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Optimization of Process Parameters for Metal Ion Remediation using Agricultural Waste materials

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ABSTRACT: Present study shows the ability of sugarcane bagasse, to remove Zn (II) from aqueous solutions by varying the pH, adsorbent dose and agitation time. The Central Composite Face-Centered Experimental Design in Response Surface Methodology (RSM) by Design Expert Version 6.0.10 (Stat Ease, USA) was used to analyze the influence of metal ion concentration, pH and adsorbent dose on the removal of Zn (II), designing the experiments and for full response surface estimation. Batch made experiments were also carried out to access the adsorption equilibrium. The optimum conditions for maximum removal of Zn (II) from an aqueous solution of 50mg/L were as follows: adsorbents dose, 2000mg/L; pH; 6.5; and stirring speed: 250 rpm for the biosorbent. This was evidenced by the higher value of coefficient of determination (R^2= 0.9995) for sugarcane bagasse.

Keyword: Central composite face-centered design (CCFD), Biosorption, Sugarcane Bagasse, optimization

I. INTRODUCTION

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. These toxic metal ions such as zinc(Zn), chromium (Cr), lead (Pb), copper (Cu), nickel (Ni), cobalt (Co), silver (Ag), cadmium (Cd) get introduced to the aquatic streams by means of various industrial activities viz. metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic, chlor-alkali, radiator manufacturing, alloy industries, storage batteries industries, etc (Kadirvelu *et al.,* 2001a; Williams *et al.,* 1998) and these usually contain metal-ion concentrations much higher than the permissible levels and do not degrade easily into harmless end products (Gupta *et al.,* 2001), thus causing serious threats to human beings and organism.

The main source of zinc in waste water is discharging waste streams from metals, chemicals, pulp and paper manufacturing processes, steel works with galvanizing lines, zinc and brass metal works, zinc and brass plating, viscose rayon yarn and fiber production, etc. Zinc occurs in the nature as sulfide, carbonate, silicate and oxide. Zinc hydrolyzes negligibly at pH<7 but it forms different species at pH>7.

The WHO recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg/l (Dinesh Mohan *et al.,* 2002). Even acute dose of this heavy metal result in the severe gastrointestinal inflammation and liver and kidney damage dizziness, intense thirst, abdominal pain, vomiting and shock.

From wastewater, heavy metals are usually removed by precipitation technology using hydroxides, carbonates and sulphides [E.R. Christensen, *et al.,* 1982; K.A. Brantner, *et al.,* 1981; and C. Namasivayam, *et al.,* 1992) Each method has its own benefits and limitations (E. Sandau, *et al.,* 1992; J.A. Brierley, *et al.,* 1986). A variety of microbial and other biomass types has been reported to have good biosorption potential and such materials have been suggested for use in wastewater treatment for metal removal (B. Volesky, 2004; J. Wase, *et al.,* 1997; A.C.A. Costa, *et al.,* 1995; E. Rubin, *et al.,* 2005; E.W. Wilde, *et al.,* 1993).However, these procedures have significant disadvantages, namely removing metal incompletely, high reagent requirement, less efficiency, sensitive operating conditions, generation of toxic sludge or are very expensive when the contaminant concentrations are less than 100 mg L^{-1}. Otherwise, additional chemical dosage may impact the microorganism activity of subsequent activated sludge process for removal of COD.

Another powerful technology is adsorption of heavy metals by activated carbon; however the high cost of activated carbon and its loss during the regeneration restricts its application. Since 1990's the adsorption of heavy metal ions by low cost renewable organic materials has gained momentum. The utilization of seaweeds, moulds, yeasts, dead microbial biomass, insoluble starch xanthate, tree barks, onion skin, straw, coconut shell, apple residues materials for removal of heavy metals has also been explored but the problem like less efficiency, sensitive operating conditions again persisted.

