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Optimization of parameters for adsorption of metal ions onto rice husk ash using Taguchi's experimental design methodology

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Abstract

The present paper deals with optimization of various batch parameters for the simultaneous removal of cadmium (Cd(II)), nickel (Ni(II)) and zinc (Zn(II)) metal ions from aqueous solutions by rice husk ash (RHA) using Taguchi's optimization methodology. Various adsorption parameters such as initial metal concentration of each metal ion ($C_{0,i}$), temperature (T), initial pH (pH_0), adsorbent dosage (m) and contact time (t) were varied at three levels to see their effects on the total adsorption of metals onto RHA (q_{tot}). L_{27} orthogonal array (OA) has been used for experimental design, and the results have been analyzed using signal-to-noise (S/N) ratio and Pareto analysis of variance (ANOVA). The parameter m has been found to be the most significant parameter with 47.38 and 37.78% contribution to the q_{tot} and S/N ratio data. It is also observed that the interactions between $C_{0,i}$'s (i.e. $C_{0,Cd} \times C_{0,Ni}$, $C_{0,Cd} \times C_{0,Zn}$ and $C_{0,Ni} \times C_{0,Zn}$) contribute significantly to both raw and S/N ratio data for simultaneous metal ions removal by RHA. All the parameters and their interactions considered are found to be statistically significant at 95% confidence level for the desired response characteristic, q_{tot}. The study shows that the Taguchi's method is suitable to optimize the experiments for total metal ions removal. The total optimum adsorptive removal of metal ions were obtained with $C_{0,i} = 0\text{–}100$ mg/l, $T = 40\,^{\circ}$C, $pH_0 = 6$, $m = 10$ g/l and $t = 60$ min. The results showed that a multi-staged adsorptive treatment is necessary to meet the minimal discharge standards of metal ions in the effluent.

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1. Introduction

In the past few decades, the uncontrolled discharge of heavy metals from plating/rinsing industries and various other manufacturing process industries has resulted in serious contamination of numerous sites. The heavy metal ions are often encountered at elevated levels and their exposure is likely to persist for a prolonged time. Cadmium (Cd(II)) is a non-essential and a non-biodegradable metal ion which slowly accumulates in the body of living creatures, usually through food chain [1]. Nickel (Ni(II)) is also toxic (in concentrations more than 15 mg/dm^3), especially to activated sludge bacteria. The presence of Ni(II) is detrimental to the operation of anaerobic digesters used in wastewater treatment plants [2]. In humans, zinc [Zn(II)] occurs in over 20 metalloenzymes, including several that are involved in nucleic acid metabolism; its excess ingestion may result in acute gastrointestinal disturbances accompanied with nausea. Instances of acute toxicity have occurred from ingestion of fruit juices that were stored in galvanized (zinc plated) steel containers [3,4]. Due to toxicity of metals, the Central Pollution Control Board (CPCB), Ministry of Environment and Forests (MOEF), Government of India has set Minimal National Standards (MINAS) of 1.0, 3.0, 5.0 mg/l, respectively, for Cd(II), Ni(II) and Zn(II) for safe discharge of the industrial effluents containing these metal ions into surface waters. The safe discharge limit for these metals into marine coastal areas is 2.0, 5.0, 15.0 mg/l, respectively [5]. CPCB has set MINAS of 2.0, 3.0, 5.0 mg/l; and 0.2, 2.0, 5.0 mg/l, for discharge of Cd(II), Ni(II) and Zn(II) for the effluents of electroplating and inorganic chemical industries, respectively.

Amongst the most commonly used methods for the treatment of wastewaters, adsorption on activated carbon (AC) has gained prominence. However, high costs of activated carbon and 10–15% loss during regeneration and the difficulties faced in the recovery/disposal of metals make the utilization of activated carbon prohibitive in the developing countries. This has led to a search for cheaper agri-based substitutes to activated

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carbon. Rice husk ash (RHA) is one such alternative material that is available in plenty, being a waste and has a very high potential as an adsorbent. RHA is collected from the particulate collection devices attached downstream to the boiler furnaces and upstream to the flue gas stacks of the rice husk fired boilers. Our previous studies [1,6] showed the characterization of low-cost RHA, and the efficacy of RHA as an adsorbent for the individual removal of Cd(II), Ni(II) and Zn(II) metal ions from aqueous solutions. Optimum conditions for metal ions removal were found to be $pH_0 \approx 6.5$, adsorbent dose $\approx 10\,kg/m^3$ of solution. The equilibrium between the adsorbate in the solution and on the adsorbent surface was practically achieved in 5 h. The kinetics of adsorption showed the metal ions adsorption to be a gradual process with quasi-equilibrium being attained in 5 h. The pseudo-second-order kinetics represented the equilibrium data well. The effective diffusion coefficient of the cations onto the RHA is of the order of $10^{-13}\,m^2/s$. An increase in temperature was found to induce a positive effect on the sorption process. Toth isotherm best represented the equilibrium adsorption of single components onto RHA. The heat of adsorption (ΔH_0) and change in entropy (ΔS_0) for metal adsorption onto RHA were found in the range of 127–194 kJ/mol K. The isosteric heat of adsorption was quantitatively correlated with the fractional loading of metal ions onto adsorbents. The results showed that the RHA possessed heterogeneous surface with sorption sites having different activities.

Industrial effluents generally contain several metals. Therefore, it is necessary to study the simultaneous sorption of two or more metals. It is also essential to quantify the interactive effect of one metal on the sorption of the other. No information is available in literature on the simultaneous adsorptive removal of Cd(II), Ni(II) and Zn(II) ions by RHA.

