# Remediation of Cadmium Ions from Aqueous Media through Chemically Modified *Saccharum arundinaceum*: Prediction through Modeling Techniques

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**Summary:** Adsorption is a cost effective and green technology for the removal of hazardous chemicals from aqueous media. In current work, remediation of cadmium ions from aqueous media is performed by employing chemically modified *Saccharum arundinaceum*. Sorbent was pretreated with acid and base, separately, to check the effect of these chemicals on its adsorption potential and base treated sorbent was selected for further analysis, due to its higher sorption potential (97.5%) for $Cd^{2+}$. Characterization of sorbent was carried out by recording FTIR spectra for determination of functional groups and SEM for evaluation of surface morphology. FTIR spectra reflect suitability of sorbent material for removal of $Cd^{2+}$ due to presence of abundant –OH groups on sorbent surface, which may develop strong binding with sorbate. SEM results exhibited presence of cylindrical cavities on sorbent surface, endorsing viability of sorbent for the removal of $Cd^{2+}$. $2^4$ full factorial design (FFD) was employed to optimize the experimental conditions. Experimental results of adsorption process were compared with the predicted results; obtained by first-order model of FFD and Artificial Neural Network (ANN). In FFD, all the possible combinations were used and predicted model was generated for application on experimental setup. Similarly, ANN was used to obtain predicted response by multi-layer perceptron (MLP) method. Predictive analysis, carried out by both the modeling techniques, yielded comparable results, i.e. FFD (0.9852) and ANN (0.9788); revealing good prediction ability of both the modeling techniques.

**Key Words**: *Saccharum arundinaceum*, Adsorption, ANN, Full Factorial Design, Sorbent Modification.

## Introduction

Rapid increase in urban population has resulted in proportionate inadequacy of water resources to fulfill the requirement of human consumption as well as of industrial processes. Among different strategies to overcome this alarming situation, there is dire need to review our utilization patterns of water resources [1]. Among the different sources of water pollution, industrial effluents contribute potential hazards to ecosystem. They introduce a range of contaminants such as heavy metals, dyes or phenolics to soils and different water bodies [2]. Toxic metals are frequently discharged by various industrial units such as mining, painting, coating, extractive metallurgy and nuclear units, which cause contamination of freshwater and marine environment [3, 4]. These heavy metals are the major pollutants in marine and groundwater [5]. Heavy metals have long biological half-lives, usually get accumulated in different body parts causing side effects and are non-biodegradable [6]. Arsenic, copper and cadmium are particularly reported as toxic metals for humans as well as for animals. Cadmium is one of the toxic metals, present in water, in the form of organic and inorganic compounds [7]. It is toxic even at trace level and is involved in causing renal toxicity, hypertension, weight loss, fatigue, lymphocytosis, pulmonary fibrosis, atherosclerosis, peripheral neuropathy, lung cancer, osteoporosis, and hyperuricemia [8]. All these effect reveal the dire need to remove it from all aqueous media. Heavy treatment cost of industrial effluents is the main restriction in its removal. In order to develop cost-effective alternatives, natural processes and agrowaste materials are potentially used [9].

Adsorption is considered cheaper and green technology for the remediation of $Cd^{2+}$ as well as other toxic heavy metals from industrial effluents [10]. It is a surface phenomenon; effectively used in industrial processes for purification of underground water and wastewater [11]. Zero cost of raw materials, used as sorbents; make it convenient, economical in addition to being comparably effective and green technique [12]. Activated carbon is reported to be one of the most potential sorbents but its cost warrants its usage at major scale. Therefore, there exists a need for the exploration of low-cost and abundantly available materials, preferably agrowastes, which may be opted at large scale [13]. Number of waste biomasses such as rice husk, lemon peel, moringa leaves has been successfully explored as potential sorbents [14, 15]. In continuation of these series of investigations, sorption potential of *Saccharum* is planned to be evaluated for the removal of $Cd^{2+}$ from aqueous media. It is an important genus of grass family, which is abundantly available in Pakistan. This genus includes variety of plants like *Saccharum bengalense*, *Saccharum narenga*, *Saccharum munja*, and *Saccharum officinarum* [16].

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To evaluate the sorption potential, it is necessary to optimize different parameters affecting the efficiency of sorption process. For the purpose, full factorial design (FFD) is considered an effective statistical approach to optimize experimental conditions with minimum experimental data [16]. It is also applied on experimental results to generate predictive models to predict adsorption potential of a particular sorbent. However, in recent studies, Artificial Neural Network (ANN) has got recognition for model development and prediction. ANN is based on idea of human brain, which involves input neurons, hidden neurons and output neurons. Experimental data utilized for FFD is considered sufficient for generation and development of ANN models [16-18].

To evaluate possible improvement in sorption potential of *Saccharum arundinaceum*, it is chemically modified and potential is determined by employing full factorial design of experiment. Viability of both the techniques, i.e. ANN and FFD was compared for predictive power and experimental design. These predictive models can be applied, on other elements, for prediction of their adsorption potential onto *Saccharum arundinaceum*, without experimentation. Predictive models, generated in present study, are a significant contribution as cheaper and time saving methods for prediction of adsorption potential of unexplored materials.

## Experimental

*Saccharum arundinaceum* stem was used as sorbent in present study and was collected from vicinity of Sargodha city, Pakistan. After collection, sample was properly washed with deionized water followed by drying at 105 °C for 24 h in an electric oven (Model, LEB-1-20). Dried adsorbent material was ground to appropriate particle size and stored at -4 ºC till further analyses.