Recently attention has been diverted towards the biomaterials which are byproducts or the wastes from large scale industrial operations and agricultural waste materials. An abundant source of potentially metal-sorbing biomass is agricultural wastes viz. rice husk (Bansal, *et al.,* 2009), groundnut shells, saw dust, sugarcane bagasse, corncob (U.K. Garg, *et al.*, 2007), groundnut hulls, and wheat bran etc. These are widely available, inexhaustible, and inexpensive material that exhibit significant specificity for the targeted heavy metal ions. All lignocellulosic resources contain polyphenolic compounds such as tannins and lignins as common properties which are believed to be the active sites for attachment of heavy metal cations. These are effective adsorbents for a wide range of solutes, particularly for divalent metal cations. These resources, once used for heavy metal removal, can be regenerated by eluting the metal ions using different dilute acids to get soluble metal salts, and can be used repeatedly. The process involves application of various low cost agricultural waste materials either in the raw /natural form or doping with some chemical groups. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, and regeneration of biosorbents and possibility of metal recovery.

In the present study a natural low cost biosorbent viz; sugarcane bagasse (SCB), have been selected for the removal of the toxic metal such as zinc from the simulated solutions using Central Composite Design, which is a useful mathematical and statistical method for analyzing the effects of several independent variables on process outcomes (response) (Myers and Montgomery, 2002; Draper and John, 1988). Usually, this process employs a low-order polynomial equation in a pre-determined region of the independent variables, which is subsequently analyzed to identify the optimum values of the independent variables for the best response. The efficiency of this process depends on various factors varying from the type of metal ion studied and the type of biosorbent material used. The classical method involves changing one independent variable parameter while maintaining all others at a fixed level which is extremely time consuming and expensive for a large number of parameters. To overcome this difficulty, some statistical methods have been used. RSM can be employed to optimize the biosorption of heavy metal. The design experiments were already used to recover metals from industrial effluents (Kaminar, Ruotolo and N.M.S. Kaminari, 2007). Optimization process involves three major variations: performing the statistically designed experiments, estimating the coefficient in a mathematical model, and predicting the response and checking the adequacy of the model (Muthukumar, 2004).

II. MATERIALS AND METHOD

A. Materials

SCB used in the study was procured from a sugar-mill located in Punjab (India). The collected bagasse was dried under sun and pith was separated manually. Pith was boiled with distilled water for 30 min to remove soluble sugars present in it. The material so obtained was dried at 120°C in hot air oven for 24 h, and then the material was grinded and sieved through the sieves of 150 microns size.

B. Methods

All standard Zn (II) solutions were prepared from Zn $(NO_3)_2{\cdot}6H_2O$and the solution Ph was adjusted with 0.01M HCl and NaOH solutions (AR Grade, Merck). The concentration of Zn (II) in aqueous solution was determined by atomic absorption spectroscopy (Draper & John, 1988) using a Varian, double beam, atomic absorption spectrophotometer, model SpectrAA-20. The Zn (II) concentration of a sample was estimated using a calibration curve (absorbance versus concentration) prepared using standard concentration of Zn (II) solutions. Calibration curves were prepared for each of the different pH values tested since the curves varied with pH.

The adsorption of Zn (II) from aqueous solution on to sugarcane bagasse was performed in a static mode. Experiments were performed according to the central composite design (CCD) matrix as per the design expert. To Each 50 Ml solution of known Zn (II) concentration and pH, a desired quantity of the adsorbents was added in 250 mL Erlenmeyer flask.

The mixture was agitated in an orbital shaker at room temperature at desired speed for predetermined time intervals (60 min). The supernatant was separated by centrifugation at 4000 rpm for 10 min. The residual concentration in supernatant was determined. The response, i.e., removal efficiency of Zn (II) was calculated as;

$$Y(\%) = \frac{(C_o - C_t)}{C_o} x100 \qquad \ldots(1)$$

All experiments were carried out in triplicate and the mean values are reported. The maximum deviation was found to be 3%, which is non significant.

C. Experimental design for optimization of parameters

The optimization of Zn (II) uptake was carried out by three chosen independent process variables with six star points (a=1) and six replicates at centre points, according to central composite face-centered (CCFD) design. The range and the level of the variables are given in Table 1. The amount of metal uptake (Y) was taken as the response of the design experiments. The quadratic equation model for predicting the optimal point was expressed according to Eq. (2).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta x_i x_j + \varepsilon \qquad (2)$$

Table 1: The central composite design for three independent variables and different adsorbents.