The adsorption of metal ions from aqueous solution by any adsorbent is affected by several parameters such as the initial concentration of metal ion (C_0), temperature (T), initial pH (pH_0) of the solution, adsorbent dosage (m) and contact time (t). These parameters need to be optimized for attaining maximum sorptive removal of the adsorbate. The experiments are, generally, conducted in such a manner as to optimize 'one-factor-at-a-time'. This methodology overlooks the interactive effects of various factors on the sorption process. Fractional factorial design based on Taguchi's orthogonal array can be a very effective methodology to investigate the effects of multiple factors as well as potential interactions between these factors in a time and cost effective manner [7]. It has been used extensively in carrying out experiments and devising a strategy for quality control in the manufacturing industries. Recently, chemical and environmental engineers have started applying Taguchi's design of experimental methodology in various studies. Kim et al. [8] optimized the experimental conditions based on the Taguchi robust design for the formation of nano-sized silver particles by chemical reduction method; Mohammadi et al. [9] separated copper ions by electrodialysis; and Madaeni and Koocheki [10] optimized the conditions for wastewater treatment using spiral-wound reverse osmosis element. Kaminari et al. [11] used an electrochemical reactor for recovering heavy metals from acidified aqueous solutions for different process parameters as metallic ion concentration, current density and bed expansion. Plessis and Villiers [12] applied Taguchi's method in the evaluation of mechanical flotation in waste activated sludge thickening. Moghaddama et al. [13] used Taguchi's design methodology to determine the optimum purification conditions for minimizing the lead, cadmium, nickel and cobalt contents in the leaching solutions obtained from ammoniacal ammonium carbonate leaching of non-sulphide zinc ores. Srivastava et al. [14] recently applied this methodology for multi-component adsorption of metal ions onto bagasse fly ash (BFA).

This papers aims at using Taguchi's fractional factorial experimental design to screen significant factors, which would have significant impact on the multi-component adsorption efficiency of metal ions from aqueous solution using RHA as an adsorbent. The aim of the present study is to maximize the selected response characteristic (total adsorptive removal of metal ions by RHA (q_{tot})) by optimizing various parameters affecting the simultaneous adsorption of Cd(II), Ni(II) and Zn(II) metal ions from aqueous solutions. The effects of individual parameters and their interactions on q_{tot} will be examined by employing the standard procedure suggested by Taguchi.

2. Material and methods

2.1. Adsorbent and adsorbates

RHA was used as obtained from a nearby paper mill without any pretreatment except sieving to remove very fine particles. Detailed physico-chemical characterization of RHA has already been presented in our earlier publications [1,6]. The average particle size of RHA was 150.47 μm. Bulk density and the heating value of RHA were $104.9\,kg/m^3$ and 9.68 MJ/kg, respectively. The pore size distribution results showed that the RHA was predominantly mesoporous. The Brunauer–Emmett–Teller (BET) surface area was $36.44\,m^2/g$. The average pore diameter by BET was 42.603 Å. The Barrett–Joyner–Halenda (BJH) pore area showed 80% of the pore area due to the mesopores. The polar groups present on the RHA surface imparted considerable cation exchange capacity to RHA.

All the chemicals used in the study were of analytical reagent grade. Nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) (CAS #7791-20-0) was procured from Qualigens Fine Chemicals, Mumbai, India. Cadmium sulphate octahydrate ($3CdSO_4{\cdot}8H_2O$) (CAS #7790-84-3), zinc sulphate heptahydrate ($ZnSO_4{\cdot}7H_2O$) (CAS #7446-20-0), NaOH and HCl were obtained from S.D. Fine Chemicals, Mumbai, India. Stock solutions of Cd(II), Ni(II) and Zn(II) were made by dissolving exact amount of $3CdSO_4{\cdot}8H_2O$, $NiCl_2{\cdot}6H_2O$ and $ZnSO_4{\cdot}7H_2O$ in distilled water (DW), respectively. The stock solution for each metal salt was diluted with DW to have metal ion concentration in the range of 10–100 mg/l for use in the experiments.

2.2. Analysis of metal ions

The concentration of Cd(II), Ni(II) and Zn(II) in the aqueous samples was determined with reference to the appropriate standard metal ion solutions using a flame atomic absorption

Table 1
Process parameters for multi-component adsorption study of metal ions onto RHA using Taguchi's OA

	Parameters	Units	Levels		
			0	1	2
A	Initial concentration of cadmium ($C_{0,\mathrm{Cd}}$)	mg/l	0	50	100
B	Initial concentration of nickel ($C_{0,\mathrm{Ni}}$)	mg/l	0	50	100
C	Initial concentration of zinc ($C_{0,\mathrm{Zn}}$)	mg/l	0	50	100
D	Temperature (T)	°C	20	30	40
E	Initial pH of solution (pH_0)	–	4	6	8
F	RHA dose (m)	g/l	5	10	15
G	Contact time (t)	min	30	60	90

spectrophotometer (GBC Avanta, Australia) with the detection limit of 0.009, 0.040 and 0.008 mg/l at the wavelength of 228.8, 232 and 213.9 nm, for Cd(II), Ni(II) and Zn(II), respectively, by using air–acetylene flame. Before the analysis, a sample was diluted, if necessary, with DW to a concentration in the range of 0.2–1.8 mg/l for Cd(II), 1.8–8 mg/l Ni(II) and 0.4–1.5 mg/l Zn(II).