### *Pretreatment of Sorbent Material*

*Saccharum arundinaceum* stem were pretreated with HCI (0.1 M) and NaOH (0.1 M), separately, to evaluate the effects of acid- and base-treatments on pore size, i.e. pore area, pore volume and sorption capacity. For chemical treatment, ground sorbent (20 g) was stirred for 4 h in NaOH (0.1 M, 1L) or HCl (0.1 M, 1L) followed by filtration and extensive washing with distilled water to remove any residual traces of acid/base. After washing, treated sorbent material was dried at 110 °C and stored in airtight zipper bags at -4 ºC till further use.

### *Characterization of Sorbent*

To determine physical and chemical characteristics of sorbent material, affecting efficiency of adsorption process, it is necessary to characterize the sorbent. Therefore, chemical characterization of sorbent was carried out by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR).

### *Scanning Electron Microscopy (SEM)*

Surface analysis was performed using Scanning Electron Microscope (SEM) JEOL model 2300. Sorbent material was scanned under optimized set of conditions, under Argon atmosphere by employing platinum coating to avoid charge indulgence at 6 mA.

### *Fourier Transform Infrared Spectroscopy (FTIR)*

For the determination of structural functional groups, Fourier Transform Infrared Spectrophotometric analysis was conducted (Model Shimadzu AIM-8800). Diffused Reflectance Infrared Technique (DRIFT) was used for analysis, using KBr as background reagent. Purpose of using KBr was to facilitate the passage of IR radiations through sample, as IR radiations can pass through ionic salts like KBr. For this purpose, sample was finely ground and mixed with KBr under high pressure for the development of pellets, which were then subjected to spectrometer for analysis.

### *Instruments and Chemicals*

Adsorption of $Cd^{2+}$ was determined by using Flame Atomic Absorption Spectrometer (FAAS), Model Schimadzu AA 6300. All the chemicals used, in present work, were of analytical grade. Working solutions of cadmium were prepared by diluting the stock solution (1000 mg/l) of Cd $(NO_3)_2.4H_2O$, in deionized water.

### *Adsorption Experiments*

Adsorption experiments were carried out, in batch process, by using aqueous solution of $Cd^{2+}$. For this purpose, 100 ml standard solution of Cd was taken in 250 ml Erlenmeyer flask, containing known amount of sorbent (0.5-2 g) followed by shaking the contents of flask at 150 rpm for 40-120 min. Variable parameters were sorbate concentration (30-90ppm), pH (3-12), contact time (40-120 min) and sorbent dose (0.5-2 g). Adsorbent (0.5-2 g) was added in $Cd^{2+}$solution (100 mL) and resulting mixture was shaken at constant speed of 150 rpm for required interval (40-120 minutes), followed by filtration. Adsorbed amount of $Cd^{2+}$ was determined, by determining the remaining amount of $Cd^{2+}$in filtrate, by Flame atomic absorption spectrometry (FAAS). Parameters were set one by one and efficacy of sorption process was evaluated.

*Predictive Modeling and Optimization*

Two types of predictive models, i.e. Full factorial design (FFD) and Artificial Neural Network (ANN) were applied on the experimental data to predict the sorption potential of sorbent employed:

*Full Factorial Design*

To determine the adsorption of $Cd^{2+}$ onto *Saccharum arundinaceum*, a $2^4$ full factorial design was applied. Factorial design of analysis facilitates to check the effect of all the parameters on adsorption phenomenon and mutual interaction of these parameters as well. Four independent variables including, pH ($X_1$), initial concentration ($X_2$), contact time ($X_3$) and sorbent dose ($X_4$) were used in this study. Predicted response *i.e.* adsorption was taken as dependent variable and it was calculated by employing equation 1 generated by employing all the possible combinations of variable parameters.

*Artificial Neural Network*

Artificial Neural Network (ANN) is considered a valuable technique for data analyses by linear and non-linear mechanisms [19]. Concept of this model is taken from human nervous system and is based on several neurons, which are organized in the form of layers. These layers include input layer, hidden layer and output layer. Neurons are used to transfer signals from input layer to output layer through hidden layer. It generates relationship between dependent and independent variables through interconnected neurons [20]. In present study, selected descriptors were taken as continuous input signal and adsorption as output signal in ANN development. Statistica 10 was applied for generation of automated artificial neural network.

**Results and Discussion**

*Effect of Pretreatment*

To estimate the effect of acid and base treatments on adsorption potential of *Saccharum arundinaceum* stem, sorbent material was pretreated following the above mentioned procedure. Results reveal that base-treated Saccharum *arundinaceum* exhibited the highest sorption efficiency for $Cd^{2+}$ (97.5%) as compared to raw (91.15%) and acid treated (57.6) forms of the same sorbents (Fig. 1). Adsorption capacity of sorbent depends upon its structural functional groups and its microporous structure [21]. Enhancement of sorption capacity, upon treatment with base, may be due to increase in concentration of hydroxyl groups on sorbent surface or modification of sorbent cell wall by base-action [22]. As cell wall is porous in nature and allows the accessibility of aqueous solution to cell components. Base treatment is reported to be enhancing the adsorption potential of cell wall by affecting area exposed for sorption [23]. Decrease in adsorption efficiency of sorbent, upon acid-treatment, was found because the surface binding sites get significantly reduced due to action of acid; as acid removes hydroxyl groups from the surfaces, which are mainly responsible for attachment on sorbent surface [24]. So base-treated *Saccharum arundinaceum* was used for generation of predictive models by factorial design of analysis.

