**N-(((2-((2-Aminoethyl)amino)ethyl)amino)methyl)-4-sulfamoylbenzamide Impregnated Hydrous Zirconium Oxide as a Novel Adsorbent for Removal of Ni(II) from Aqueous Solutions: Optimization of Variables Using Central Composite Design**

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**ABSTRACT:** In this study, N-(((2-((2-aminoethyl)amino)ethyl)amino)methyl)-4-sulfamoylbenzamide was impregnated into the hydrous zirconium oxide matrix to yield N-(((2-((2-aminoethyl)amino)ethyl)amino)methyl)-4-sulfamoylbenzamide/hydrous zirconium oxide composite (AESB/HZO). The composite material was used to remove Ni(II) from aqueous environment. AESB/HZO was characterized using Fourier transform infrared, scanning electron microscopy with energy dispersive X-ray, and thermogravimetry–differential thermal analyses. An experimental design approach was utilized to model and optimize the variables of adsorption of Ni(II) onto the AESB/HZO composite. Four experimental parameters were selected as independent variables: contact time, pH, adsorbent dose, and initial Ni(II) concentration. A multivariable experimental design was used to establish quadratic model to describe the relationship between percent removal of Ni(II) and four independent variables. At the optimum conditions (contact time: 85 min, pH: 6, adsorbent dose: 10 mg/20 mL, and initial Ni(II) concentration: 20 mg L\(^{-1}\)), high removal efficiency (99.35%) was achieved, which is reasonably well predicted by the quadratic model. The sorption of Ni(II) is dependent on pH and ionic strength at pH < 6.0. At low pH, \(-\text{NH}\) and \(-\text{NH}_2\) groups are protonated, whereas the \(-\text{SO}_2^-\) group is available for binding with Ni(II) and the sorption of Ni(II) is mainly governed by outer-sphere surface complexation. In the pH range 6.0–7.5, \(-\text{NH}\), \(-\text{NH}_2\), and \(-\text{SO}_2^-\) groups are available for binding with Ni(II) and the sorption is mainly governed by inner-sphere surface complexation. Adsorption isotherm data fitted well to the Langmuir model and the maximum adsorption capacity was found to be 96.03 mg g\(^{-1}\) at 303 K. The results of present investigation demonstrated that AESB/HZO has a good potential for Ni(II) removal from aqueous solution.

**INTRODUCTION**

Many industrial processes release effluents containing heavy metal ions/and other pollutants into aquatic environment, which present a threat to the human health due to their toxicity and accumulation in human organisms. Nickel is a toxic heavy metal, which is associated with a large number of industrial applications such as electroplating, mining, printing, batteries, metal finishing, silver refineries, phosphate fertilizers, coinage, food processing, and pulp and paper. These industries release nickel into the environment. The maximum concentration of total nickel allowed by WHO and Bureau of Indian Standards is 70 and 20 \(\mu\)g L\(^{-1}\) Ni(II) in drinking water, respectively. The pollution caused by nickel has been reported from across the world including Asia.\(^{10-14}\) Strict environmental regulations on the discharge of heavy metals have forced to treat the wastewater and bring the level of heavy metals content under permissible limit.

Several approaches have been utilized for removal of Ni(II) from water and wastewater, which include nanofiltration,\(^{15}\) coagulation–floculation,\(^{16}\) electrocoagulation,\(^{17}\) electrofloitation,\(^{18}\) ion exchange,\(^{19}\) photocatalytic removal,\(^{20}\) adsorption,\(^{21}\) and so forth. Among these treatment technologies, adsorption is recognized as a highly potential process for removal of Ni(II) from wastewater. Activated carbon has been found as an efficient adsorbent for the removal of different types of pollutants including heavy metal ions.\(^{22}\) Activated carbon...
obtained from different sources such as graphite,23 Nigerian bamboo,24 doum palm seed,25 cucumis melo peel,26 olive stone,27 and rice husk28 has been used as sorbent for removal of Ni(II) from aqueous systems.

Inorganic−organic hybrid materials have been examined as potential adsorbents for the removal of toxic cationic and anionic species from water and wastewater.29−33 Recently, some critical reviews dealing with layered double hydroxide-based nanomaterials,34 polymer-based nanocomposites,35 and metal organic framework-based materials36 for removal of radionuclides, heavy metal ions, and toxic metal ions have appeared. Silica gels (MCM-41) functionalized with aminopropyl group,37 poly (ethyleneimine),38 and 2-((1H-pyrrol-2-yl) methylene) hydrazine carbothioamide39 were employed as adsorbents for removal of Ni(II) from aqueous solution. Carboxymethyl-chitosan deposited onto functionalized Aerosil 200 silica particles and colloidal silica were used as effective adsorbents40,41 for retention of Ni(II) from aqueous solution.

