Removal of Zinc from Aqueous Solution on HCl Impregnated Sponge Iron Plant Waste: Optimization by DOE

Deepthi Tirumalaraju and Susmita Mishra

Abstract—Adsorption capability of Sponge Iron Plant (SIP) waste was explored using Zn metal solution. Surface modification of sponge iron plant (SIP) waste was achieved by impregnation with dilute HCl which resulted in improvement of BET surface area by 29%. This surface modification is further authenticated by FTIR and SEM study. Influence of various parameters such as pH, Temperature, Initial Zn Concentration and Adsorbent Dosage on adsorption process was studied. A 2⁴ full factorial design of experiments (DOE) was used to ascertain the significance of each factor and their mutual interactions on the adsorption process. The two levels of pH, Initial metal Concentration, Temperature and Adsorbent Dosage considered were 6 & 8, 20ppm & 100ppm, 30°C & 40°C and 0.5g/L & 1.5g/L respectively. All the main effects were found to be statistically significant while none of their interactions showed any significance. The difference between the average of combinations and the average of center points was found to be 2.75% showing there was no significant curvature present. Among all the parameters pH was found to be most significant parameter while Adsorbent dosage was least affected. The experimental data were fitted to various isotherm models. Maximum adsorption capacity 128.20 mg/g was observed using Langmuir model at pH 8 and temperature 30°C. The sorption reaction fitted well to a pseudo second-order rate model.

Index Terms— Sponge Iron Plant Waste, Adsorption, Impregnation, DOE, Isotherm.

I. INTRODUCTION

Rapid industrialization and urbanization has lead to excessive release of heavy metals into aquatic systems. Due to their toxicity and non-biodegradability they can accumulate in food chain posing a severe damage to the living organisms. Thus, treatment of industrial wastewater containing soluble heavy metals has become essential in order to increase the quality of water. Conventional methods for the heavy metal removal from water and wastewater include hydrometallurgical techniques, oxidation, reduction, precipitation [1], electro dialysis, membrane filtration [2], flotation [3], ion exchange, reverse osmosis [4,5], and adsorption [6]. However, all these methods have their inherent advantages and limitations in application. Adsorption is considered quite attractive in terms of removing the metals from dilute solutions effectively and economically compared to other techniques [7, 8, 9].

Although some of the metals are involved in the metabolism

of human beings, ingestion of those metals in excess amounts will cause abnormalities in their bodies. One such metal is zinc. Zinc is an essential trace element used for enzymatic reactions in humans [10] and its extended and excessive ingestion may lead to toxic effects such as carcinogenesis, mutagenesis and teratogenesis as a result of its bioaccumulation [11]. Intake of zinc ranging from 100 to 150 mg/day interferes with copper metabolism and causes low copper status, reduced iron function, red blood cell microcytosis, and neutropenia, reduced immune function, and reduced levels of high-density lipoproteins. Ingesting 200–800 mg/day of zinc can cause abdominal pain, nausea, vomiting, and diarrhea. There are other reported effects including lethargy, anaemia, and dizziness [12]. According to the WHO standards the maximum contamination level of zinc is 5.0 mg/L.

Zinc is one of the heavy metal which is often detected in industrial wastewaters, which originate from electroplating, mining activities, smelting, battery manufacture, metallurgical processes, galvanizing plants, stabilizers, thermoplastics, pigment manufacture, etc., in addition to the discharges of municipal wastewater treatment plants [13, 14]. Different adsorbents typically used to remove zinc from wastewater include activated carbon [15], modified flax shive [16], rice husk ash [17], waste biomass [14], waste activated sludge [14], wood sawdust Modified Sugarcane Bagasse [18] and Lignite [19]. In spite of several investigations using different adsorbents still new adsorbents are sorted due to increasing demand for treatment of industrial effluents. Some of the industrial solid waste materials are being used as adsorbents these days. One of such kind is the waste produced by sponge iron plants. Sponge iron plant waste is major dust pollution and it needs to be treated well before disposal. It has been found out that around 1.6-1.75 tonne of Fe, 1.2- 1.5 tonne of coal & 0.035 tonne of dolomite are required for production of one tonne of sponge iron. This results in production of 0.54 tonne of solid waste which includes 0.25 tonne of dust and 0.29 tonne of coal char. Due to non- availability of good grade of coal, the amount of char fines increases. The size of char varies from 0.5 mm to 3 mm causing difficulty to handle. Apart from this, it occupies a lot of area for disposal. A 100 TPD plants requires 10 acres of land annually for disposal of solid waste [20].

In the present study the adsorption of zinc from aqueous solution using HCl treated sponge iron plant waste (char) as an adsorbent was investigated. One of best optimization tools being used now-a-days is statistical design of experiments

Manuscript received June 1, 2011

D. Tirumalaraju is with the Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa- 769008, India (e-mail: tirumalaraju.deepthi@gmail.com).

S. Mishra, Associate Professor, Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa- 769008, India (e-mail: smishra@nitrkl.ac.in).