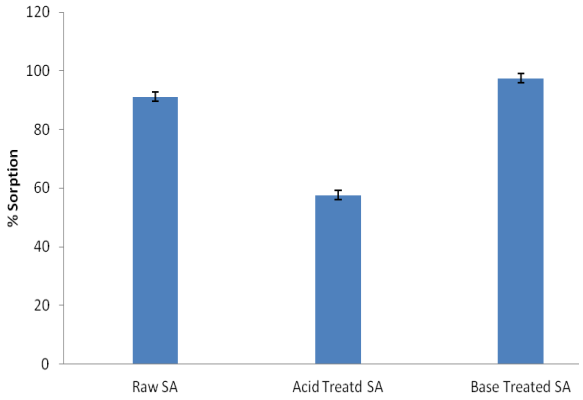


Fig. 1: Effect of chemical treatment on sorption potential of *Saccharum arundinaceum* stem for the removal of $Cd^{2+}$ from aqueous solutions.

*Characterization of Sorbent*

*Saccharum arundinaceum* stem was characterized for assessment of surface morphology and functional group determination by Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR), respectively.

*Scanning Electron Microscope (SEM)*

For morphological surface analysis, Scanning Electron Microscope (SEM) JEOL model 2300 was utilized. Raw, acid-treated and base-treated forms of *Saccharum arundinaceum* stem were analyzed to study surface morphology. Micrographs (Fig. 2) reveal the presence of hollow cavities in the structure of raw sorbent, which are assumed to be responsible for binding of sorbate onto sorbent surface. Acid-treatment decreased these cavities by deforming sorbent surface, surface becomes smooth and thin adsorption layer is formed on the sorbent surface, so magnitude of adsorption decreased. Surface of raw and base-treated sorbent was found rough, containing cylindrical pores, which makes possible multilayer and thick adsorption on sorbent surface as compared to smooth surface. Results obtained in SEM micrograph are in good agreement with the previously reported data [25].

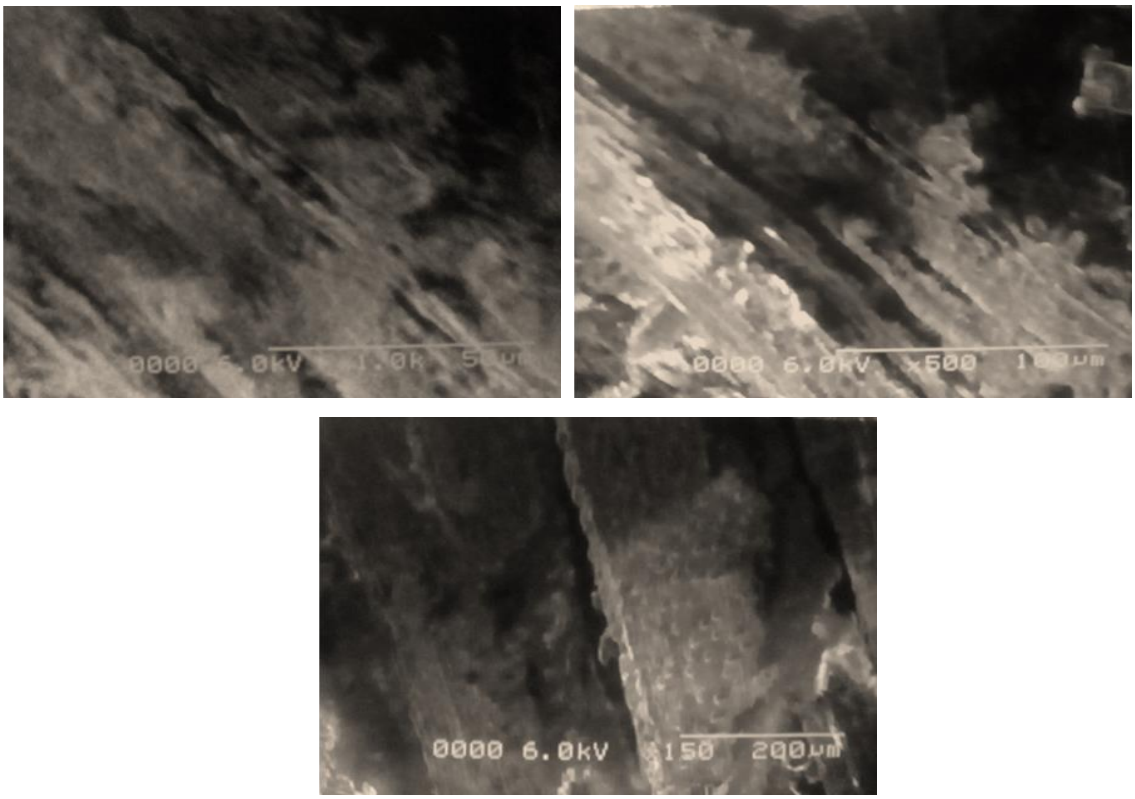


Fig. 2: (a) SEM image of raw *Saccharum arundinaceum* at three different resolutions.