2.3. Taguchi's methodology of experimental design

Taguchi's methodology adopted in this study consists of four phases [15], as explained in our earlier study [14]. The various factors to be optimized for the simultaneous adsorptive removal of Cd(II), Ni(II) and Zn(II) metal ions from aqueous solutions by RHA, were selected and the ranges were assigned on the basis of the detailed experiments carried out earlier for metal removal by RHA [1,6]. Based on the experience, the process parameters having significant impact on adsorption have been selected and are given in Table 1. To understand the interactive effects of initial concentration of metal ions, three interactive parameters, namely, $C_{0,\mathrm{Cd}} \times C_{0,\mathrm{Ni}}$, $C_{0,\mathrm{Cd}} \times C_{0,\mathrm{Zn}}$ and $C_{0,\mathrm{Ni}} \times C_{0,\mathrm{Zn}}$, have also been studied.

With seven parameters, each at three levels and three second-order interactions, a L_{27} (3^{13}) OA was selected, and the experiments under the same conditions were carried out in triplet. Table 2 shows the selected L_{27} OA with assignment of parameters and interactions.

2.4. Batch experimental adsorption studies

Batch adsorption experiments were performed for simultaneous metal removal by RHA employing selected 27 experimental trials in combination with seven parameters at three levels (Table 1) and the results obtained from each set as the total amount of metal ion adsorbed onto RHA, q_{tot} are shown in Table 2. The results presented in the table are of three individual determinations.

For each experimental run, 150 ml aqueous solution having 50 ml of each metal ion solution (i.e. Cd(II) or Ni(II) or Zn(II)) of known concentration was taken in a 500 ml conical flask containing specific amount of RHA. These flasks were agitated at a constant shaking rate of 150 rpm in a temperature controlled orbital shaker (Remi Instruments, Mumbai) maintained at 20, 30 or 40 °C, as the case may be. The initial pH of the adsorbate solution was adjusted using 1N (36.5 g/l) HCl or 1N (40 g/l) NaOH aqueous solution without any further adjustment during the sorption process. The samples withdrawn after appropriate contact time were centrifuged using Research Centrifuge (Remi Instruments) at 5000 rpm for 5 min and then the supernatant liquid was analyzed for the residual concentration of metal ions.

The removal of metal ions from the solution and the equilibrium adsorption uptake in the solid phase, q_{tot} (mg/g), was calculated using the following relationships:

$$q_{\mathrm{tot}} = \sum_{i=1}^{3} \frac{(C_{0,i} - C_{e,i})}{m} \tag{1}$$

where, $C_{0,i}$ is the initial metal ion concentration (mg/l), $C_{e,i}$ the equilibrium metal ion concentration (mg/l) and m is the adsorbent dose (g/l).

2.5. Analysis of experimental data and prediction of performance

The experimental data were processed with 'higher-is-better' quality characteristic (i) to determine the optimum conditions for the adsorption, (ii) to identify individual parameters of significance for adsorption, and (iii) to estimate total metal uptake (q_{tot}) at the optimum conditions. The detailed methodology for analysis of experimental data are explained by many investigators [14,16,17]. The plot of average response curves, analysis (ANOVA) for raw data and signal-to-noise ratio (S/N) data have been used for the data analysis. The mean at the optimal condition (optimal value of the response characteristic) is estimated as

$$\mu = \bar{T} + (\bar{A}_2 - \bar{T}) + (\bar{B}_2 - \bar{T}) = \bar{A}_2 + \bar{B}_2 - \bar{T} \tag{2}$$

where, $\bar{T}$ is the overall mean of the response, and $\bar{A}_2$ and $\bar{B}_2$ represent average values of response at the second levels of parameters A and B, respectively.

The confidence intervals as suggested by Taguchi, i.e. $\mathrm{CI}_{\mathrm{POP}}$ (confidence interval for the population), and $\mathrm{CI}_{\mathrm{CE}}$ (confidence interval for a sample group) in regard to the estimated mean of the optimal treatment condition have been used. The expressions for computing the confidence interval are [14,18]

$$\mathrm{CI}_{\mathrm{POP}} = \sqrt{\frac{F_\alpha(1,\ f_e)V_e}{n_{\mathrm{eff}}}} \tag{3}$$

$$\mathrm{CI}_{\mathrm{CE}} = \sqrt{F_\alpha(1,\ f_e)\left[\frac{1}{n_{\mathrm{eff}}} + \frac{1}{R}\right]} \tag{4}$$

where, F_α $(1, f_e)$ is the F-ratio at a confidence level of $(1-\alpha)$ against degree of freedom (DOF) 1 and error DOF f_e, V_e is the error variance (from ANOVA),

$$n_{\mathrm{eff}} = \frac{N}{1 + [\text{Total DOF associated in the estimate of the mean}]} \tag{5}$$

Table 2
Column assignment for the various factors and three interactions in the Taguchi's L_{27} (3^{13}) orthogonal array and Experimental q_{tot} values for multi-component metal ions adsorption onto RHA