(DOE). The present article also reports the use of statistical design of the experiments to reduce the total number of attempts for optimizing the operating conditions of the batch adsorption system, and it is expected that this statistical tool will contribute in suggesting the best experimental conditions for removing the zinc from aqueous solution. Statistical design of experiments [21] determines the important effects of factors on a response as well as the interaction effects among the factors. Although statistical experimental design has largely been employed in the optimization of industrial processes [22], it has been rarely applied to adsorption [23, 24]. So there is a need for more implementation to determine the potential of DOE in adsorption studies. The rate kinetics and adsorption isotherms have also been mentioned for the present adsorbent.

II. MATERIALS AND METHODS

2.1. Preparation of adsorbent

Sponge iron plant waste from a local sponge iron industry, Mahavir Fero Pvt. Ltd., situated at Kalunga was collected. The collected sample was pulverized to pass through a set of sieves according to the ASTM Method D 2013 and was dried in an oven at $100 \pm 5^\circ\text{C}$ for 24 hr. It was then subjected to surface modification process by soaking in HCl, which increases the proportion of active surface [25]. The oven dried adsorbent was washed several times with distilled water, to remove any particles adhering to the surface. The dried adsorbent was added to 500ml conical flask containing 250 ml of 1N HCl solution. The mixture was left overnight and filtered to remove the sorbent, followed by washing several times with distilled water to make it neutral. The adsorbent was again dried at an oven temperature of 85°C for 2hr.

2.2. Chemicals

All the chemicals used were of analytical reagent grade purchased from Merck, India. Zinc metal was used for preparation of zinc stock solution. Hydrochloric acid and Sodium hydroxide were used to adjust the solution pH. Distilled water was used throughout the experimental studies.

2.3. Stock solution preparation

Stock zinc solution (100mg/L) was prepared by dissolving 100 mg zinc dust powder in a slight excess of 1+1 HCl and diluted to 1000ml with distilled water.

2.4. Instrumentation

Atomic Absorption Spectrophotometer (A Analyst 200, Perkin Elmer) operating with an air-acetylene flame was used to estimate zinc metal ion concentration. Solution pH was measured in a pH meter (EUTECH Instruments, model 510). Adsorption study was performed in a temperature controlled shaker (Lab Companion model SI-300R). Fourier transform infrared spectrometry (Perkin Elmer, resolution at 4cm^{-1}) was used to analyze the organic functional groups present in the adsorbent. The surface texture and elemental analysis of the sample was displayed through Scanning electron microscope/Energy dispersive X-ray (SEM - JEOL, JSM 6480 LV). The surface area of the adsorbent was determined by using BET (Autosorb-1, Quantachrome)

2.5. Adsorption Experiment

Batch adsorption experiments were carried out in a shaker at room temperature using a series of conical flasks containing desired dose of adsorbent in a predetermined concentration of zinc metal solution for a fixed duration. Samples were collected at different time interval. The supernatant was separated by filtration and analyzed through AAS to estimate the zinc ion concentration. The percentage removal of metals from the solution was calculated by the following equation.

$$\% \text{removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where C_0 (mg/L) is the initial metal ion concentration and C_e (mg/L) is the final metal ion concentration in the solution. Isotherm studies were recorded by varying the initial concentration of metal solution from 10 to 100 mg/L. The amount of the metal uptake was calculated by the difference between the equilibrium concentration and the initial concentration. The amount of metal retained in the solid phase q_e (mg/g) was calculated using the relation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Where m is the mass of adsorbent (g), V is the volume of the solution (L), C_0 is the initial concentration of metal (mg L^{-1}), C_e is the equilibrium metal concentration (mg L^{-1}) and q_e is the metal quantity adsorbed at equilibrium (mg/g).

2.6. Statistical design of experiments

Statistical design of experiments is a simultaneous study of several process variables [22, 26]. Several factors were changed in a systematic way so as to ensure the reliable and independent study of the main factors and interactions which are sensitive to the process. The present study focused on the influence of factors on the adsorption of zinc metal ions on SIP waste. The purpose was to identify only the important variables that affect the response variable i.e. percentage removal and their interactions if any which may alter the response significantly [22, 26]. The significance of each factor and their interaction effects were evaluated by using two-level full factorial design of experiments. This study determines the influence of some of the factors in the adsorption of zinc on SIP waste and quantifies them to ensure that the influence is getting transformed into a measurable response. The potential factors (or parameters) were classified as controlled factors and held-constant factors. The controlled factors were those selected for this study (Table I). The held-constant factors like speed of agitation and contact time were held at a specific level i.e. 120 rpm and 10 min respectively, though their effect on the response cannot be completely overruled. Each variable was kept at three levels, high level (+1), center point (0) and a lower level (-1) as listed in Table I. After conducting all the runs according to the design of experiments, the results were analyzed using Analysis of Variance (ANOVA) technique. Statistica 9.0 software was utilized for statistical and mathematical calculations.

TABLE I: VARIABLES CONSIDERED FOR THE DESIGN OF EXPERIMENTS AND THEIR LEVELS.