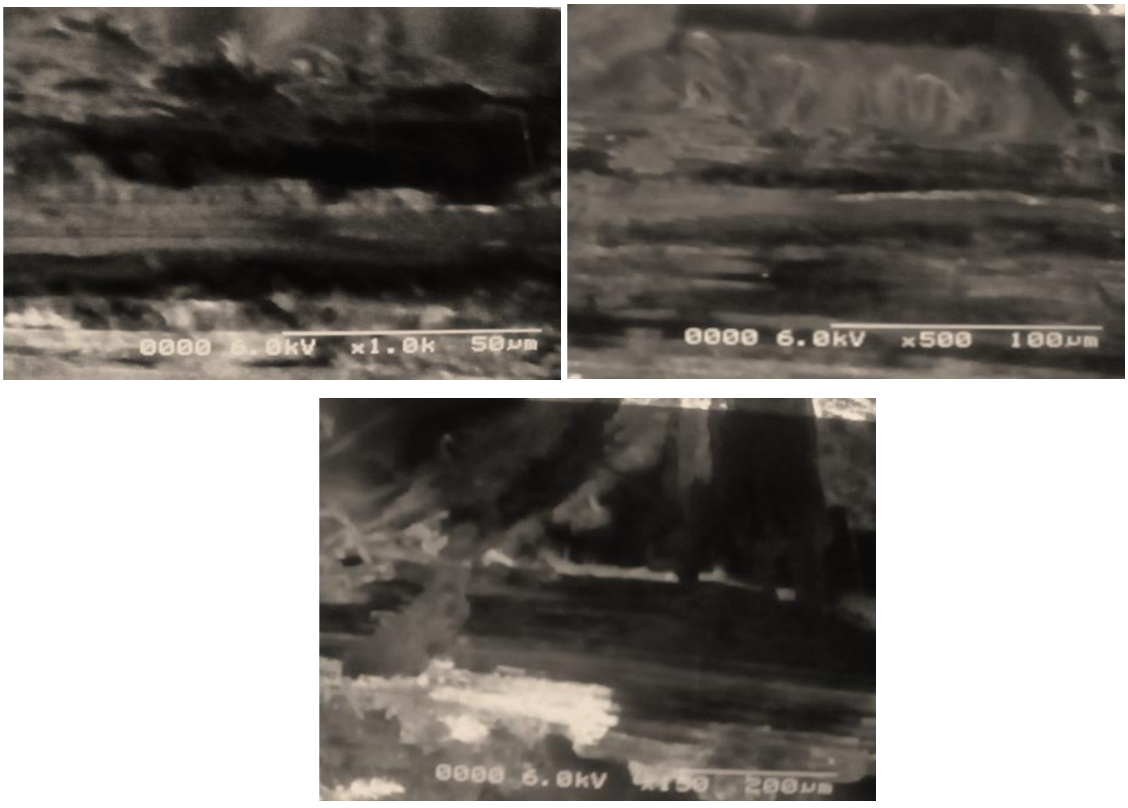


Fig. 2: (b) SEM image of base-treated *Saccharum arundinaceum* at three different resolutions.

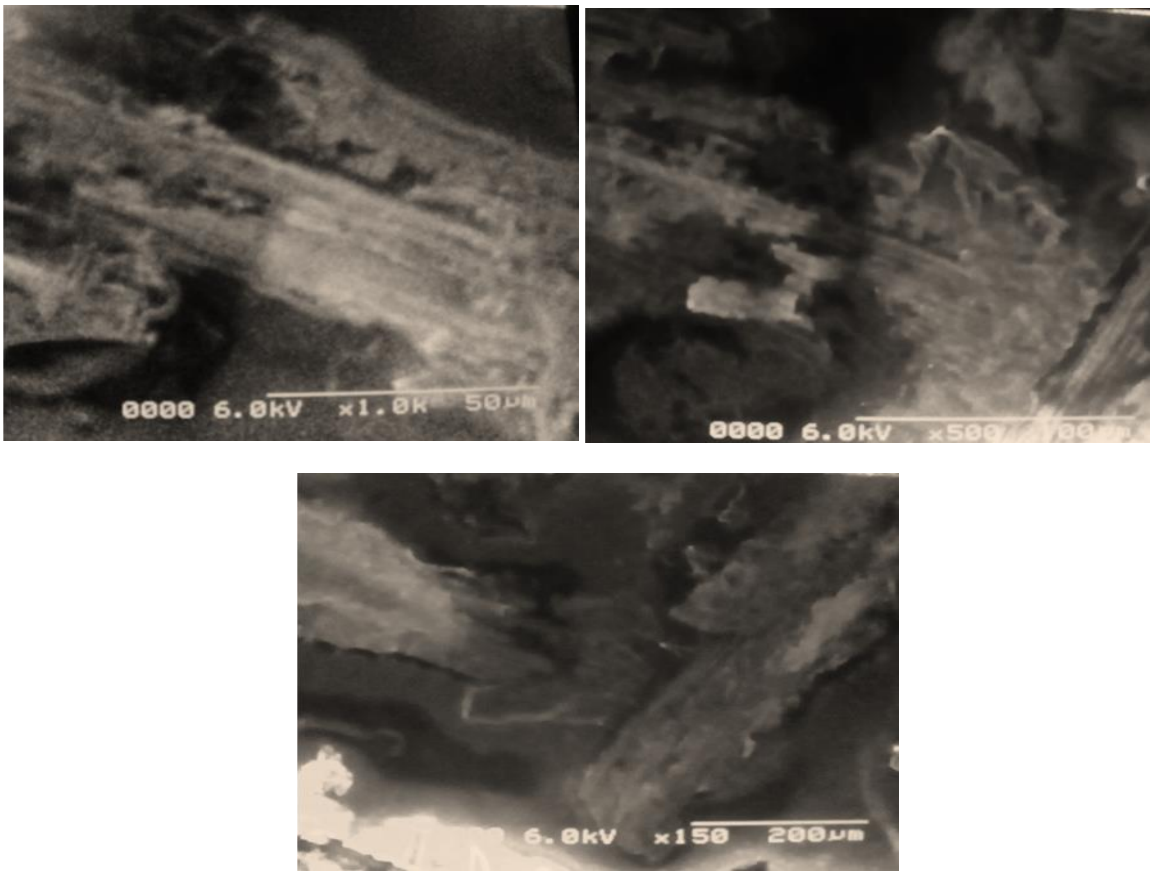


Fig. 2: (c) SEM image of acid-treated Saccharum arundinaceum at three different resolutions.