Values of the Variables			Adsorption (%)
Dose (A)	**pH** (B)	**rpm** (C)	**SCB**
2000.00	3.60	100.00	19.38
1250.00	5.05	175.00	46
1250.00	5.05	175.00	45
1250.00	5.05	48.87	31.07
500.00	3.60	100.00	12
500.00	3.60	250.00	13.74
1250.00	5.05	301.13	52.5
500.00	6.50	250.00	21.45
1250.00	5.05	175.00	45
11.34	5.05	175.00	9
1250.00	7.49	175.00	64.17
500.00	6.50	100.00	35.4
2000.00	6.50	250.00	95
2511.34	5.05	175.00	73.8
1250.00	5.05	175.00	45.5
1250.00	5.05	175.00	45
1250.00	2.61	175.00	15
2000.00	6.50	100.00	68.45
2000.00	3.60	250.00	57
1250.00	5.05	175.00	45

Three factors were studied and their low and high levels are given in Table 1. Percentage adsorption was studied with a standard RSM design called central face composite design (CCD). Twenty experiments were conducted in duplicate according to the scheme mentioned in Table 2. Design Expert Version 6.0.10 (Stat Ease, USA) was used for regression and graphical analysis of the data obtained. The results for each trial performed as per the experimental plan. The application of the response surface methodology based on the estimates of the parameters indicated an empirical relationship between the response and input variables expressed by the following quadratic models.

Response SCB = $45.26 + 19.56A + 14.17B + 6.44C - 1.54A^2 - 2.05B^2 - 1.27C^2 + 7.0AB + 9.55AC - 3.35BC$ …(3)

Where A, B and C are three independent variables

Table 2: Experimental range and levels of independent variables.

		Range and levels (coded)				
Factors		−1.682	−1	0	+1	+1.682
Adsorbent dose (mg/L)	A	159.10	500	1000	1500	1840.9
pH	B	2.48	3.5	5.0	6.5	7.52
Stirring speed (rpm)	C	65.91	100	150	200	234.09

The statistical significance of the quadratic model was evaluated by the analysis of variance (ANOVA) as presented in Table 3. The results showed that this regression was statistically significant at *F* value of 2833for SCB and values of prob>*F* (<0.0001). Value of coefficient of Variance, Predicted R^2 and adjusted R^2 showing values close to 1 shows high significance of the model. The ANOVA has also been analyzed on for second-order response surface model and the results are given in Table 3. The significant of each coefficient was determined by *F*-values and *p*-values, which are listed in Table 3. The larger the magnitude of the *F*-values and the smaller *p*-values, the more significant is the corresponding coefficients. In this case, the first-order main effects, square effects and interaction effects of initial solution pH, stirring speed and biomass dosage were significant model terms. The p-value in the Analysis of Variance (ANOVA) was less than 5% of the computed F-values indicating that both models were significant at a high confidence level (95%). The p-value probability was also relatively low ($p < 0.05$), indicating the model's significance. Therefore indicating a moderate degree of correlation between the response and the independent variables in Fig. 1a, and a high degree of fitting in Fig 1b demonstrate this correlation between predicted and experimental values.