Variables	Low level (-1)	Center point (0)	High level (+1)
pH	6	7	8
Initial metal concentration(mg/L)	20	60	100
Temperature(°C)	30	35	40
Adsorbent Dose(g/L)	0.5	1	1.5

a) Normal Probability Plots of effects

When analyzing data from factorials, occasionally, high-order interactions occur, and as such, normal probability plots are used to estimate the significant factors [27]. This is the plot of the actual value of the estimated effects against their cumulative normal probabilities [27]. The nominal effects are normally distributed with mean zero and variance (σ^2) and will tend to fall along a straight line, whereas significant effects will have nonzero means and will not lie along the straight line. Effects in the statistical designs are done by averaging the responses that are applicable to the level of each factor. The difference between the average responses at the two levels of each factor is an indication of the significance of that factor in influencing the response measured. Expressed mathematically, the single effects caused by the variation of the input parameters are calculated with the help of the following formula:

$$\text{Effect} = \frac{2}{m} \sum_{i=1}^m (\text{Algebraic sign of constant} \times R_{i, \text{observed}}) \quad (3)$$

Where m is the number of runs and R is the response.

b) Pareto Plots of Effects

A Pareto chart is a special type of bar chart where the values being plotted are arranged in descending order. As we study the effects of different factors on the response, it will give us the descending order of effects exerted by different variables and the interactions between them. It helps us to set the priority levels while designing the process. These Pareto charts were prepared based on 80-20 rule, which states that 80% of effects come from 20% of the various causes [28].

c) Graphical Residual Analysis

The normal plotting of residuals provides a diagnostic test for any uncertainly diverted model [22, 29]. The normal probability plots of the residuals for the data test the hypothesis that the residuals have a normal distribution. This should be a straight line if the residuals have a normal distribution. A plot of residuals versus fits (fitted model values) tests the assumption or the hypothesis that the variations are the same in each combination.

d) Test for Curvature Using 'Centre Points'

Adding centre points to the design provides protection against curvature from second-order effects as well as allows an independent estimation of error [22]. If $\bar{Y}_C$ is the average percentage leaching of zinc from N_C runs at the centre, $\bar{Y}_F$ the average percentage leaching of zinc from the runs at the

factorial points under study, and the difference $(\bar{Y}_F - \bar{Y}_C)$ is small, then the centre points lie on or near the plane passing through the factorial points, and hence, there is no quadratic curve. On the other hand, if $(\bar{Y}_F - \bar{Y}_C)$ is large, then quadratic curvature is present [28].

2.7. Adsorption isotherms

The study of the adsorption equilibrium was carried out for metal concentrations varying from 10 to 100mgL⁻¹. The obtained experimental data were fitted with the linearized form of Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin models.

a) Langmuir isotherm model

Langmuir adsorption isotherm model exhibits the monolayer coverage of the sorption surfaces and assumes structurally homogeneous adsorbent. It also assumes that all the adsorption sites are energetically identical. The Langmuir equation is given by [30].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

The linearization of it leads to the following form:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \frac{1}{C_e} + \frac{1}{q_m} \quad (5)$$

Where C_e , equilibrium metal concentration, q_m and K_L are the Langmuir constants related to maximum adsorption capacity (mg/g), and the relative energy of adsorption (1/mg), respectively. The essential characteristics of Langmuir isotherm model can be explained in terms of a dimensionless constant separation factor, R_L , defined by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

The values of R_L indicates the type of Langmuir isotherm to irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linear ($R_L=1$) or unfavorable ($R_L > 1$).

b) Freundlich isotherm model

Freundlich equation is derived to model the multilayer adsorption and for the adsorption on heterogeneous surfaces. The Freundlich equation is given by [31]:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

The logarithmic form of equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

Where q_e is the amount of metal ion adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration (mg/L), K_F and n are freundlich equilibrium constants.

c) Dubinin –Radushkevich isotherm(D-R)

The D-R isotherm is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant sorption potential. The D-R equation is:

$$q_e = q_m e^{\left\{ -\beta \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \right\}} \quad (9)$$

The linear form of this model is expressed by [32]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (10)$$

Where β is a constant related to the adsorption energy, R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the gas constant, and T (K) is the absolute temperature; and $\varepsilon = RT \ln (1 + 1/C_e)$. The constant β ($\text{mol}^2 \text{ KJ}^{-2}$) reflects the mean free energy E (KJ mol^{-1}) of sorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship.

$$E = (2\beta)^{-1/2} \quad (11)$$

This parameter gives information about chemical or physical adsorption. With the magnitude of E , between 8 and 16 KJ mol^{-1} , the adsorption process follows chemical ion-exchange, while for the values of $E < 8 \text{ KJ mol}^{-1}$, the adsorption process is of a physical nature.

d) Temkin isotherm

Temkin isotherm assumes that decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm is given by the following equation [33]:

$$q_e = \frac{RT}{b} \ln(aC_e) \quad (12)$$

Linear form of Temkin isotherm is given by the following equation:

$$q_e = a + b \ln C_e \quad (13)$$

Where q_e is the amount of metal ion adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration (mg/L), a is equilibrium binding constant (g^{-1}) and b is related to heat of adsorption (J/mol) which are Temkin constants.