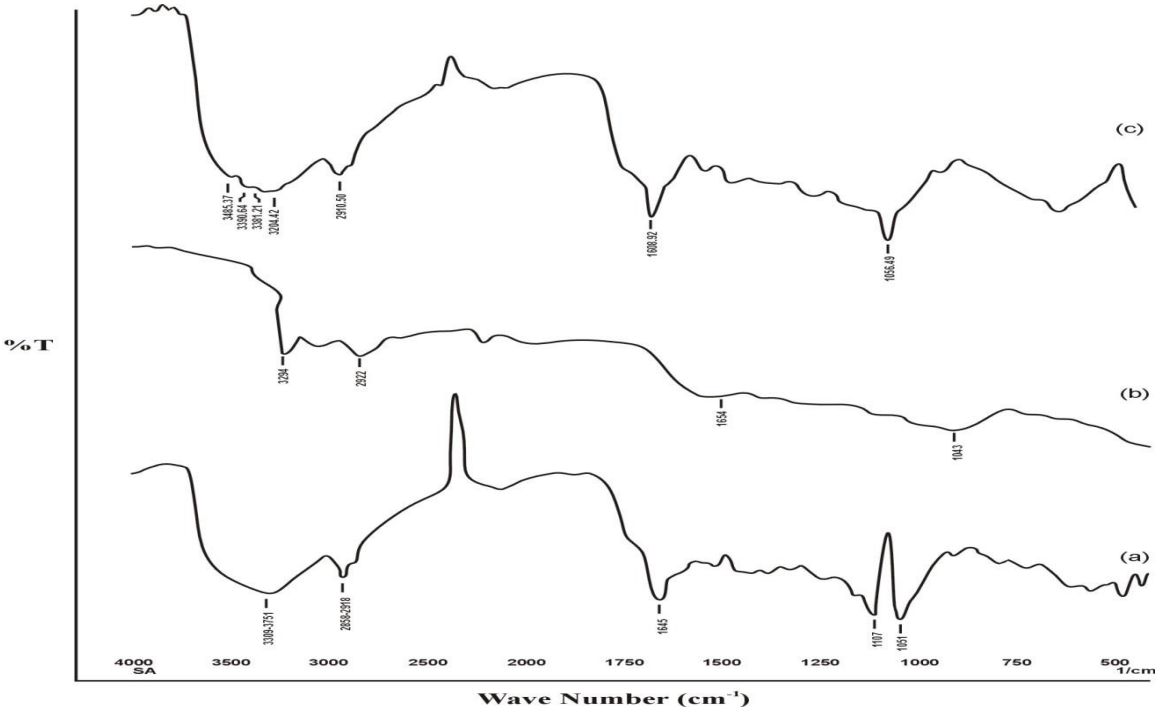


Fig. 3: FTIR spectra of *Saccharum arundinaceum* (a) base-treated (b) acid-treated (c) raw.

*Fourier Transform Infrared Spectroscopy (FTIR)*

Fourier transform infrared spectrometric (Model Shimadzu AIM-8800) analysis was carried out to determine the structural functional groups present in *Saccharum arundinaceum* stem. Nature of functional groups, especially surface active part of a functional group, determines the ease and strength of binding between sorbent and sorbate species [26]. Major functional groups identified in FTIR spectra of *Saccharum arundinaceum* stem are presented as Fig. 3. A broad band present at 3000-3700 $cm^{-1}$ may be due to stretching vibrations of hydroxyl group, which may develop hydrogen bonding with sorbates. This band appeared in FTIR spectra of raw and base-treated forms of sorbent but, amazingly, disappeared in acid-treated form of *Saccharum arundinaceum*, which may be attributed to the reaction between –OH group of sorbent with hydrogen ions contributed by acid. Stretching band of –CH appears in 2900-3000 $cm^{-1}$ wavenumber range for all the sorbents. Peak at 1750 $cm^{-1}$ appear due to C=O and 1200 $cm^{-1}$ due to C-O functional group. In some cases, –CN bending bands also appear at 1049 $cm^{-1}$. Absorption band due to stretching of secondary amides appears at 1645 $cm^{-1}$. For the purpose of adsorption, significant role is played by –OH group and heteroatoms to attach the sorbate on sorbent surface.

*Predictive Modeling by Full Factorial Design*

Adsorption experiment was carried and experimental results obtained for adsorption of $Cd^{2+}$ onto *Saccharum arundinaceum* are listed in Table-1. To check the effect of all the four parameters on adsorption process, $2^4$ full factorial design was employed. Equation used for this purpose is as follows,

*Predicted Response (Rp)* = $b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_1X_2 + b_6X_1X_3 + b_7X_1X_4 + b_8X_2X_3 + b_9X_2X_4 + b_{10}X_3X_4 + b_{11}X_1X_2X_3 + b_{12}X_2X_3X_4 + b_{13}X_1X_3X_4 + b_{14}X_1X_2X_3X_4$ **1**

Here $X_1$, $X_2$, $X_3$ and $X_4$ represent pH, initial concentrate of sorbate, contact time and amount of sorbent, respectively while their products in various combinations represent the interaction of parameters [27]. A linear model given in equation 1 was applied for regression fit and predictive response was calculated, as presented in Table-2. Results of model are found very close to experimental results with low value of % variance.