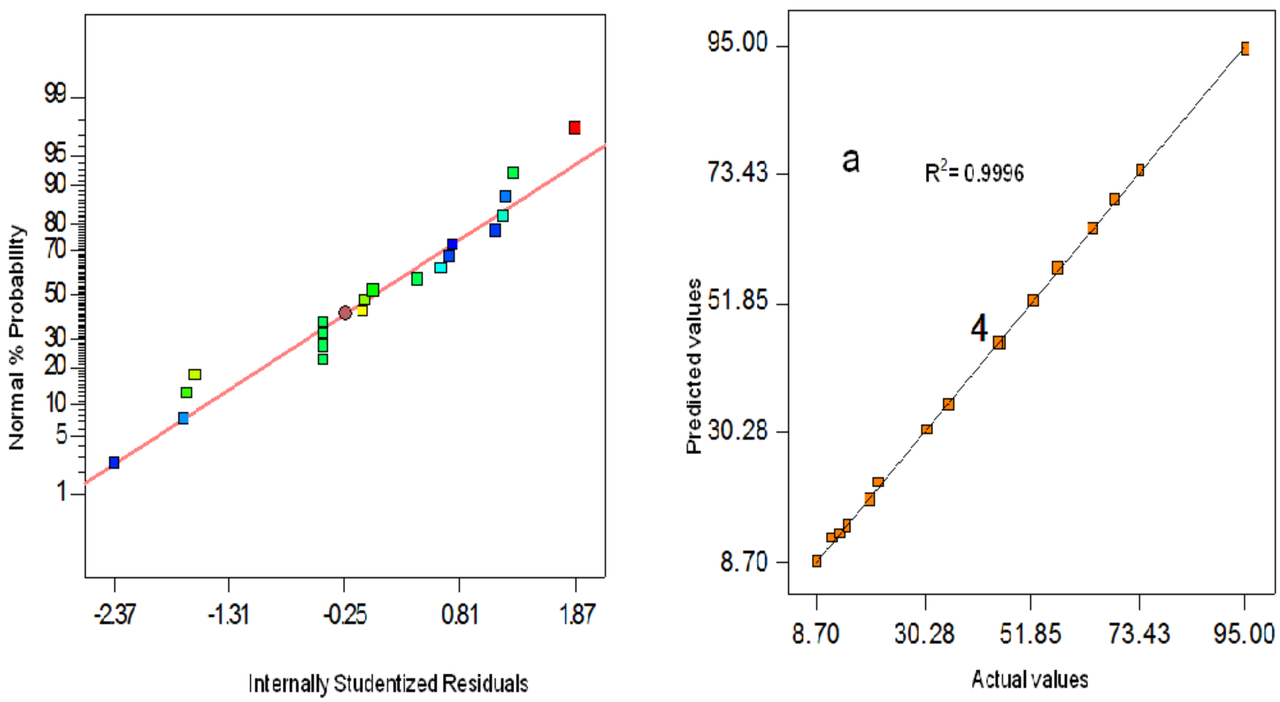


Fig. 1. a) Normal probability plot of residuals b) Actual Vs Predicted value plot.

Table: 3: Analysis of Variance (ANOVA) for Quadratic Model for Zinc Adsorption

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	10020.53	9	1113.39	2833.88	< 0.0001	S
Lack of Fit	3.05	5	0.61	3.49	0.0982	NS
Mean	35234.65	1	35234.65			
Quadratic	99.62	3	33.2184.52		<0.0001	S

R^2= 0.9928; Adjusted R^2=0.9995; Predicted R^2= 0.9982;CV: 1.24

Table 4: Optimal Zn (II) adsorption conditions from the model.

Parameters	Adsorbent dose	pH	Stirring speed	Response (%)
Parameters(given by model)	2000	6.5	250	95
Suggested solution		6.5	200	96
Actual results obtained after	1500	6.5	200	96

D. Optimization of Process Parameters

After optimizing the process parameters viz; stirring speed, adsorbent dose and pH, experiments were performed and effect of each parameter separately as well as combined effect was analyzed using contour and 3-D models. In the numerical optimization, a minimum and a maximum range has been selected for each parameter included. Each point on this range has given some weight to adjust the shape of its particular desirability function. The ouput desired is then combined into an overall desirability function. This range has been selected from minimum to maximum. In this study particularly the program seeks to maximize this function. The goal seeking begins at a random starting point and proceeds up the steepest slope to a maximum. Central face design response method was applied for optimization any combination of three parameters, namely the pH, stirring speed and adsorbent dose. The range of process parameters is shown in Fig. 1 with desirability of around 95 % with SCB.

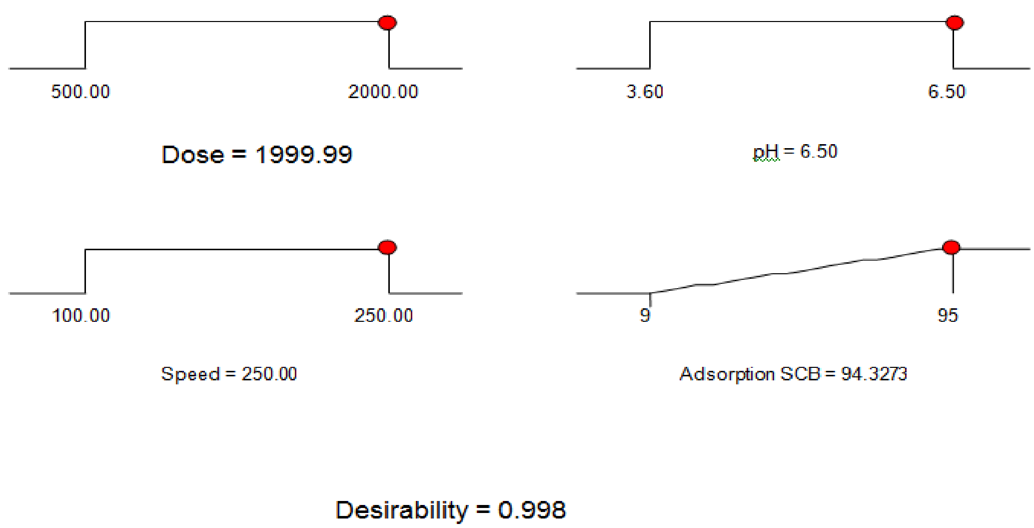


Fig. 2. Range of Process Variables with Metal Ion Removal Desirability.