2.8. Adsorption kinetics model:

Kinetic models such as pseudo-first order and pseudo-second order; etc are available to find out the best fit kinetic model for adsorption of Zn on SIP waste.

a) Pseudo-first order model

The model of the pseudo-first order used is that of Lagergren given by the following equation [34]:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (14)$$

Where k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption, q_t (mg/g) denotes the amount of adsorption at time t (min) and q_e (mg/g) is the amount of adsorption at equilibrium.

After definite integration by application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (14) becomes.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t \quad (15)$$

The adsorption rate constant, k_1 , can be calculated by plotting $\log(q_e - q_t)$ versus t .

b) Pseudo-second order model

The pseudo-second-order equation can be written as [35, 36]:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad (16)$$

Integration of Eq. (16) and application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (17)$$

Where k_2 ($\text{g} / (\text{mg min})$) is the rate constant, k_2 and q_e can be obtained from the intercept and slope.

III. RESULTS AND DISCUSSION

3.1. Characterization of adsorbent:

The physical properties of the adsorbent before and after the acid treatment were presented in Table II. The results clearly indicate an increase in the available surface area of the adsorbent.

TABLE II: CHARACTERISTICS OF UNTREATED AND HCl TREATED SIP WASTE.

Property	Untreated SIP waste	HCl treated SIP waste
Moisture (%)	2.49	2.46
Volatile matter (%)	1.9	1.85
Ash content (%)	69.9	60.2
Fixed Carbon (%)	25.71	35.49
Iodine no(mg/g)	141	145
BET surface area (m^2/g)	118.5	143.3

a) FTIR analysis:

The FTIR results for both HCl treated and untreated SIP waste were presented in figures 1(a) & (b). It was observed that the acid treatment process did not affect the contentedness of functional groups in the adsorbent.

Figure 1. FTIR Spectrum of (a) Untreated SIP waste. (b) HCl treated SIP waste.

The four major peak ranges were almost unchanged before and after the treatment. The peaks in the ranges $1000\text{--}1300 \text{ cm}^{-1}$ and $1600\text{--}1750 \text{ cm}^{-1}$ is attributed to the C-O and C=O of esters and ketones groups respectively. A very broad band near to the 3600 cm^{-1} indicates the presence of hydrogen bonded OH group which is due to the adsorption of water on the adsorbent [37,38]. The peaks near to 2300 cm^{-1}

are attributed to the presence of nitrile ($C\equiv N$) groups to some extent. The presence of $C=O$ shows very high affinity towards metal adsorption [39], that reflects the sorption capacity of the adsorbent.

b) Analysis of SIP waste by SEM/EDX:

Scanning electron microscopic photographs of SIP waste and impregnated SIP waste illustrated the figure 2 reveal the structure and indicates that the adsorbents had a porous and homogeneous structure with a deep pore. A progressive change in the surface of the particles had been observed (fig 2(a) & 2(b).)

Figure 2. Scanning electron micrographs of the adsorbent, (a) untreated SIP waste, (b) HCl treated SIP waste.

The energy dispersive X-ray microanalysis of both the samples were shown in Table III & indicate the presence of carbon and oxygen in larger percentage with other metals such as Al, Si and Fe etc.

TABLE III: ELEMENTAL COMPOSITION OF ADSORBENTS.

Elements	C	O	Al	Si	Fe	S
SIP waste (wt %)	53.06	31.61	2.36	3.67	7.16	0.68
Impregnated SIP waste (wt %)	67.37	19.79	3.31	5.31	1.18	--

3.2. Assessment of effects of parameters using Design of Experiments:

The matrix for four variables varied at two levels (+,-) and corresponding metal removal percentage Y_{Zn} is shown in

Table IV. According to the DOE principle, six experiments were carried out at base level i.e. at center points to estimate error and standard deviation. The regression model equation with interaction terms can be written using Taylor series of expansion as:

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{14} x_1 x_4 + b_{23} x_2 x_3 + b_{24} x_2 x_4 + b_{34} x_3 x_4 + b_{123} x_1 x_2 x_3 + b_{124} x_1 x_2 x_4 + b_{234} x_2 x_3 x_4 + b_{1234} x_1 x_2 x_3 x_4 \quad (18)$$

where Y =% of metal adsorbed; b =model coefficients; and x_1, x_2, x_3 , and x_4 = dimensionless coded factors for pH, initial Zn concentration, adsorbent dose and temperature respectively.

TABLE IV: ZN ADSORPTION RESULTS FROM THE EXPERIMENTAL RUNS OF 2^4 FULL FACTORIAL DESIGN.

