95 % confidence level for all considered parameters. pH was found to be the most important parameter for removal of As(III) from aqueous solution. The optimum results were obtained at pH 7; adsorbent dose 0.7 g/50 mL; metal ion concentration 20 mg/L and contact time 120 min. SEM and FTIR studies of khangar before and after As(III) adsorption were made in order to understand the nature of adsorption. Comparison of adsorption on different adsorbents has also been included in the manuscript.

Keywords: As(III), Khangar, Optimization, Taguchi's method, SEM, FTIR.

INTRODUCTION

The heavy metals discharged by the industries are accumulated in natural resources and interfere the metabolism of the human body and ecosystem [1,2]. Arsenic is one of the most toxic elements and it is a worldwide problem. In India, according to Central Pollution and Control Board (CPCB) and Minimal National Standards (MINAS) the permissible limit of arsenic is 0.5mg/L for the discharge of industrial effluents [3]. Arsenic(III) is known to cause various health problems [4,5]. Many methods such as membrane filtration, coagulation, electro dialysis and adsorption have been used to remove toxic elements from aqueous solutions. In recent years adsorption method has attracted interest in wastewater treatment process and the most commonly used adsorbent is activated carbon [6-8]. In this study, we used khangar as adsorbent for the removal of As(III) ions from the aqueous solution of sodium arsenite. Adsorption studies have been made and optimum conditions for As(III) removal have been found out by batch adsorption method as well as by Taguchi's method. In the analysis of results powerful statistical tools; S/N ratio, ANOVA with F-test, have been used to obtain significant results [9].

EXPERIMENTAL

Carbon waste (khangar) obtained from thermal power plant (UP), India was used as an adsorbent. The collected material was washed with deionized water and then air dried for several days. It was oven dried at 110 °C for 2 h. The dried khangar was crushed in a mechanical grinder and sieved through 350 μm mesh sieve to obtain fine powder [10]. A stock solution of sodium arsenite (1000 mg/L) for determination of As(III) ions was prepared in double distilled water.

Characterization of adsorbent (khangar): FTIR spectra of khangar before and after adsorption of As(III) were recorded in KBr phase in the wavelength range 4000-400 cm^{-1}. SEM pictures of khangar before and after As(III) adsorption were recorded.

Adsorption study: Adsorption experiments of As(III) over khangar were performed at different pH (1-7), initial metal ion concentration (1.0-30 mg/L), time (60-150 min) and different amounts of adsorbent (0.1-0.7 g)/50 mL. 0.1 N HCl and 0.1 N NaOH were used to adjust the pH. The batch sorption was carried out in 250 mL iodine flask at room temperature by taking 50 mL of As(III) solution at 150 rpm. After a particular interval of time iodine flask was removed, solution was allowed to settle down and then filtered through Whatman filter paper No. 1. As(III) in the filtrate was estimated by atomic absorption spectrometer. Adsorption capacity and percent removal after adsorption were calculated by using eqns. 1 and 2 [11,12].

$$q_{eq} = \frac{(C_o - C_e)}{M} V \tag{1}$$

TABLE-1
TAGUCHI METHOD EXPERIMENTAL PARAMETERS AND THEIR LEVELS

Factors	Designation	Level 1	Level 2	Level 3	Level 4
pH	A	1	3	5	7
Adsorbent dose (g/50 mL)	B	0.1	0.3	0.5	0.7
Metal ion concentration (mg/L)	C	1	10	20	30
Interaction time (min)	D	60	90	120	150

$$\text{Removal (\%)} = \left(\frac{C_o - C_e}{C_e}\right) \times 100 \qquad (2)$$

where, q_{eq} is the equilibrium concentration, C_o is initial concentration of the metal ion, C_e is concentration of metal ion after adsorption, V is volume of the solution, M is mass of the adsorbent in g.