Removal of Zn (II) using sugarcane bagasse

Fig. 3 shows the individual as well as combined trend of metal removal by varying pH, adsorbent dose and stirring speed. This is very clear from the figure that with increase in pH and SCB dose, the removal efficiency increases. Contour plots also shows outward trend, indicating that at pH 6.5, adsorbent dose of 20g/L and stirring speed of 250 rpm removal efficiency is maximum.

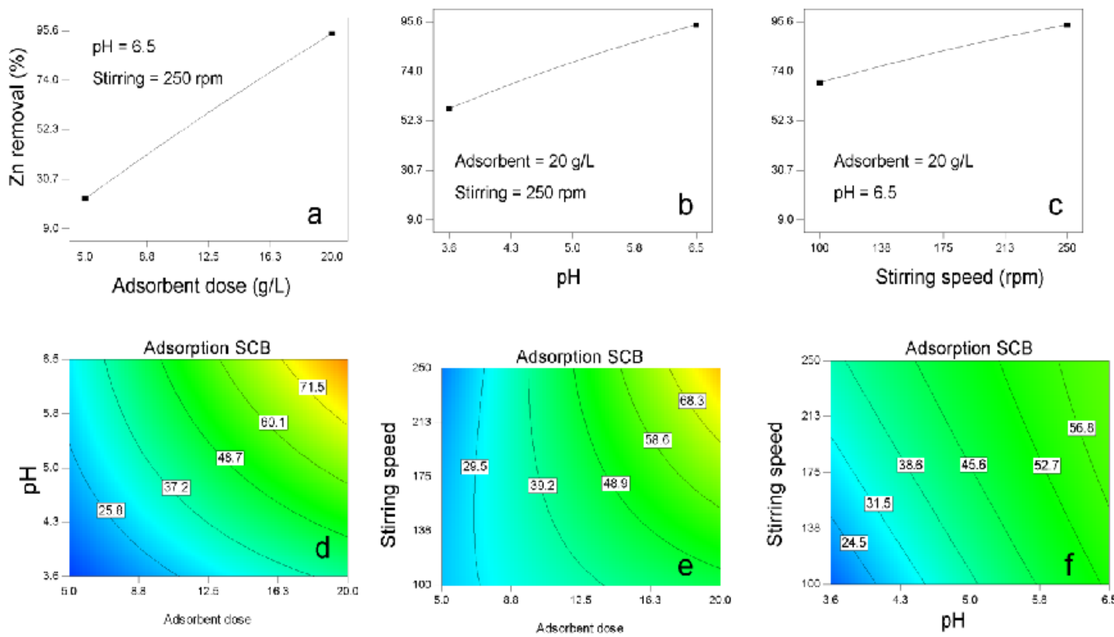


Fig. 3. One Variable Plot and Contour Plot Showing effect of different Process Variables using SCB Adsorbent.

III. RESULTS

A. Effect of pH and Adsorbent Dose

To investigate the combined effect of pH of the system and adsorbent dose, the RSM was used and results were shown in the form of contours and 3D plots. Figs. 3 and 4 show that with increase in pH, the removal efficiency increases with adsorbent dose. For instance from Fig. 3, (at pH _5.0, adsorbent dose 500 mg) the removal efficiency was 48% which increased to 65% with pH 6.0 and adsorbent dose1000 mg. The optimum value of both the factors, viz, pH and adsorbent dose can be analyzed by saddle point or by checking the maxima formed by the X and Y coordinates.