Exp. no.	1	2	3	4	5	6	7	8	9	10	11	12	13	R1	R2	R3	S/N ratio (dB)
	A	B	$A \times B$	$A \times B$	C	$A \times C$	$A \times C$	$B \times C$	D	E	$B \times C$	F	G				
1	0	0	0	0	0	0	0	0	0	0	0	0	0	0.00	0.00	0.00	0.00
2	0	0	0	0	1	1	1	1	1	1	1	1	1	3.68	3.69	3.77	11.39
3	0	0	0	0	2	2	2	2	2	2	2	2	2	4.22	4.12	4.14	12.38
4	0	1	1	1	0	0	0	1	1	1	2	2	2	2.25	2.30	2.26	7.11
5	0	1	1	1	1	1	1	2	2	2	0	0	0	7.89	7.88	7.93	17.95
6	0	1	1	1	2	2	2	0	0	0	1	1	1	5.45	5.32	5.35	14.60
7	0	2	2	2	0	0	0	2	2	2	1	1	1	4.69	4.71	4.80	13.50
8	0	2	2	2	1	1	1	0	0	0	2	2	2	3.26	3.18	3.19	10.13
9	0	2	2	2	2	2	2	1	1	1	0	0	0	10.11	9.86	9.91	19.96
10	1	0	1	2	0	1	2	0	1	2	0	1	2	2.35	2.36	2.36	7.44
11	1	0	1	2	1	2	0	1	2	0	1	2	0	2.44	2.46	2.47	7.80
12	1	0	1	2	2	0	1	2	0	1	2	0	1	9.15	8.93	8.97	19.10
13	1	1	2	0	0	1	2	1	2	0	2	0	1	6.42	6.48	6.51	16.22
14	1	1	2	0	1	2	0	2	0	1	0	1	2	3.14	3.22	3.16	10.03
15	1	1	2	0	2	0	1	0	1	2	1	2	0	3.27	3.26	3.34	10.34
16	1	2	0	1	0	1	2	2	0	1	1	2	0	1.72	1.73	1.76	4.80
17	1	2	0	1	1	2	0	0	1	2	2	0	1	7.07	7.25	7.10	17.07
18	1	2	0	1	2	0	1	1	2	0	0	1	2	4.65	4.54	4.56	13.22
19	2	0	2	1	0	2	1	0	2	1	0	2	1	2.14	2.19	2.15	6.68
20	2	0	2	1	1	0	2	1	0	2	1	0	2	6.93	6.96	7.11	16.90
21	2	0	2	1	2	1	0	2	1	0	2	1	0	4.03	3.93	3.95	11.97
22	2	1	0	2	0	2	1	1	0	2	2	1	0	1.96	1.92	1.91	5.72
23	2	1	0	2	1	0	2	2	1	0	0	2	1	1.52	1.56	1.53	3.75
24	2	1	0	2	2	1	0	0	2	1	1	0	2	10.15	10.40	10.20	20.21
25	2	2	1	0	0	2	1	2	1	0	1	0	2	3.74	3.84	3.76	11.55
26	2	2	1	0	1	0	2	0	2	1	2	1	0	2.30	2.36	2.31	7.33
27	2	2	1	0	2	1	0	1	0	2	0	2	1	1.81	1.82	1.85	5.23
Total														116.35	116.28	116.32	
Mean															4.31		

N: total number of results and R: sample size for confirmation experiment.

It can be seen from Eq. (4) that as R approaches infinity, i.e. the entire population, the value $1/R$ approaches 0 and then $CI_{CE} = CI_{POP}$. As R approaches 1, the CI_{CE} becomes wider.

2.6. *Confirmation experiment*

In order to verify the conclusions drawn from the experiments, certain confirmation experiments in triplet were carried out at the optimum conditions for the significant parameters (the insignificant parameters are set at economic levels). The average of the results of the confirmation experiments is compared with the anticipated average based on the parameters and levels tested.

3. Results and discussion

3.1. *Effect of process parameters*

Table 3 shows the raw data for the average value of q_{tot} and S/N ratio for each parameter at the three levels and interactions at the assigned levels. It is found that the parameters: $C_{0,i}$, T, pH$_0$, m and t significantly affect the q_{tot} values. Also, the interaction effect of concentration of one metal ion with respect to (w.r.t) other metal ion also has significant influence on q_{tot} values.

Individually, at levels 1, 2 and 3; parameters m (F), pH$_0$ (E) and $C_{0,Zn}$ (C) have highest influence, respectively, with q_{tot} as the desired response characteristic. The difference between levels 2 and 1 (L2-L1) of each factor indicates the relative influence of the effect. The larger the difference, the stronger is the influence. Table 3 shows that m (parameter F) has good influence over others for the removal of Cd(II), Ni(II) and Zn(II) from aqueous solution by RHA. $C_{0,i}$ also shows strong influence on q_{tot} than that of other parameters. With an increase in the $C_{0,i}$, the mass transfer driving force increases giving increased values of q_{tot}.

The response curves for the individual effects of various parameters on q_{tot} and the respective S/N ratios are given in Fig. 1. An increase in the levels of factors such as $C_{0,i}$, and T from 1 to 2 and from 2 to 3 results in an increase in the q_{tot} values.

Sorption is, generally, an exothermic process. However, if the adsorbate diffusion controls the sorption process, the overall process will be endothermic in nature resulting in an increase in q_{tot} with an increase in T. A temperature increase favours the mobility of the metal ions resulting in an enhancement in the sorptive capacity of the adsorbents. However, the diffusion of the metal ions into the pores of the RHA is not the only rate-