Taguchi's methodology of experimental design: Taguchi's method used orthogonal array for laying out experiments. Number of process parameters and their levels were used to select the array [13-15]. For this experiment, four process parameters such as pH, adsorbent dose, metal ion concentration and contact time with four levels were chosen (Table-1). In this experiment L_{16} array was chosen, which provided the interactions of process parameters and their levels (Table-2). Experiments were conducted as per the combinations shown in the Table-2. For each interaction, a batch of three samples were made and the percent removal of As(III) after adsorption was calculated by eqn. 2. The collected data was analyzed for mean response and Signal to Noise ratio (S/N) with higher characteristics. Analysis of variance, ANOVA was applied to data to determine the importance of each factor on the arsenic adsorption capacity of khangar.

TABLE-2
EXPERIMENTATION DATA OF ORTHOGONAL ARRAY L_{16}

S. No.	Operating factors and their levels				Removal (%)
	A	B	C	D	
1	1	0.1	30	60	59.46
2	1	0.3	20	90	62.96
3	1	0.5	10	120	65.66
4	1	0.7	1	150	65.08
5	3	0.1	10	120	67.74
6	3	0.3	1	150	68.48
7	3	0.5	30	60	70.84
8	3	0.7	20	90	72.81
9	5	0.1	20	150	75.18
10	5	0.3	30	120	76.95
11	5	0.5	1	90	77.14
12	5	0.7	10	60	77.58
13	7	0.1	30	90	81.89
14	7	0.3	1	60	83.78
15	7	0.5	10	150	85.57
16	7	0.7	20	120	86.12

A = pH, B = adsorbent dose, C = initial metal ion concentration, D = contact time.

RESULTS AND DISCUSSION

Characterization of adsorbent: The FTIR spectrum of khangar [Fig. 1(a)] shows a broad vibrational band at 3420.18 cm^{-1} indicating the presence of bound OH group, which could be due to adsorption of moisture on the surface of khangar. Band at about 2900 cm^{-1} is due to CH stretching modes. A strong band at 1091.09 cm^{-1} may be due to =C=O stretching vibrations. Fig. 1(b) shows the FTIR spectra of khangar after adsorption of As(III). Two new intense bands at 3130.05 cm^{-1} and 1400.64 cm^{-1} are seen [10]. The bands indicate some sort of interaction of As(III) on the surface of khangar. SEM of khangar before adsorption (Fig. 2) shows flaky morphology which on adsorption (Fig. 3) became completely compact. This indicates that khangar before adsorption was porous and when it adsorbs As(III), the pores are filled and the morphology is changed.

Effect of process parameters on adsorption: Percentage removal of As(III) ion was determined by eqn. 2 and the values are given in Table-2. Effect of pH on arsenic removal for khangar is shown in Figs. 4 and 5. Adsorption increased with the increase of pH and was almost maximum at pH = 7. The arsenic exists into two forms, As(V) (arsenate) and As(III) (arsenite) but mostly as arsenate (AsO_4^{3-}). This in neutral medium is reduced in the following way [16].

$$AsO_4^{3-} + 2H_2O + 2e^- \rightleftharpoons AsO_2^- + 4OH^- \qquad (3)$$

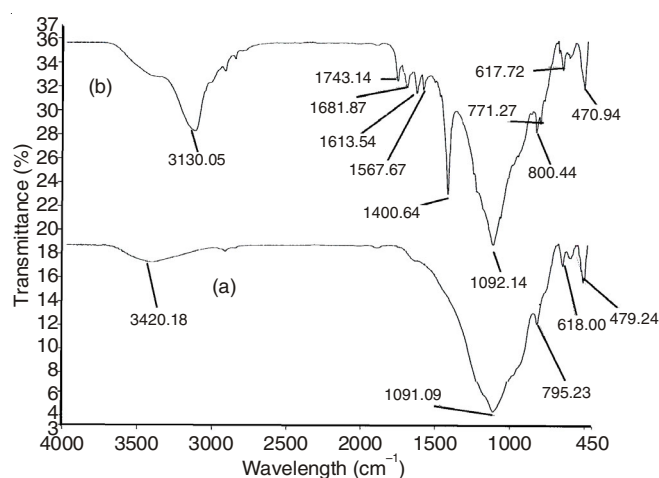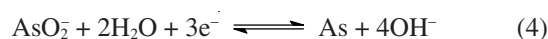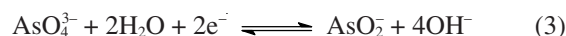$$AsO_2^- + 2H_2O + 3e^- \rightleftharpoons As + 4OH^- \qquad (4)$$