Table-1: Design matrix and results for adsorption of $Cd^{2+}$ on *Saccharum arundinaceum.*

| Run | $X_1$ (pH) | $X_2$ (Time) | $X_3$ (Initial Conc.) | $X_4$ (Sorbent dose) | Measured Response (% Sorption) |
|---|---|---|---|---|---|
| 1 | -1 (3) | -1 (30) | -1 (40) | -1 (0.5) | 40.3965 |
| 2 | -1 (3) | -1 (30) | +1 (120) | -1 (0.5) | 65.6525 |
| 3 | -1 (3) | +1 (90) | -1 (40) | -1 (0.5) | 90.2175 |
| 4 | -1 (3) | +1 (90) | +1 (120) | -1 (0.5) | 98.1455 |
| 5 | +1 (12) | -1 (30) | -1 (40) | -1 (0.5) | 36.0945 |
| 6 | +1 (12) | -1 (30) | +1 (120) | -1 (0.5) | 34.4225 |
| 7 | +1 (12) | +1 (90) | -1 (40) | -1 (0.5) | 98.6055 |
| 8 | +1 (12) | +1 (90) | +1 (120) | -1 (0.5) | 93.4295 |
| 9 | -1 (3) | -1 (30) | -1 (40) | +1 (2) | 18.069 |
| 10 | -1 (3) | -1 (30) | +1 (120) | +1 (2) | 7.949 |
| 11 | -1 (3) | +1 (90) | -1 (40) | +1 (2) | 53.211 |
| 12 | -1 (3) | +1 (90) | +1 (120) | +1 (2) | 28.931 |
| 13 | +1 (12) | -1 (30) | -1 (40) | +1 (2) | 11.85 |
| 14 | +1 (12) | -1 (30) | +1 (120) | +1 (2) | 6.986 |
| 15 | +1 (12) | +1 (90) | -1 (40) | +1 (2) | 55.146 |
| 16 | +1 (12) | +1 (90) | +1 (120) | +1 (2) | 40.874 |

Table-2: Validity of the FFD model by experimental and calculated response.

| Run | $X_1$ | $X_2$ | $X_3$ | $X_4$ | Experimental Response | Calculated Response by FFD | % Variation |
|---|---|---|---|---|---|---|---|
| 1 | 3 | 30 | 40 | 0.5 | 35.2 | 40.3965 | 5.1965 |
| 2 | 3 | 30 | 120 | 0.5 | 67.06 | 65.6525 | 1.4075 |
| 3 | 3 | 90 | 40 | 0.5 | 95.26 | 90.2175 | 5.0425 |
| 4 | 3 | 90 | 120 | 0.5 | 96.18 | 98.1455 | 1.9655 |
| 5 | 12 | 30 | 40 | 0.5 | 40.86 | 36.0945 | 4.7655 |
| 6 | 12 | 30 | 120 | 0.5 | 31.66 | 34.4225 | 2.7625 |
| 7 | 12 | 90 | 40 | 0.5 | 93.36 | 98.6055 | 5.2455 |
| 8 | 12 | 90 | 120 | 0.5 | 94.55 | 93.4295 | 1.1205 |
| 9 | 3 | 30 | 40 | 2 | 23.13 | 18.069 | 5.061 |
| 10 | 3 | 30 | 120 | 2 | 6.1 | 7.949 | 1.849 |
| 11 | 3 | 90 | 40 | 2 | 48.16 | 53.211 | 5.051 |
| 12 | 3 | 90 | 120 | 2 | 30.73 | 28.931 | 1.799 |
| 13 | 12 | 30 | 40 | 2 | 6.56 | 11.85 | 5.29 |
| 14 | 12 | 30 | 120 | 2 | 8.1 | 6.986 | 1.114 |
| 15 | 12 | 90 | 40 | 2 | 60.46 | 55.146 | 5.314 |
| 16 | 12 | 90 | 120 | 2 | 39.67 | 40.874 | 1.204 |

The results were also analyzed by ANOVA. Coefficients of all the possible combinations of variables, their standard error, t-stat and *p*-value were calculated. The *p*-value is considered important to diagnose the importance of individual parameters and their interactions. Smaller the value of *p*, more significant will be the variable for calculation of response [28]. In this context, $X_2$ (0.3899) and $X_3$ (0.44611) were therefore found significant. By increasing contact time ($X_2$) and initial concentration of sorbate ($X_3$) adsorption of sorbent also increase, as sorbent got more time to attach on the surface of agrowaste and high concentration of sorbate makes more ions available for attachment purpose [29]. Results are summarized in Table-3 along with standard error. Validity of model was assessed by applying model Equation and determining the calculated response as given in Table-6. Difference of experimental and calculated results was determined by calculating percent variation. Calculated results were found in good agreement with experimental values and percent variation was found less than 5.5 showing validity of the model for present study. Experimental data was plotted vs calculated results and $R^2$ value was found to be 0.9852; as shown in Fig 5.

Table-3: Statistical parameters for $2^4$ full factorial design.

| Terms | Coefficients | Standard Error | t-Stat | p-value |
|---|---|---|---|---|
| $X_1$ | 1.364166667 | 5.272507538 | 0.258732047 | 0.83882059 |
| $X_2$ | 1.033388889 | 0.726081638 | 1.423240631 | 0.389919071 |
| $X_3$ | 0.770256944 | 0.649771045 | 1.185428236 | 0.446113435 |
| $X_4$ | 6.333333333 | 31.63504523 | 0.200199914 | 0.874211714 |
| $X_1X_2$ | 0.0107500 | 0.063018519 | 0.170584778 | 0.892437707 |
| $X_1X_3$ | -0.064960648 | 0.066841233 | -0.971864904 | 0.509082845 |
| $X_1X_4$ | -1.334444444 | 2.520740741 | -0.529385836 | 0.690043215 |
| $X_2X_3$ | -0.005023843 | 0.009022879 | -0.55678933 | 0.676571181 |
| $X_2X_4$ | -0.180777778 | 0.378111111 | -0.478107552 | 0.716079827 |
| $X_3X_4$ | -0.410055556 | 0.401047396 | -1.022461583 | 0.492929952 |
| $X_1X_2X_3$ | 0.000394522 | 0.000878751 | 0.448957088 | 0.731355177 |
| $X_2X_3X_4$ | 0.000868519 | 0.005272508 | 0.164725894 | 0.896065605 |
| $X_1X_3X_4$ | 0.034085185 | 0.037811111 | 0.901459497 | 0.53296245 |
| $X_1X_2X_3X_4$ | -0.000135988 | 0.000420123 | -0.323684984 | 0.80071124 |