The conventional one-variable-at-a-time (OVAT) approach has been utilized most frequently to optimize the adsorption processes.42−44 However, the OVAT approach does not consider the interactions between the variables of the adsorption processes and requiring large number of experimental runs. The application of experimental design in the optimization of adsorption processes makes it feasible to achieve maximum useful information through fewer experiments. Response surface methodology (RSM) can derive an empirical model, which includes the most important variables and their effects. More recently, RSM based on Box−Behnken design has been utilized for optimization of Cd(II) removal using poly (o-phenylenediamine)/hydrous zirconium oxide.45 In addition, central composite design (CCD) with RSM has been applied to optimize the conditions for maximum removal of Zn(II) from contaminated soil.46

In this study, N-(((2-((2-aminoethyl)amino)ethyl)amino)-methyl)-4-sulfamoylbenzamide impregnated hydrous zirconium oxide (AESB/HZO) was synthesized and characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) coupled with energy dispersive X-ray (EDX) analysis, and thermogravimetry−differential thermal analyses (TGA−DTA). RSM combined with CCD was employed to design and optimize the removal of Ni(II) from aqueous solution by AESB/HZO. The adsorption equilibrium data were analyzed by different isotherm models.

RESULTS AND DISCUSSION

Characterization. The FTIR spectrum of HZO (Figure 1a) displayed absorption bands peaking at 3371 and 1623 cm\(^{-1}\), which correspond to stretching vibration of O−H of coordinated water and H−O−H bending vibration, respectively.47 The absorption band observed at 1402 cm\(^{-1}\) is resulting from the O−H bending vibration from Zr−OH.48 The absorption band centered at 670 cm and 474 cm\(^{-1}\) indicated the lattice vibration of Zr−O.49 The FTIR spectrum of AESB/HZO is shown in Figure 1b. The bands observed at 1413 and 1105 cm\(^{-1}\) are assigned to the asymmetric and symmetric stretching modes of O=S=O group, respectively.50 The band peaking at 1051 cm\(^{-1}\) indicated C−S stretching vibration along with the ring vibration.51 The band
observed at 928 cm\(^{-1}\) is assigned to S–N stretching vibration.\(^{52}\) A broad band within 3500–3300 cm\(^{-1}\) is assigned to N–H stretching vibration. The absorption band centered at 1644 cm\(^{-1}\)\(^{151}\) indicated the amide C=O stretching vibration. The band observed at 1567 cm\(^{-1}\) corresponds to Zr–N and Zr–O stretching vibration, respectively. The surface morphology of AESB/HZO was characterized by SEM. The SEM image (Figure 1c) revealed the presence of pores of varying dimensions. Figure 1d shows the energy-dispersive system (EDS) peaks corresponding to carbon, nitrogen, oxygen, sulfur, and zirconium, which confirmed the synthesis of AESB/HZO.

The TGA curve (Figure 1e) shows a steep slope between 50 and 130 °C with mass loss of 11.34%, which corresponds to the loss of H\(_2\)O molecules. The number of water molecules was calculated using the equation\(^{53,54}\)

\[
18n = \frac{X(M + 18n)}{100} \tag{1}
\]

where \(n\) is the number of water molecules; \(X\) and \(M\) are the percent weight loss and molecular weight of compound, respectively. The number of water molecule was found to be 3.28. The DTA curve exhibited an endothermic peak at 88.92 °C, which also confirmed the loss of water molecules. The anhydrous AESB/HZO shows decomposition from 130 to 250 °C with a mass loss of 17.48%. This loss in weight may be due to the decomposition of sulfonamide group.\(^{55}\) The second step decomposition was observed from 250 to 390 °C with 31.37% weight loss, which may be due to decomposition of benzamide group. In third step, the degradation occurs from 390 to 590 °C with 25.71% weight loss, which may be due to decomposition of remaining organic moiety. Lastly, the weight loss was observed from 590 to 650 °C. At 650 °C, the material is converted to zirconium oxide.

**RSM and Model Fitting.** The experimental results in terms of percentage removal of Ni(II) obtained from 30 runs of CCD are presented in Table 1. The experimental data were fitted to different regression models (Table 2). The quadratic model was selected as the best model on the basis of low \(p\)-value (0.0001) and high values of \(F\) adjusted \(R^2\), and predicted \(R^2\). The relationship between the percentage removal and independent variables can be described by the following quadratic equation

\[
\text{Removal (\%)} = +99.35 + 5.55X_1 + 13.41X_2 + 3.45X_3
+ 6.45X_4 + 3.95X_5X_2 - 2.13X_3X_4
+ 1.61X_1X_4 - 1.17X_3X_5 - 1.86X_4X_5
- 2.73X_1^2 - 13.94X_2^2 - 9.45X_3^2
- 9.96X_4^2 \tag{2}
\]