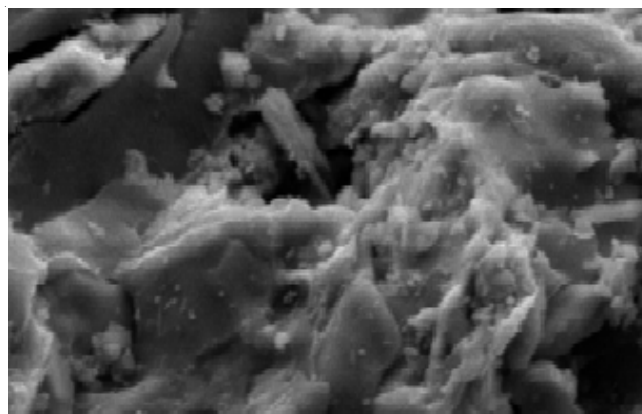Fig. 1. FTIR spectra of khangar (a) before and (b) after adsorption

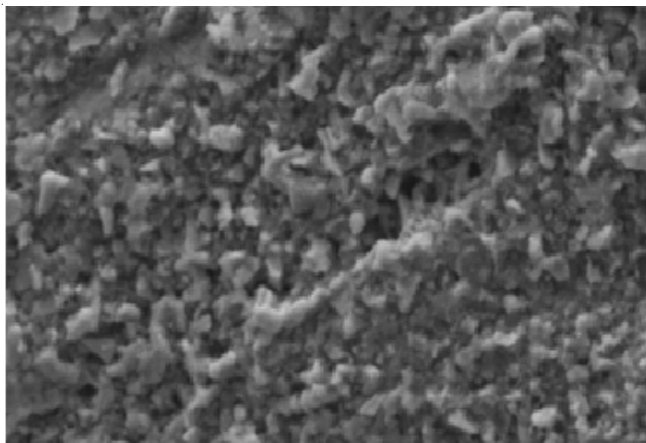Fig. 2. SEM of khangar before adsorption
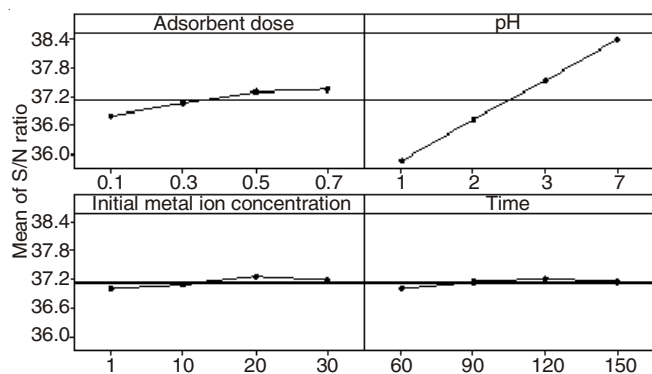
Fig. 3. SEM of khangar after adsorption

Fig. 4. Variation of S/N ratio with pH, adsorbent dose, initial metal ion concentration and time
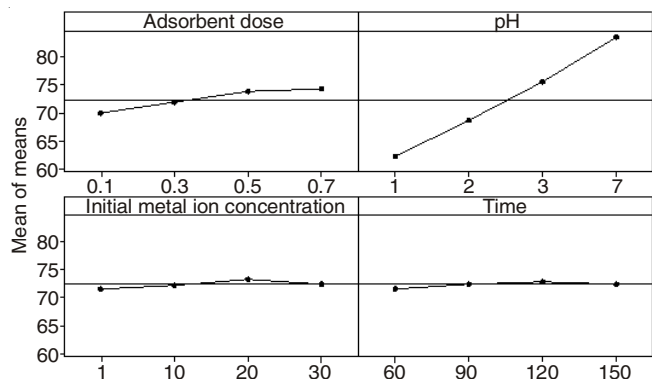