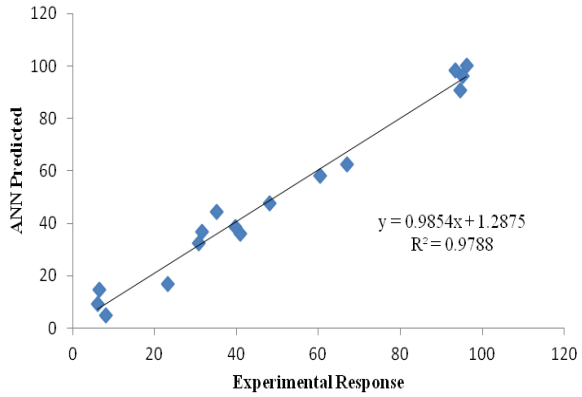


Fig 4 Plot of experimental response vs ANN predicted for adsorption of $Cd^{2+}$ on *Saccharum arundinaceum*

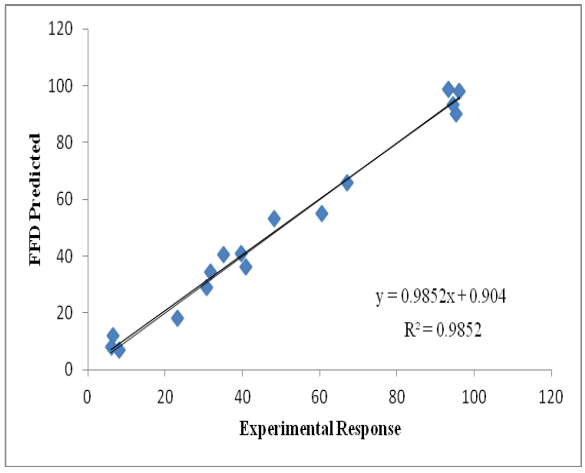


Fig 5 Plot of experimental response vs FFD predicted for adsorption of $Cd^{2+}$ on *Saccharum arundinaceum*

Another important parameter to check adequacy of any model is residual analysis. Residuals are expected to occur according to normal distribution if any element of variation remains unexplained by the fitted model. For this purpose, residuals are calculated and then plotted against predicted results.

$$\text{Residual} = \frac{(Y_{exp} - Y_{pred})}{Y_{exp}} \times 100 \qquad 4$$

Plot of residual and FFD predicted data (Fig 6) was found random with no usual pattern which shows that developed model is adequate and there is no element of variation in present model [30].

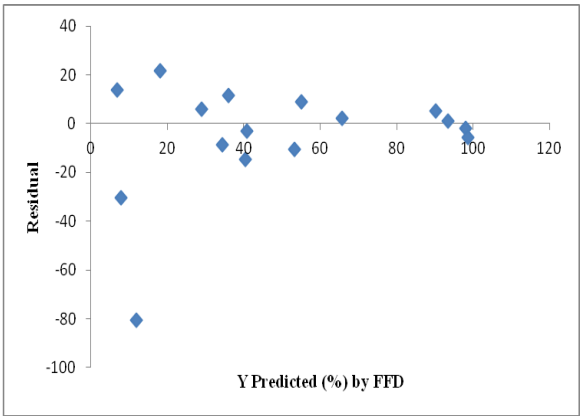


Fig. 6: Residual vs predicted response by FFD for adsorption of $Cd^{2+}$.

*Artificial Neural Network for Predictive Modeling*

For generation of ANN model, same DoE was applied which was used for FFD model generation. Architecture and specifications for ANN model generation are given in Table-4. For this purpose, multi-layered perceptron (MLP) with four neurons in input layer and one which is % sorption in output layer was used. Input layer contain pH, contact time, initial concentration of sorbate and amount of sorbent as input feed. Automated neural network procedure was implemented in STATICA 10 was used. Number of hidden layers and neurons play important role in topology and optimization of ANN model. Number of neurons was varied in hidden layer by changing various combinations, so as to develop the best fit model. Weights of neurons were adjusted in such a way to minimize error. The architecture of the best fit model was 4-7-1 with seven hidden neurons. Values of weights are given in Table-5. Predicted value of percent sorption, calculated through ANN, is given in Table-6 with % variance. Plots of experimental and predicted results express closeness of calculated results with experimental findings; as shown in Fig. 4.