Run number	pH (X_1)	Initial Concentration (X_2)	Adsorbent Dosage (X_3)	Temperature (X_4)	% Adsorption (Y_{Zn})
15	-	+	+	+	43.62
19	0	0	0	0	57.28
21	0	0	0	0	57.9
14	+	-	+	+	91.12
5	-	-	+	-	41.125
7	-	+	+	-	35.9
9	-	-	-	+	48.75
8	+	+	+	-	75.89
12	+	+	-	+	76.54
2	+	-	-	-	74.77
3	-	+	-	-	33.31
20	0	0	0	0	56.75
16	+	+	+	+	80.25
18	0	0	0	0	59.02
17	0	0	0	0	57.63
13	-	-	+	+	51.21
11	-	+	-	+	39.24
6	+	-	+	-	82.2
1	-	-	-	-	38.825
4	+	+	-	-	67.93
22	0	0	0	0	58.7
10	+	-	-	+	90.22

a) ANOVA (Analysis of the variance)

The determination of the significant factors affecting the removal efficiency was done by performing two-way analysis of variance (ANOVA). In Table V, the column labeled “F” presents the F statistic for testing the null hypothesis that states that the main effects and the two-way are equal to zero, respectively. The column labeled “P” presents the P-value for the F test. The small P values (<0.05) mean that not all the main effects and interactions are zero at the 5% significance level. In other words, there is reasonably strong evidence that at least some of the main effects and interactions are not equal to zero.

The data given in Table IV was used to estimate the main and binary interaction effects, as plotted in figure 3. The determination of the significant effects as analyzed by the probability plots are shown in the figure. When the effects of the individual factors were assessed using the factorial design pH, Initial concentration, Adsorbent dosage and Temperature showed that they were statistically significant factors since they have nonzero means. All the binary interactions were statistically insignificant because they did not differ much from normal distribution (zero mean). So, there were no significant interactions between individual factors.

TABLE V: Zn ANOVA TABLE FOR Zn ADSORPTION.

Factors/ Interactions	SS	df	MS	F	P
(1)pH	5888.260	1	5888.260	1277.761	0.000000
(2)Initial Concentration	268.468	1	268.468	58.258	0.000010
(3)Adsorbent Dosage	62.925	1	62.925	13.655	0.003531
(4)Temperature	315.063	1	315.063	68.369	0.000005
1 by 2	6.076	1	6.076	1.319	0.275211
1 by 3	4.275	1	4.275	0.928	0.356186
1 by 4	0.846	1	0.846	0.184	0.676510
2 by 3	1.925	1	1.925	0.418	0.531310
2 by 4	19.714	1	19.714	4.278	0.062957
3 by 4	4.873	1	4.873	1.057	0.325877
Error	50.691	1	4.608		
Total SS	6623.1	2			
	15	1

Figure 3. Normal Plot of Effects of Main Factors and Their Interactions. Produced by Statistica 9.0

Figure 4 shows the Pareto chart of standardized effects. It gives the factors which have a standardized effect beyond 95% confidence level (beyond the line at 2.10). The figure represents the descending order of significant factors; hence pH is the most significant factor in adsorption of Zinc using SIP waste.

Figure 4. Pareto Chart of standardized effects generated by STATISTICA 9.0

From both the figures 3&4 one can say that no interaction term is statistically significant in influencing the Zn adsorption. The standardized effects, standardised errors and coefficients of equation (18) (up to 2-way interactions) are presented in the Table VI.

TABLE VI: STANDARDIZED EFFECTS, STANDARDISED ERRORS AND MODEL COEFFICIENTS

Factors	Effect	Std. Err.	Coefficients (b)	Std.Err. (Coeff.)
Mean	59.91727	0.457675	59.91727	0.457675
(1)pH	38.36750	1.073343	19.18375	0.536672
(2)Initial Concentration	-8.19250	1.073343	-4.09625	0.536672
(3)Adsorbent Dosage	3.96625	1.073343	1.98313	0.536672
(4)Temperature	8.87500	1.073343	4.43750	0.536672
1 by 2	-1.23250	1.073343	-0.61625	0.536672
1 by 3	1.03375	1.073343	0.51688	0.536672
1 by 4	0.46000	1.073343	0.23000	0.536672
2 by 3	0.69375	1.073343	0.34687	0.536672
2 by 4	-2.22000	1.073343	-1.11000	0.536672
3 by 4	-1.10375	1.073343	-0.55187	0.536672

Neglecting the coefficients of non significant terms at 95% confidence level, the regression equation (18) becomes

$$Y = 59.91727 + 19.18375x_1 - 4.09625x_2 + 1.98313x_3 + 4.43750x_4 \quad (19)$$

b) Graphical analysis:

Figure 5 shows the normal plot of residuals and figure 6 shows the residuals vs. predicted values. Figure 5 depicts that all residuals lie on a straight line with linear correlation coefficient of 0.9639, which shows that the residuals were distributed normally. A plot of residuals vs. predicted values tests the assumptions that the variations are the same in each combination (Figure 4). Figure 4 shows that all the residuals were distributed between -3 and $+3$. Since the residuals were distributed normally with constant variance, mean zero and independently (Figures 5 and 6); it can be concluded that Equation (19) was in excellent agreement with the experimental data. In other words, the underlying assumptions about the errors were satisfied.

Figure 5. Normal plot of residuals.

Calculated from Table IV the difference ($\bar{Y}_F - \bar{Y}_C$) is found to be 2.8% which confirms that there is no much significant curvature present.