Fig. 5. Variation of means of means with pH, adsorbent dose, initial metal ion concentration and time

The removal of As(III) was conducted with respect to adsorbent dose in the range 0.1 to 0.7 g/50 mL. The results showed that the rate of adsorption of As(III) ions increased when mass of the adsorbents increased from 0.1 to 0.7 g/50 mL. The graphs shown in Figs. 4 and 5 also revealed the similar results [17].

Experiments were conducted with initial metal ion concentration ranging from 1 to 30 mg/L. Figs. 4 and 5 clearly shows that the metal ion adsorption firstly increased with the increase in concentration, but after 20 mg/L concentration it became constant and then decreased as adsorption sites get blocked by the metal ions already present in the solution, so there is no effect of increased concentration on maximum removal of As(III) ions [8].

Adsorption isotherm: Langmuir adsorption isotherm was allowed to fit the data and is expressed as:

$$1/Q_e = 1/Q_0 + 1/Q_0.b.C_e \qquad (5)$$

where C_e is the equilibrium concentration (mg/L), Q_e the amount of Cu(II) ions adsorbed at equilibrium (mg/g), Q_0 is the maximum adsorption capacity (mg/g), b is constant (L mg^{-1}) [18]. A plot of $1/Q_e$ *versus* $1/C_e$ gives straight line (Fig. 6). The values of correlation coefficient (R^2) and adsorption capacity are 0.988 and 7.35 mg/g, respectively. To investigate the favourability of a process, the dimensionless separation factor R_L was calculated from eqn. 6 [19].

$$R_L = 1/(1 + bC_o) \qquad (6)$$

where b is Langmuir constant and C_o is optimum initial concentration of As(III). The values of R_L is 0.892 indicating that adsorption of As(III) on khangar is favourable.
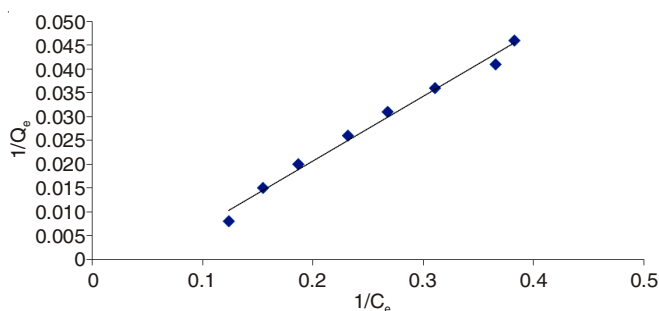

Fig. 6. Langmuir isotherm for removal of As(III) using khangar

Statistical analysis of Taguchi method experiment: The results of Taguchi method experiment are given in Table-2. Table-2 gives optimum values as pH 7, adsorbent dose 0.7 g/ 50 mL, initial As(III) concentration 20 mg/L and contact time 120 min. Under this condition, the percent removal can reach 86.12 %. MINITAB-15 software [20] was used to calculate S/N ratio and mean response of percent removal of As(III) from the effluent. The value of S/N ratio was calculated by using eqn. 7.

$$\left(\frac{S}{N}\right)_{HB} = -10\log\left(1/R\sum\nolimits_{j=1}^{R} 1\Big/Y_j^2\right) \qquad (7)$$