Table 3
Average and main effects of q_{tot} values for RHA—raw and S/N data

	Raw data, average value			Main effects (raw data)		S/N data, average value			Main effects (S/N data)	
	L1	L2	L3	L2-L1	L3-L2	L1	L2	L3	L2-L1	L3-L2
A	4.59	4.47	3.86	−0.12	−0.60	11.89	11.78	9.93	−0.11	−1.85
B	3.87	4.69	4.37	0.82	−0.32	10.41	11.77	11.42	1.36	−0.35
C	2.83	4.27	5.82	1.45	1.55	8.11	11.37	14.11	3.26	2.74
D	3.70	4.22	5.00	0.53	0.78	9.61	11.18	12.81	1.56	1.63
E	3.49	4.96	4.48	1.47	−0.47	9.92	11.85	11.84	1.93	−0.01
F	6.84	3.57	2.52	−3.26	−1.06	15.44	10.58	7.58	−4.86	−3.00
G	3.73	4.66	4.53	0.93	−0.13	9.54	11.95	12.11	2.41	0.16
$A \times B$	3.54	4.41	4.97	0.87	0.55	9.61	11.58	12.41	1.97	0.83
$A \times C$	3.92	4.50	4.50	0.58	0.00	10.23	11.75	11.62	1.51	−0.12
$B \times C$	3.87	4.59	4.47	0.72	−0.11	9.89	11.93	11.78	2.03	−0.14

controlling step [1], and the diffusion resistance can be ignored with adequate contact time. Therefore, an increase in the sorptive uptake of metal ions with an increase in *T* may be attributed to chemisorption. In our earlier studies, it has been shown that the desorption efficiency of metal ions from the spent (loaded) RHA using various solvents (acids, bases and water) is poor [1,19]. This confirms chemisorptive nature of adsorbate uptake. The heat of adsorption (ΔH_0) values between 20 and 400 kJ/mol, are generally taken as to indicate chemisorptive characteristics. ΔH_0 values for the sorption of the studied metal ions onto RHA were found in the range of 33.3–40.2 kJ/mol [6]. This reinforces that chemisorption is responsible for the metal ions uptake.

Fig. 1 shows an increase in q_{tot} with an increase in the level of *t* from 1 to 2, however, q_{tot} decreases with further increase in *t* from levels 2 to 3. During the initial stage of sorption, a large number of vacant surface sites are available for adsorption. However, as the sorption progresses, the occupation of the vacant sites becomes difficult because of the repulsive forces acting between the adsorbate molecules present on the solid surface and in the bulk liquid phase. The easily accessible mesopores get almost saturated with metal ions during the initial stage of adsorption. Thereafter, the metal ions have to travel further deep into the pores with much larger resistance. This results in a decrease in the rate of adsorption later on [1]. Therefore, the adsorption of metal ions increases with *t* until equilibrium is reached between the solute molecules in the liquid and the solid phases.

An increase in pH_0 showed higher adsorption up to level 2. But further increase in pH_0 to level 3 showed a decrease in q_{tot}; q_{tot} increases with an increase in the pH_0 from 4 to 6. The maximum uptake of metal ions was obtained at $pH_0{\sim}6$ and the q_{tot} decreased above this pH_0. Adsorption at low pH_0 ($pH_0 \leq 6.0$) is, however, lower than that at higher pH_0 (≥ 6.0). The point of zero charge (pH_{PZC}) of the RHA is 8.3 [1]. Adsorption of cations is favoured at $pH > pH_{PZC}$, while that of anions is favoured at $pH < pH_{PZC}$. The specific sorption of cations shifts pH_{PZC} towards lower values, whereas that of anions shifts pH_{PZC} towards higher values. For $pH_0 < 6$, a significant electrostatic repulsion exists between the positively charged surface of the RHA and the metal ions in the solution. A higher concentration of H^+ in the solution competes with metal ions for the active sorption sites, resulting in the reduced uptake of cations. As the pH_0 of the system increases, the number of positively charged sites decreases and the number of negatively charged sites increases. A negatively charged surface site on the RHA favours the sorption of cationic metal ions.

As *m* increases from levels 1 to 2 and then to level 3, q_{tot} decreases. This is attributed to the decrease in unit adsorption as *m* increases, even though, the metal ions removal increases due

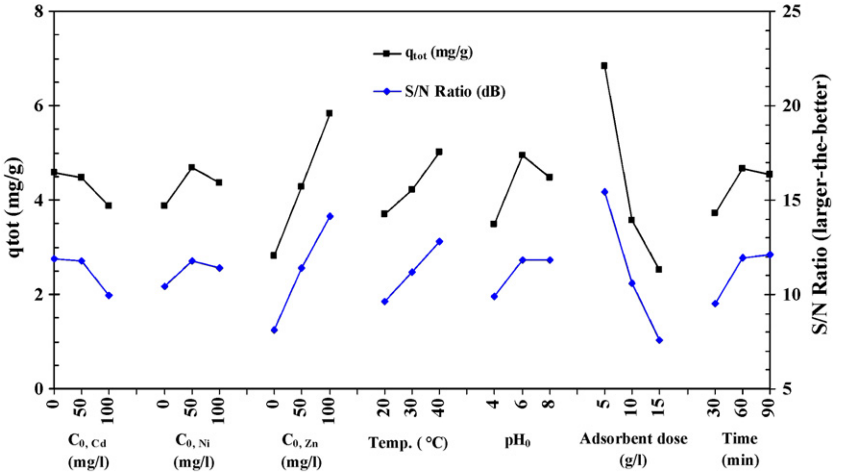

Fig. 1. Effect of process parameters on q_{tot} and S/N ratio for multi-component adsorption of metal ions by RHA.