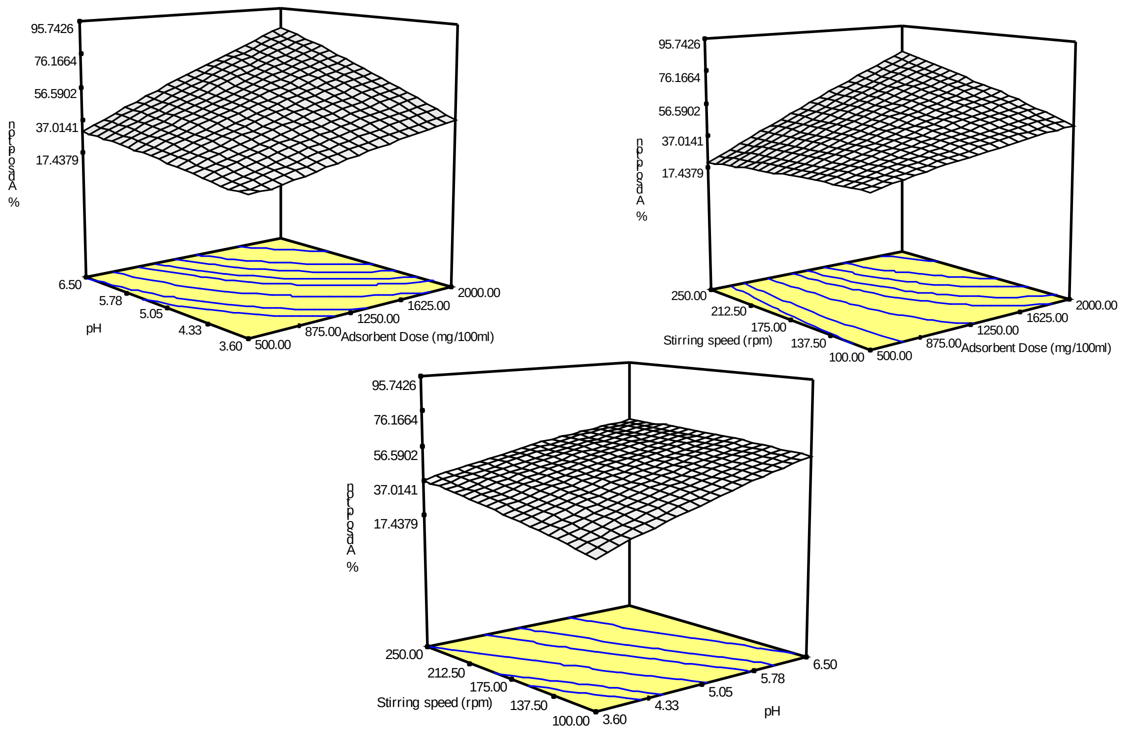
B. Effect of stirring speed and Ph

Fig. 3 show the effect of stirring speed on the percentage adsorption of Zinc metal ions under the predefined conditions given by Design Expert Version 6.0.10.

Graphs show that the maximum adsorption occurs under the medium stirring conditions (150 rpm) at pH 6.5 which is in accordance with the model.

C. Effect of stirring speed and adsorbent dose

Combined effect of stirring speed and adsorbent dose has been analyzed from the CCFD and it has been estimated that the points of maxima for stirring speed and adsorbent dose are at 150 rpm and 2000 mg, respectively. Figs. 2 and 3 shows that stirring speed has minimum impact of all the three parameters as two maxima has been found in case of stirring speed, so from the contour plots and 3D graphs the optimum value of the stirring speed has been found at 150 rpm.



3-D Plots Showing effect of different Process Variables using SCB Adsorbent

Fig. 4. 3-D Plots Showing effect of different Process Variables using SCB Adsorbent.

IV. CONFIRMATION EXPERIMENTS

Further to support the optimized data as given by numerical modeling under optimized condition, the confirmatory experiments were conducted with the parameters as suggested by the model (pH 6.5, adsorbent dose 1500 mg and stirring speed 200 rpm) and the removal efficiency was found to be 79% (Table 4). The effect of pH, stirring speed and adsorption dose were also studied to support the results and data is in accordance with the results obtained from optimized conditions. Further studies on the adsorption kinetics of the system and effect of the metal ion concentration on the removal efficiency was also analyzed and it was found that results are in accordance with the suggested model given by RSM software.

V. CONCLUSIONS

Study showed that sugarcane bagasse is a potential biosorbent for the removal of Zinc from aqueous solution with a percentage removal efficiency of 95% with an adsorbant dose of 2 gm/L, ph 6.5 and 250 rpm.

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