Response of various parameters on percentage removal of As(III) ions (Table-3) clearly shows that the maximum efficiency for removal of As(III) is at pH 7-level 4, adsorbent dose 0.7 g/50 mL-level 4, initial metal ion concentration 20 mg/L-level 3 and contact time 120 min-level 3. The optimum removal efficiency of 86 % is found (Table-2). The S/N ratio also suggests the same levels for the optimum adsorption of the As(III) ions. ANOVA for S/N ratios are given in Table-4. The sum of squared deviation for pH parameter is 987.68 for percent removal and its percentage contribution is 94.61 % (Table-5). The percentage contributions of adsorbent dose, initial metal ion concentration and contact time are 4.42, 0.55 and 0.035 respectively. The study showed that in the removal of As(III) from the solution, pH has the maximum contribution. Coefficient of determination (R^2) from the model is 1.000 whereas the adjacent R^2 value comes to be 0.999. The result shows high correlation between observed and predicted value.

TABLE-3
EFFECT OF VARIOUS FACTORS ON S/N RATIO AND AVERAGE RESPONSE

Levels of parameters	S/N ratio				For mean			
	A	B	C	D	A	B	C	D
1	36.85	37.83	38.11	37.05	63.17	70.26	72.22	72.46
2	37.72	38.08	38.17	37.17	69.12	72.14	73.16	73.84
3	38.56	38.31	38.36	37.3	76.82	74.23	74.42	74.75
4	39.42	38.37	38.26	37.6	84.59	75.30	73.82	74.23
Delta	2.55	0.55	0.25	0.18	21.38	4.64	1.98	1.39
Rank	1	2	3	4	1	2	3	4

A = pH, B = Adsorbent dose, C = Initial metal ion concentration, D = Contact time

TABLE-4
ANOVA FOR S/N RATIO FOR VARIOUS PARAMETERS AT LEVELS WHERE MAXIMUM REMOVAL OCCURS

Source	dof	SSD	F value	P	PC
A	3	19.235	4731.8	0	95.21
B	3	0.947	351.6	0	4.69
C	3	0.138	43.7	0.009	0.68
D	3	0.074	23.4	0.031	0.36
Residual error	3	0.004			
Total	15	20.198			

Significance level at 95 % confidence interval, dof = degree of freedom, SSD = sum of squares of deviations, F value = Fisher's value, P = probability value, A = pH, B = Adsorbent dose, C = Initial metal ion concentration, D = Contact time, PC = Contribution (%)

TABLE-5
ANOVA FOR MEAN (% REMOVAL) FOR VARIOUS PARAMETERS AT LEVELS WHERE MAXIMUM REMOVAL OCCURS

Source	dof	SSD	F value	P	PC
A	3	987.68	2971.84	0	94.61
B	3	46.19	139.65	0.002	4.42
C	3	5.84	16.89	0.025	0.55
D	3	3.74	11.08	0.043	0.035
Residual error	3	0.34			
Total	15	1043.79			

Significance level at 95 % confidence interval, dof = degree of freedom, SSD = sum of squares of deviations, F value = Fisher's value, P = probability value, A = pH, B = Adsorbent dose, C = Initial metal ion concentration, D = Contact time, PC = Contribution (%)

Optimum performance characteristics for removal of As(III) ions: Statistical ANOVA results shown in the Tables 4 and 5 clearly indicate that the process parameters significantly affect the process responses. The Fischer ratio (or F test) of the ANOVA is used to determine significant process factors. The F value for each process factor is ratio of mean of the squared deviations to the mean of the squared error. The significant parameters and their optimum levels have already been chosen as pH of the solution = 7, adsorbent dose = 0.7 g/50 mL, Initial metal ion concentration = 20 mg/L and contact time = 120 min. The estimated mean of percent removal characteristic can be computed in the following manner [20,21]:

$$\mu_{\%removal} = \overline{T} + (\overline{A} - \overline{T}) + (\overline{B} - \overline{T}) + (\overline{C} - \overline{T}) + (\overline{D} - \overline{T}) \quad (8)$$

where, $\overline{T}$ is the overall mean of the response = 73.57 and $\overline{A}$ is the average removal of metal ion concentration at level four of parameter pH of the solution = 84.59, $\overline{B}$ is the average removal of metal ion concentration at level four of parameter Adsorbent dose = 75.30, $\overline{C}$ is the average removal of metal ion concentration at level three of parameter. Initial metal ion concentration = 74.42 and $\overline{D}$ is the average removal of metal ion concentration at level three of parameter contact time = 74.75.