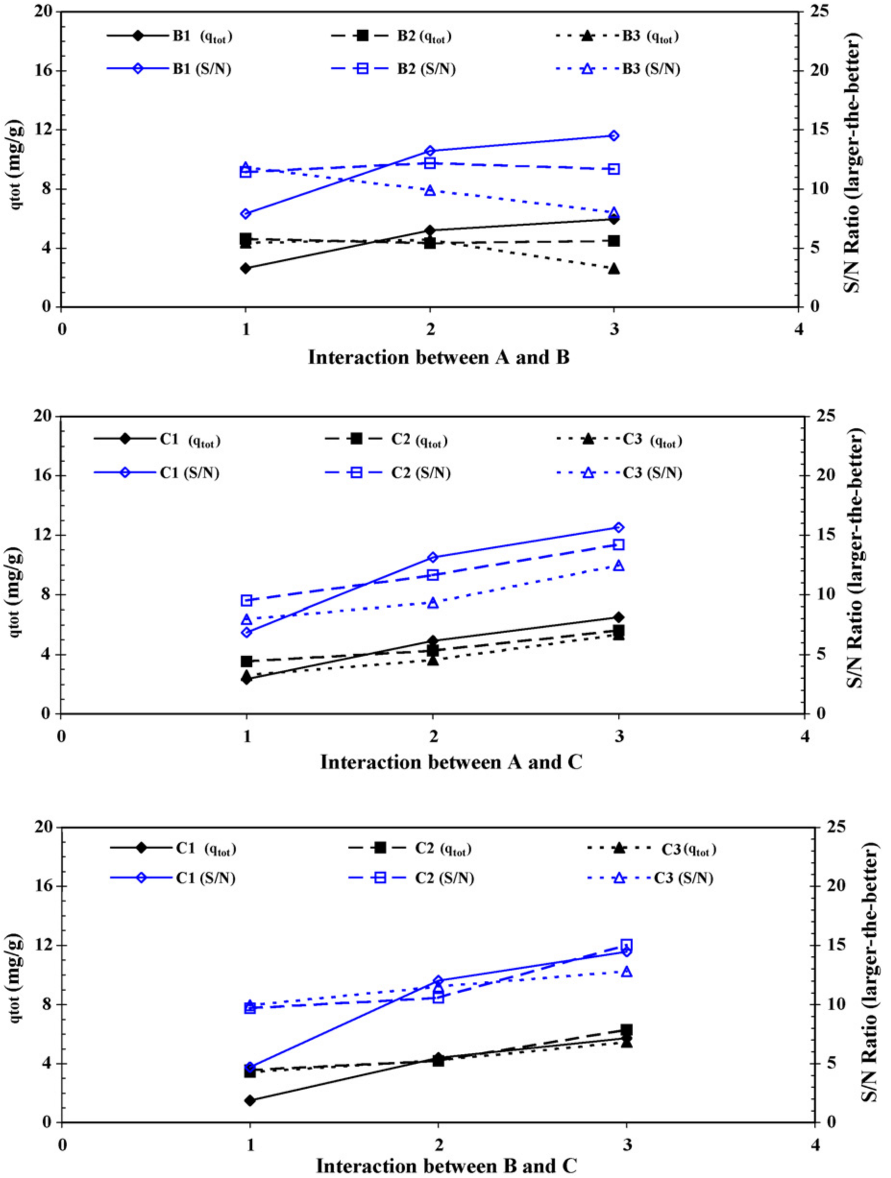

Fig. 2. The interaction between parameters A, B, C at three levels on q_{tot} and S/N ratio for multi-component adsorption of metal ions by RHA.

to availability of larger surface area and more adsorption sites [20].

The interaction between initial concentrations of Cd(II), Ni(II) and Zn(II) metal ions [$(A \times B)$, $(A \times C)$ or $(B \times C)$] significantly affects the average value of q_{tot} (Table 3, Fig. 2). Fig. 2 shows that the effect of initial concentration of one metal ion ($C_{0,\mathrm{Cd}}$ or $C_{0,\mathrm{Ni}}$) on other metal ions ($C_{0,\mathrm{Ni}}$ or $C_{0,\mathrm{Zn}}$) at lower concentrations is more pronounced for all possible interactions. Srivastava et al. [20] showed the antagonistic effect of one metal ion on the simultaneous sorption of another metal ion. This is because of the competition between the different metal ions to occupy vacant adsorption sites on the surface. It was reported that Cd(II), Ni(II) and Zn(II) ions share the same binding sites on the surface of adsorbents, and, therefore, the sorption of one metal ion reduces the number of binding sites available for the sorption of the other metal ions. This leads to the antagonistic sorption behavior. The screening effect of metal ions that are not adsorbed may be another possible explanation for the observed behavior of antagonism. This behavior is generally not observed at lower values of $C_{0,i}$. However, as $C_{0,i}$ increases from levels 1 to 2, q_{tot} shows highest rate of increase. With further increase in $C_{0,i}$ to level 3, this rate of increment in q_{tot} decreases.

The contribution of individual factors is the key for the control to be enforced on the adsorption of various metal ions onto RHA. ANOVA results for raw and S/N ratio data with q_{tot} are given in Table 4. From the calculated F-ratios, it can be inferred that the parameters and the interactions considered in the experimental design are statistically significant at 95% confidence level. The contribution of each parameter for q_{tot} is shown in Fig. 3. It can be observed from Table 4 that the parameter m (F) is the most significant factor with 47.4 and 37.8% contribution to the raw and S/N ratio data, respectively, for the metal adsorption with q_{tot} as the desired characteristic within the assigned levels for each factor. It can also be observed that the interactions between

Table 4
ANOVA of q_{tot} and S/N ratio data for multi-component adsorption of metal ions by RHA