Table-4: Architecture and specifications used for ANN model generation.

| Specifications | |
|---|---|
| No. of neurons in input layer | 4 |
| No. of neurons in hidden layer | 7 |
| No. of neurons in output layer | 1 |
| Training error | 0.00046 |
| Test error | 0.00098 |
| Validation error | 0.0017 |
| Hidden activation | Logistic |
| Output activation | Identity |

Table-5: Parameters of ANN (Weights of hidden and output layer) utilized for model generation.

| Neurons | Parameters of Hidden Layer | | | | | Parameters of Output Layer | |
|---|---|---|---|---|---|---|---|
| | Weights of Hidden Layer | | | | | bias | -0.16794 |
| | | | | | | Weights of Output Layer | |
| | X1 | X2 | X3 | X4 | Input bias | Neurons | Weights |
| 1 | 0.15659 | -1.32620 | -0.49609 | -0.51075 | -0.93242 | 1 | -0.06002 |
| 2 | 0.01570 | -0.48560 | -1.62112 | 1.20030 | 0.58479 | 2 | -0.34248 |
| 3 | -0.59463 | 0.93884 | -0.19874 | -3.53515 | 0.22925 | 3 | 0.33235 |
| 4 | -0.14972 | -0.01122 | 0.67250 | -0.21881 | -1.68732 | 4 | 1.26510 |
| 5 | -0.00646 | 0.16033 | -0.23765 | 0.59551 | -0.32965 | 5 | 0.17530 |
| 6 | 0.01684 | 0.65227 | -0.66064 | 0.06804 | -1.41913 | 6 | 1.34280 |
| 7 | 1.03307 | 2.02847 | -1.12669 | 0.15706 | 0.33487 | 7 | 0.16424 |

Table-6: Comparison of experimental and predicted results for adsorption of $Cd^{2+}$ on *Saccharum arundinaceum.*

| Run | X1 | X2 | X3 | X4 | Experimental Response | ANN Predicted | % Variation for ANN | FFD Predicted | % Variation for FFD |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3 | 30 | 40 | 0.5 | 35.2 | 44.22 | -9.02 | 40.3965 | 5.1965 |
| 2 | 3 | 30 | 120 | 0.5 | 67.06 | 62.4 | 4.66 | 65.6525 | 1.4075 |
| 3 | 3 | 90 | 40 | 0.5 | 95.26 | 96.06 | -0.8 | 90.2175 | 5.0425 |
| 4 | 3 | 90 | 120 | 0.5 | 96.18 | 99.98 | -3.8 | 98.1455 | 1.9655 |
| 5 | 12 | 30 | 40 | 0.5 | 40.86 | 36.14 | 4.72 | 36.0945 | 4.7655 |
| 6 | 12 | 30 | 120 | 0.5 | 31.66 | 36.71 | -5.05 | 34.4225 | 2.7625 |
| 7 | 12 | 90 | 40 | 0.5 | 93.36 | 98.2 | -4.84 | 98.6055 | 5.2455 |
| 8 | 12 | 90 | 120 | 0.5 | 94.55 | 90.64 | 3.91 | 93.4295 | 1.1205 |
| 9 | 3 | 30 | 40 | 2 | 23.13 | 16.82 | 6.31 | 18.069 | 5.061 |
| 10 | 3 | 30 | 120 | 2 | 6.1 | 9.38 | -3.28 | 7.949 | 1.849 |
| 11 | 3 | 90 | 40 | 2 | 48.16 | 47.57 | 0.59 | 53.211 | 5.051 |
| 12 | 3 | 90 | 120 | 2 | 30.73 | 32.3 | -1.57 | 28.931 | 1.799 |
| 13 | 12 | 30 | 40 | 2 | 6.56 | 14.59 | -8.03 | 11.85 | 5.29 |
| 14 | 12 | 30 | 120 | 2 | 8.1 | 4.8 | 3.3 | 6.986 | 1.114 |
| 15 | 12 | 90 | 40 | 2 | 60.46 | 57.96 | 2.5 | 55.146 | 5.314 |
| 16 | 12 | 90 | 120 | 2 | 39.67 | 38.55 | 1.12 | 40.874 | 1.204 |

ANN model was evaluated by calculating residual analysis as shown in Fig. 7.

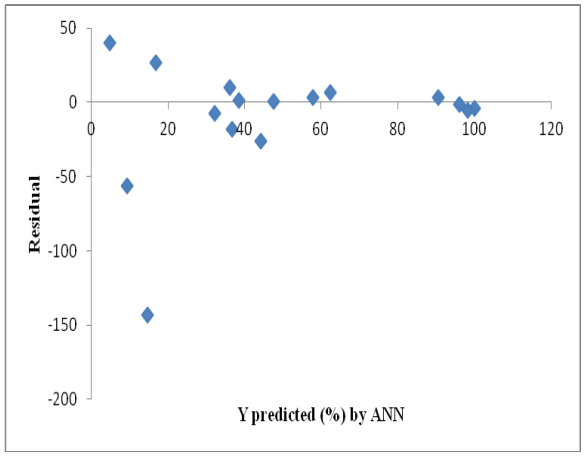


Fig. 7: Residual vs predicted response by ANN for adsorption of $Cd^{2+}$

A comparison of predictive ability of ANN and FFD was made. For this purpose, experimental results were plotted against predicted results (ANN & FFD) as shown in Fig. 4, 5. Results for FFD were found close to experimental results, i.e. $R^2$ value was 0.9852 for FFD and 0.9788 for ANN; however, the difference was very small. Both the predictive techniques yielded results close to experimental findings and low value of % variance was achieved for both of these methodologies. Thus it can be concluded that both FFD and ANN are suitable models to predict % sorption with reasonable accuracy.

*Desorption Method*

Desorption potential of a sorbent material, for a specific metal ion, is necessary to be determined to regenerate adsorbent for reuse. This feature adds worth to sorbent in terms of viability and cost-effectiveness. In current work, desorption ratio of

$Cd^{2+}$ was carried out for the recovery of adsorbed amount of $Cd^{2+}$, from the surface of sorbent, by using HCl (0.1-1 M) solution. Maximum desorption was found out to be 97.1%, which was achieved on treating sorbent with 0.1 M HCl.

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