Hence, $\mu_{\%removal} = 88.87$ MPa

The confidence intervals CI_{pop} (confidence interval for population) and CI_{CE} (confidence interval for a sample group) for the predicted mean for the confirmation experiment can be calculated by following equations [15,22].

$$CI_{pop} = \sqrt{F_\alpha(1, f_e) V_e \left(\frac{1}{\eta_{eff}} \right)} \quad (9)$$

$$CI_{CE} = \sqrt{F_\alpha(1, f_e) V_e \left(\frac{1}{\eta_{eff}} + \frac{1}{R} \right)} \quad (10)$$

where, $F_\alpha(1, f_e)$ is variance ratio at the level of significance α (where, α = 95 %) and the confidence level is (1-α) against degree of freedom (DF) 1& error DF (f_e), V_e = Error variance (from ANOVA); and η_{eff} is calculated from eqn. 11:

$$\eta_{eff} = \frac{N}{1 + \text{Total DF involved in estimation of mean}} \quad (11)$$

where, N = Total number of results; R = Sample size for the confirmation experiment; By substituting values N: total no of results = 16 × 3 = 48; f_e = 3 and V_e = 0.11 (from Table-4); $F_{0.05}(1,3)$ = 10,1 (tabulated F-value) in equations 9 to 11. At 95 % confidence intervals CI_{pop} and CI_{CE} of the predicted ranges for adsorption of As(III) ions onto khangar are 88.05 < $\mu_{\% Removal}$ < 89.68 (CI_{CE}) and 88.32 < $\mu_{\% Removal}$ < 89.41 (CI_{pop}). In

TABLE-6
COMPARISON OF VARIOUS LOW COST ADSORBENTS FOR As(III) ADSORPTION

Adsorbent used	pH	Concentration (mg/L)	Temperature (°C)	Model used to calculate adsorption capacity	Adsorption capacity (mg/g)	Ref.
Olive pulp	7.2	5-20	25	Langmuir	1.393	[23]
Activated alumina	7.0	0.79-4.90	25	Langmuir	3.480	[24]
Nanoscale zero-valent iron	7.0	–	35	Langmuir	2.470	[25]
Iron oxide coated cement	~ 7.0	0.7-13.5	35	Langmuir	0.670	[26]
Activated red mud	7.2	2.5-30	25	Langmuir	0.663	[27]
Khangar	7.0	1-30	27	Langmuir	7.350	Present work

Taguchi method, confirmation experiment is the last step to verify the results, which we get from Taguchi's experiment approach. The experiment is conducted by setting all the process parameters at optimum level in a batch experiment and mean value obtained is 88.43. The average values obtained are compared with the predicted values. The results are in range of predicted values. This shows the successful optimization of experiment.

Comparison with other adsorbents: Several types of activated carbons were synthesized and used for the removal of arsenic from water and wastewater (Table-6). The adsorption capacities of these adsorbents were compared with khangar [23-27]. It was found that khangar adsorbs better than any other activated carbons listed in the table.

Conclusion

From the results, it is concluded that khangar can be used as an effective low cost adsorbent for the removal of trace amount of arsenic from aqueous solution. The optimized conditions for As(III) removal was : pH-7; adsorbent dose-0.7 g/50 mL; initial metal ion concentration 20 mg/L and contact time 120 min. The pH of the solution and the adsorbent dose were found significant parameters in the removal of As(III) ions while initial metal ion concentration and contact time have less contribution. It is also found that the experi-mental values are in the predicted range. Langmuir isotherm is best fitted to the data. Adsorption capacity of khangar for As(III) removal is higher than other adsorbents used for As(III) removal.

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