Parameter	Raw data					S/N data				
	Sum of squares	DOF	Mean square	% Contribution	*F*-value	Sum of squares	DOF	Mean square	% Contribution	*F*-value
A	8.16	2	4.08	1.41	1073.15	21.93	2	10.97	2.92	2.43
B	9.19	2	4.60	1.59	1208.76	(9.03)	(2)	(4.52)	POOLED	-
C	121.43	2	60.71	21.02	15964.24	162.37	2	81.19	21.65	17.97
D	23.35	2	11.67	4.04	3069.36	46.01	2	23.00	6.13	5.09
E	30.35	2	15.17	5.25	3989.92	22.27	2	11.13	2.97	2.46
F	273.73	2	136.86	47.38	35987.64	283.33	2	141.67	37.78	31.36
G	13.80	2	6.90	2.39	1814.09	37.28	2	18.64	4.97	4.13
$A \times B$	66.49	4	16.62	11.51	4370.50	87.09	4	21.77	11.61	4.82
$A \times C$	13.02	4	3.26	2.25	856.00	25.92	4	6.48	3.46	1.43
$B \times C$	18.06	4	4.51	3.13	1186.95	54.71	4	13.68	7.29	3.03
Residual	0.21	54	0.00	0.04		9.03	2	4.52	1.20	
Model	577.57	26	264.39	99.96	69519.60	749.94	24	328.52	98.80	72.73
Cor. total	577.78	80	264.39	100.00		758.98	26	333.04	100.00	

the parameters *A*, *B* and *C* contribute significantly to both raw and S/N ratio data for the simultaneous removal of three metal ions by RHA.

3.2. Selection of optimal levels and estimation of optimum response characteristics

Since q_{tot} is 'higher-the-better' type quality characteristic, greatest value of q_{tot} is considered to be the optimal. The optimal level of various parameters obtained after examining the response curves (Fig. 1) of the average value of q_{tot} and S/N ratios are summarized in Table 5. It is found that the 1st level of parameter *F* (*m*); the 2nd level of parameter *E* (pH_0) and *G* (*t*); and the 3rd level of parameters *A*, *B*, *C* ($C_{0,i}$) and *D* (temperature), have higher average values of q_{tot} and S/N ratio. Thus, the significant process parameters affecting the metal removal by RHA and their optimal levels (as already selected) are *A*3, *B*3, *C*3, *D*3, *E*2, *F*1 and *G*2.

It is desired to remove maximum amount of metal ions with highest possible initial concentrations of Cd(II), Ni(II) and Zn(II) metal ions present together. Therefore, the 3rd level of parameters *A*, *B* and *C* ($C_{0,Cd}$, $C_{0,Ni}$ and $C_{0,Zn}$) have been used for further calculations.

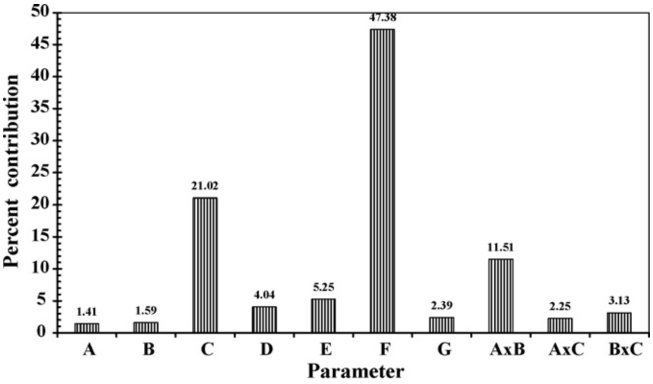

Fig. 3. Percent contribution of various parameters for q_{tot} for multi-component adsorption of metal ions by RHA (calculated based on raw data).

The predicted optimum value of q_{tot} for RHA (μ_{RHA}) as calculated from Eq. (2) following the procedure given earlier [14] is found to 9.65 mg/g. The 95% confidence intervals for the mean of the population and the three confirmation experiments (CI_{POP} and CI_{CE}) are calculated by substituting *N*: total number of results = 27 × 3 = 81; f_e(DOF error) = (80 − 26) = 54; $F_{0.05}$ (1, 54) = 4.03 (tabulated *F*-value), V_e (error variance) = 0.004 (recalculated from Table 4) in Eqs. (3)–(5). The 95% confidence intervals (CI_{POP} and CI_{CE}) of the predicted ranges of q_{tot} for simultaneous adsorption of Cd(II), Ni(II) and Zn(II) ions onto RHA are given in Table 5.

3.3. Confirmation experiments

Three confirmation experiments were conducted for simultaneous adsorption of Cd(II), Ni(II) and Zn(II) ions onto RHA at selected optimal levels of the process parameters. The average values of the characteristics are obtained and compared with the predicted values. The results are given in Table 5. The values of q_{tot} obtained through confirmation experiments are within 95% of CI_{CE}. It may be noted that that these optimal values are valid within the specified range of process parameters. Any extrapolation/interpolation should be confirmed through additional experiments.

3.4. Multi-stage adsorption

Since the wastewater treatment method employed is to ensure the compliance of the MINAS for the treated water, and the single stage treatment did not meet stipulated metal ions concentrations in the treated aqueous solution, multi-stage sorption experiments were carried out. The second to fourth stages of the experiments were carried out at the optimal conditions for all the process parameters.