Figure 6. Residuals vs predicted values.

c) Effects of Factors on Adsorption:

The effects of all the four individual factors used for the study are shown in figure 7. From the figure it can be said that except initial concentration all other parameter have positive effect on Zn adsorption percentage. Among the four factors pH has highest significance on Zn adsorption with 38.36% increase from lower level to higher level and adsorbent dose has lowest significance with only 3.966% change from lower level to higher level. The pH of solution has significant impact on the uptake of metals as it determines the surface charge of the adsorbent and degree of ionization and specification of the adsorbent [40]. The effect of initial metal ion concentration is negative because at low concentrations, metals will be adsorbed by specific sites, while with increasing metal ion concentration the specific sites are saturated and are filled [41].

3.3. Adsorption isotherms:

The equilibrium data for the adsorption are commonly known as adsorption isotherms. It is essential to know them so as to compare the effectiveness of different adsorbent materials under different operational conditions and also to design and optimize an adsorption system. Heavy metal

adsorption is usually modeled by the classical adsorption isotherms. In this study, four isotherms models were used, Langmuir, Freundlich, Dubinin-Radushkevich (DR), Temkin isotherms using Eqs (4),(7),(9),and(12) respectively. The values of various constants of the four models were calculated and were represented in the Table VII.

Figure 7. Main effect plots for Adsorption of Zn on SIP waste. Developed by using STATISTICA 9.0

TABLE VII: ISOTHERM CONSTANTS OF ZN ADSORPTION

Isotherms	8pH
Langmuir	
q_m (mg/g)	128.20
K_L (L/mg)	0.076
R^2	0.9783
Freundlich	
K_F (mg/Kg)	9.397
N	2.24
R^2	0.991
Temkin	
A	1.005
B	107.41
R^2	0.9517
D-R	
β (mol ² /kJ ²)	1.3206
q_m (mg/g)	65.32
R^2	0.9021

Adsorption isotherms for Zinc (II) adsorption from aqueous solution on SIP waste is presented in figure 8. It indicates that the experimental data fitted well to all the isotherm models expect D-R model. The adsorption constants and correlation coefficients of different isotherms studied are given in Table VII.

It is observed that the value of n is greater than unity, indicating that Zn was favorably adsorbed on the adsorbent. The maximum adsorption capacity of zinc from Langmuir isotherm was found to be 128.20mg/g and all the R_L values are within the favorable range ($0 < R_L < 1$). The free energy estimated from D-R model indicates E value as 1.6736(KJ/mol) which was less than 8 KJ/mol. It suggests

Figure 5. Normal plot of residuals.

Calculated from Table IV the difference ($\bar{Y}_F - \bar{Y}_C$) is found to be 2.8% which confirms that there is no much significant curvature present.

Figure 6. Residuals vs predicted values.

c) Effects of Factors on Adsorption:

The effects of all the four individual factors used for the study are shown in figure 7. From the figure it can be said that except initial concentration all other parameter have positive effect on Zn adsorption percentage. Among the four factors pH has highest significance on Zn adsorption with 38.36% increase from lower level to higher level and adsorbent dose has lowest significance with only 3.966% change from lower level to higher level. The pH of solution has significant impact on the uptake of metals as it determines the surface charge of the adsorbent and degree of ionization and specification of the adsorbent [40]. The effect of initial metal ion concentration is negative because at low concentrations, metals will be adsorbed by specific sites, while with increasing metal ion concentration the specific sites are saturated and are filled [41].

3.3. Adsorption isotherms:

The equilibrium data for the adsorption are commonly known as adsorption isotherms. It is essential to know them so as to compare the effectiveness of different adsorbent materials under different operational conditions and also to design and optimize an adsorption system. Heavy metal

adsorption is usually modeled by the classical adsorption isotherms. In this study, four isotherms models were used, Langmuir, Freundlich, Dubinin-Radushkevich (DR), Temkin isotherms using Eqs (4),(7),(9),and(12) respectively. The values of various constants of the four models were calculated and were represented in the Table VII.

Figure 7. Main effect plots for Adsorption of Zn on SIP waste. Developed by using STATISTICA 9.0

TABLE VII: ISOTHERM CONSTANTS OF ZN ADSORPTION

Isotherms	8pH
Langmuir	
q_m (mg/g)	128.20
K_L (L/mg)	0.076
R^2	0.9783
Freundlich	
K_F (mg/Kg)	9.397
N	2.24
R^2	0.991
Temkin	
A	1.005
B	107.41
R^2	0.9517
D-R	
β (mol ² /kJ ²)	1.3206
q_m (mg/g)	65.32
R^2	0.9021

Adsorption isotherms for Zinc (II) adsorption from aqueous solution on SIP waste is presented in figure 8. It indicates that the experimental data fitted well to all the isotherm models expect D-R model. The adsorption constants and correlation coefficients of different isotherms studied are given in Table VII.