The filtrate obtained from the first stage (after agitating the effluent with RHA at optimum *m*) was again treated with fresh adsorbent at optimum *m* in the next stage and so on. The pH_0 of the metal ions bearing solution was maintained at 6.0 in the stage 1 only. No pH adjustment was made for

Table 5
Predicted optimal q_{tot} values, confidence intervals and results of confirmation experiments

Optimal levels of process parameters	Predicted optimal values (mg/g)	Confidence intervals (95%)	Average of confirmation experiments (mg/g)
*A*3, *B*3, *C*3, *D*3, *E*2, *F*1, *G*2	9.65	$\mathrm{CI_{POP}}$: $9.58 < \mu_{\mathrm{BFA}} < 9.72$ $\mathrm{CI_{CE}}$: $9.43 < \mu_{\mathrm{BFA}} < 9.87$	9.46

Table 6
Multi-stage adsorption of metal ions from aqueous solution using RHA

Concentration (mg/l)	Cd(II)	Ni(II)	Zn(II)
C_0	100	100	100
$C_{e,\mathrm{I}}$	71.02	55.98	46.30
$C_{e,\mathrm{II}}$	35.46	19.78	11.54
$C_{e,\mathrm{III}}$	15.08	2.80	1.32
$C_{e,\mathrm{IV}}$	1.34	ND	ND

ND: not detected.

subsequent stages. C_0 was taken as100 mg/l for each metal ion.

Multi-stage treatment results for the removal of Cd(II), Ni(II) and Zn(II) ions from aqueous solution are shown in Table 6 and Fig. 4. Table 4 shows the final concentration (C_e) at the end of each treatment stage while Fig. 4 shows the removal efficiencies for each stage of treatment by RHA. The Cd(II), Ni(II) and Zn(II) ion removal efficiency by RHA for the I, II, III and IV stages are 28.98, 50.07, 57.47 and 91.11%; 44.02, 64.67, 85.84 and 100; and 53.70, 75.08, 88.56 and 100%, respectively (Fig. 4). The overall removal efficiency of Cd(II), Ni(II) and Zn(II) was 98.66, 100 and 100%, respectively, for the multi-stage treatment. It may be seen from Table 6 that the final concentrations at the end of the fourth stage ($C_{e,\mathrm{IV}}$) are 1.34 for Cd(II), non-detectable for Ni(II) and Zn(II) ions. Thus, the MINAS set by CPCB is met by Ni(II) and Zn(II) and is very near the standard value for Cd(II). Thus, it is found that the four-stage adsorption with RHA could be a good treatment to bring down the concentration of metal ions below the maximum concentration limit set by CPCB.

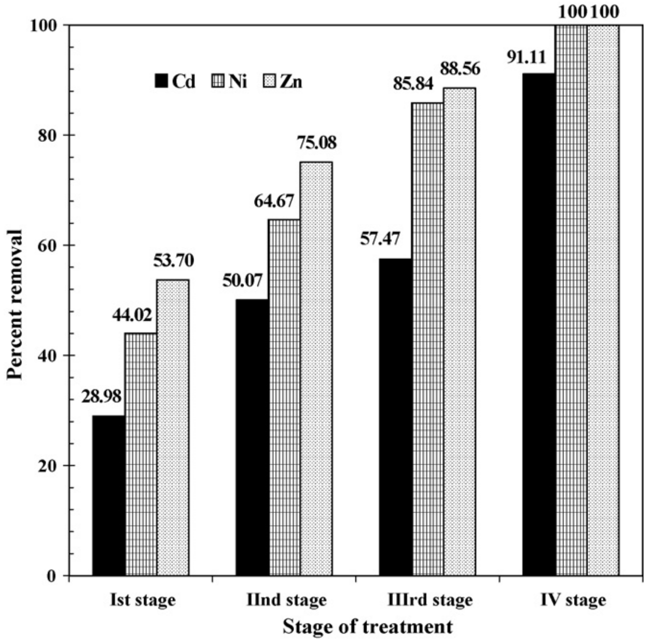

Fig. 4. Removal efficiency of RHA during various stages of multi-stage treatment. $T = 30\,^{\circ}\mathrm{C}$, $t = 5\,\mathrm{h}$, $C_0 = 100\,\mathrm{mg/l}$, $m = 10\,\mathrm{g/l}$.

4. Conclusions

The Taguchi's orthogonal array (OA) experimental design (DOE) methodology allowed fewer experiments to be conducted than the to 'one parameter at a time' optimization methodology to optimize such parameters as the $C_{0,i}$, T, pH_0, m and t that affect the simultaneous sorption of Cd(II), Ni(II) and Zn(II) metal ions from aqueous solutions by RHA. It also facilitated the understanding of the interaction of a number of variables. Maximum sorption for all the cations, viz. Cd(II), Ni(II) and Zn(II) was found to occur at pH_0 6.0. An increase in temperature is found to induce a positive effect on the sorption process. Adsorption of metal ions onto RHA is favourably influenced by an increase in the temperature of the operation. The enhanced sorption at higher temperature indicates endothermic nature of the overall sorption process. The adsorption is also found to be chemisorptive in nature. The interaction between initial concentrations of Cd(II), Ni(II) and Zn(II) metal ions [$(A \times B)$, $(A \times C)$ or $(B \times C)$] is found to be significant in affecting the average values of q_{tot}. The effect of initial concentration of one metal ion ($C_{0,\mathrm{Cd}}$ or $C_{0,\mathrm{Ni}}$) on q_{tot} values is more pronounced at the lower concentration of the other metal ions ($C_{0,\mathrm{Ni}}$ or $C_{0,\mathrm{Zn}}$) for all possible interactions. All the factors and the interactions considered in the experimental design with q_{tot} as the desired response characteristic are statistically significant at 95% confidence level. These results indicate that the use of locally available, almost free of cost, RHA could be a viable alternative to the activated carbon for the removal of metal ions from aqueous solutions.

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