It is observed that the value of n is greater than unity, indicating that Zn was favorably adsorbed on the adsorbent. The maximum adsorption capacity of zinc from Langmuir isotherm was found to be 128.20mg/g and all the R_L values are within the favorable range ($0 < R_L < 1$). The free energy estimated from D-R model indicates E value as 1.6736(KJ/mol) which was less than 8 KJ/mol. It suggests

- [6] K. O. Olyinka, B. I. Alo, and T. Adu, "Sorption of heavy metal from electroplating effluent by low cost adsorbents. I: Use of sawdust and Teak tree bark", *J. Nig. Environ. Soc.*, vol. 2, pp. 330-336, 2005.
- [7] J. H. Skinner, and N. J. Bassin, "The environmental protection agency's hazardous waste research and development program", *J. Air Pollut Control Assoc.*, vol. 38, pp. 377-387, 1988.
- [8] A. H. Mahvi, "Application of agricultural fibers in pollution removal from aqueous solution", *Int. J. Environ. Sci. Technol.*, vol. 5, pp. 275-285, 2008.
- [9] M. Malakootian, A. Almasi, and H. Hossaini, "Pb and Co removal from paint industries effluent using wood ash", *Int. J. Environ. Sci. Technol.*, vol. 5, pp. 217-222, 2009.
- [10] A. Gül, M. Yilmaz, and Z. Isilak, "Acute toxicity of zinc sulphate (ZnSO₄·H₂O) to *Guppies* (*Poecilia reticulata* P., 1859)", *G.U. J. Sci.*, vol. 22, pp. 59-65, 2009.
- [11] Agency for Toxic Compounds and Disease Registry (ATSDR), Toxicological Profile for Zinc, Public Health Service, U.S. Department of Health and Human Services, Atlanta, Georgia, 1993.
- [12] National Council of the Environment – CONAMA, Government Resolution No. 357, Ministry of the Environment, Brasília, Federal District, Brazil, www.mma.gov.br/conama (in Portuguese) 2005.
- [13] P. C. Mishra, and R. K. Patel, "Removal of lead and zinc ions from water by low cost adsorbents", *J. Hazard. Mater.*, vol. 168, pp. 319-325, 2009.
- [14] L. Norton, K. Baskaran, and T. McKenzie, "Biosorption of zinc from aqueous solutions using biosolids", *Adv. Environ. Res.*, vol. 8, pp. 629-635, 2004.
- [15] N. Kannan, and T. Veemaraj, "Adsorption behaviour of zinc (II) ions and zinc (II) – EDTA complex from aqueous solution onto lemon peel and dates nut carbons—a comparative study", *EJEA Chem.*, vol. 8, pp. 666-675, 2009.
- [16] E. I. El-Shafey, M. Cox, A. Pichugin, and Q. Appleton, "Application of a carbon sorbent for the removal of cadmium and other heavy metal ions from aqueous solution", *J. Chem. Technol. Biotechnol.*, vol. 77, pp. 429-436, 2002.
- [17] V. C. Srivastava, I. D. Mall, and I. M. Mishra, "Characterization of mesoporous rice husk ash (RHA) and adsorption kinetics of metal ions from aqueous solution onto RHA", *J. Hazard. Mater.*, vol. 134, pp. 257-267, 2006.
- [18] F. V. Pereira, L. V. A. Gurgel, S. F. de Aquino, and L. F. Gil, "Removal of Zn²⁺ from Electroplating Wastewater Using Modified Wood Sawdust and Sugarcane Bagasse", *ASCE*, vol. 135, pp. 341-350, 2009.
- [19] D. Pentari, V. Perdikatsis, D. Katsimicha, and A. Kanaki, "Sorption properties of low calorific value Greek lignites: removal of lead, cadmium, zinc and copper ions from aqueous solutions", *J. Hazard. Mater.*, vol. 168, pp. 1017-1021, 2009.
- [20] H.S. Patra, B.Sahoo and B.K. Mishra. Status of Sponge iron plants in Orissa. Research Report submitted to 'VASUNDHARA'. 2009. Available:<http://www.vasundharaorissa.org/Research%20Reports/Stat%20of%20sponge%20iron%20plant%20in%20Orissa.pdf>
- [21] R. E. Bruns, I. S. Scarminio, and B. de. Barros-Neto, "Experimental Design Chemometrics", Elsevier, Amsterdam, 2006.
- [22] D. C. Montgomery. "Design and Analysis of Experiments", John Wiley and Sons, New Jersey, USA, 2005.
- [23] L. T. Arenas, E. C. Lima, A. A dos Santos Jr, J. C. P. Vagheti, T. M. H. Costa, and E. V. Benvenuti, "Use of statistical design of experiments to evaluate the sorption capacity of 1, 4-diazoniabicyclo [2.2.2] octane=silica chloride for Cr (VI) adsorption", *Colloids Surf.*, vol. 297, pp. 240-248, 2007.
- [24] C. G. Passos, F. Ribaski, N. M. Simon, A. A. dos Santos Jr, J. C. P. Vagheti, E. V. Benvenuti, and E. C. Lima, "Use of statistical design of experiments to evaluate the sorption capacity of 7-amine-4-azaheptylsilica and 10-amine- 4-azadecylsilica for Cu (II), Pb (II) and Fe (III) adsorption", *J. Colloid Interface Sci.*, vol. 302, pp. 396-407 2006.
- [25] M. E. Argun, S. Dursun, C. Ozdemir, and M. Karatas, "Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics", *J. Hazard. Mater.*, vol. 141, pp. 77-85, 2007.
- [26] L. B. Barrentine, "An Introduction to Design of Experiments: A Simplified Approach", ASQ Quality Press, Wisconsin, USA. 1999.
- [27] C. Daniel, "Use of Half Normal Plots in Interpreting Factorial Two Level Experiments", *Technometrics*, vol. 1, pp. 311-341, 1959.
- [28] R. Koch, "The 80/20 Pinciple: The Secret of Achieving More with Less", Nicholas Breale Publishing, London, UK. 2001.
- [29] G. E. P. Box, W. G. Hunter, and J. S. Hunter, "Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building", John Wiley and Sons, New York, USA. 1978.
- [30] I. Langmuir, "The adsorption of gases on plane surface of glass, mica and platinum", *J. Am. Chem. Soc.*, vol. 40, pp. 1361-1403, 1918.
- [31] H. Freundlich and W. Heller, "Rubber die adsorption in lusungen", *J. Am. Chem. Soc.*, vol. 61, pp. 2228-2230, 1939.
- [32] J. Peric, M. Trgo, and N.V. Medvidovic, "Removal of zinc, copper and lead by natural zeolite-a comparison of adsorption isotherms", *Water Res.*, vol. 38, pp. 1839-1899, 2004.
- [33] M. I. Temkin, and V. Pyzhev, "Kinetics of ammonia synthesis on promoted iron catalysts, *Acta Physiochim*", *URSS.*, vol. 12, pp. 327-356, 1940.
- [34] Y.S. Ho, and G. McKay, "A kinetic study of dye sorption by biosorbent waste product pith", *Resour. Conserv. Recycl.*, vol. 25, pp. 171-193, 1999.
- [35] G. McKay, and Y.S. Ho, "The sorption of lead (II) on peat", *Water Res.*, vol. 33, pp. 585-587, 1999.
- [36] G. McKay, and Y.S. Ho, "Pseudo second-order model for sorption processes", *Process Biochem.*, vol. 34, pp. 451-460, 1999.
- [37] N. Azouaoua, Z. Sadaouia, A. Djaafri, and H. Mokaddema, "Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics", *J. Hazard. Mater.*, vol. 184, pp. 126-134, 2010.
- [38] P. Vinke, M. Van der Eijk, M. Verbree, A.J. Voskamp, and H. Van, Bekkum, "Modification of the surfaces of a gasactivated carbon and a chemically activated carbon with nitric acid, hypochlorite, and ammonia", *Carbon*, vol. 32, pp. 675-686, 1994.
- [39] X. Chen, S. Jeyaseelan, and N. Graham, "Physical and chemical properties study of the activated carbon made from sewage sludge", *Waste Manage.*, vol. 22, pp. 755-760, 2002.
- [40] E.-S.Z. El-Ashtouky, N.K. Amin, and O. Abdelwahab, "Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent", *Desalination*, vol. 223, pp. 162-173, 2008.
- [41] R.G. Lehman, and R.D. Harter, "Assessment of copper-soil bond strength by desorption kinetics", *Soil Sci. Soc. Am. J.*, vol. 48, pp. 769-772, 1984.
- [42] L. Norton, K. Baskaran, and T. McKenzie, "Biosorption of zinc from aqueous solutions using biosolids", *Adv. Environ. Res.*, vol. 8, pp. 629-635, 2004.
- [43] K.K. Krishnani, X. Meng, C. Christodoulatos, and V.M. Boddue, "Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk", *J. Hazard. Mater.*, vol. 153, pp. 1222-1234, 2008.
- [44] D. Pentari, V. Perdikatsis, D. Katsimicha, and A. Kanaki, "Sorption properties of low calorific value Greek lignites: removal of lead, cadmium, zinc and copper ions from aqueous solutions", *J. Hazard. Mater.*, vol. 168, pp. 1017-1021, 2009.
- [45] E.I. El-Shafey, "Removal of Zn (II) and Hg (II) from aqueous solution on a carbonaceous Sorbent chemically prepared from rice husk", *J. Hazard. Mater.*, vol. 175, pp. 319-327, 2010.
- [46] S.P. Mishra, D. Tiwari, and R.S. Dubey, "The uptake behavior of rice (jaya) husk in the removal of Zn (II) ions: a radiotracer study", *Appl. Radiat. Isot.*, vol. 48, pp. 877-882, 1997.

Mrs. Susmita Mishra.

Deepthi Tirumalaraju was born in Vizianagaram, AP, India, on 13th March 1986. She did her B.Tech in Chemical Engineering from Jawaharlal Nehru Tehnological University, Kakinada, AP, India, in the year 2009. She is currently pursuing her M.Tech (by Research) degree from National Institute of Technology, Rourkela, India, in Chemical Engineering Department, under the guidance of Dr.

Dr. Susmita Mishra, Associate Professor, Department of chemical Engineering, National Institute of Technology, Rourkela . M.Tech (R.E.C, Rourkela), PhD (I.I.T, Kharagpur), Post Doctorate (Southern Illinois University, Carbondale, U.S.A).