Analysis of variance was carried out to assess the quality and significance of the quadratic model (Table 3). The values of \(F\) and \(p\) are 1770.610 and 0.0001, respectively, which indicated that the model is highly significant. The lack of fit is insignificant which confirms the good predictability of the model. The value of determination coefficient (\(R^2 = 0.9994\)) as shown by ANOVA also indicated that the fitting is very well and only 0.06% of the total variation was not explained by the model. The high value of adjusted \(R^2\) (0.9988) indicated the high significance of the proposed model. The relationship

| Table 1. CCD Experiments with Observed and Predicted Responses* |
|---------------------|---------------------|---------------------|---------------------|---------------------|
| runs | time (min) | pH | dose (mg) | concentration (mg L\(^{-1}\)) | observed responses (% Y) | predicted responses (% Y) |
| 1 | 15 (0) | 2 | (−α) | 10 (0) | 20 (0) | 16.08 | 16.76 |
| 2 | 20 (0) | 6 | (−1) | 10 (0) | 20 (0) | 12 (−1) | 30.58 | 29.59 |
| 3 | 25 (0) | 6 | (0) | 10 (0) | 20 (0) | 4 (−α) | 99.35 | 99.35 |
| 4 | 30 (0) | 10 | (0) | 10 (0) | 20 (0) | 4 (−α) | 99.35 | 99.35 |
| 5 | 35 (0) | 10 | (0) | 10 (0) | 20 (0) | 4 (−α) | 47.01 | 46.62 |
| 6 | 40 (α) | 10 | (0) | 10 (0) | 20 (0) | 70.99 | 70.40 |
| 7 | 120 (+1) | 6 | (0) | 28 (+1) | 91.98 | 90.73 |
| 8 | 120 (+1) | 4 | (1) | 12 (−1) | 42.98 | 42.54 |
| 9 | 120 (+1) | 8 | (0) | 28 (+1) | 86.08 | 87.30 |
| 10 | 120 (+1) | 6 | (−1) | 12 (−1) | 73.82 | 73.83 |
| 11 | 120 (+1) | 4 | (0) | 28 (+1) | 33.63 | 33.84 |
| 12 | 155 (+α) | 6 | (0) | 20 (0) | 99.35 | 99.52 |
| 13 | 155 (+α) | 4 | (0) | 28 (+1) | 54.13 | 53.42 |
| 14 | 155 (+α) | 6 | (0) | 20 (0) | 99.35 | 99.35 |
| 15 | 155 (+α) | 14 | (1) | 28 (+1) | 66.21 | 65.37 |
| 16 | 155 (+α) | 6 | (0) | 36 (+α) | 71.93 | 72.41 |
| 17 | 155 (+α) | 4 | (0) | 12 (−1) | 45.88 | 46.81 |
| 18 | 155 (+α) | 6 | (0) | 20 (0) | 99.35 | 99.35 |
| 19 | 155 (+α) | 6 | (0) | 20 (0) | 68.97 | 68.47 |
| 20 | 155 (+α) | 6 | (0) | 20 (0) | 99.35 | 99.35 |
| 21 | 155 (+α) | 14 | (1) | 28 (+1) | 69.87 | 69.34 |
| 22 | 155 (+α) | 4 | (0) | 28 (+1) | 63.02 | 63.19 |
| 23 | 155 (+α) | 6 | (0) | 20 (0) | 77.39 | 77.31 |
| 24 | 155 (+α) | 8 | (1) | 12 (−1) | 81.27 | 81.33 |
| 25 | 155 (+α) | 4 | (−1) | 28 (+1) | 63.89 | 64.11 |
| 26 | 155 (+α) | 6 | (−1) | 12 (−1) | 60.78 | 61.30 |
| 27 | 155 (+α) | 8 | (0) | 20 (0) | 54.08 | 54.67 |
| 28 | 155 (+α) | 6 | (0) | 20 (0) | 99.35 | 99.35 |
| 29 | 155 (+α) | 6 | (0) | 20 (0) | 63.58 | 64.25 |
| 30 | 155 (+α) | 8 | (1) | 12 (−1) | 84.97 | 85.36 |

*Values adjusted \(R^2\)

| Table 2. Statistical Parameters of the Polynomial Models Developed for Ni(II) Removal Using AESB/HZO |
|---------------------|---------------------|---------------------|---------------------|---------------------|
| model | \(p\)-values | \(F\)-values | adjusted \(R^2\) | predicted \(R^2\) |
| linear | 0.0087 | 4.300 | 0.3129 | 0.2328 |
| 2-factor interaction | 0.9110 | 0.331 | 0.1820 | 0.1074 |
| quadratic | 0.0001 | 33194.000 | 0.9988 | 0.9965 |
between the experimental values and the predicted values of percent removal of Ni(II) obtained from eq 2 is shown in Figure 2. It can be seen in Figure 2 that the developed model is adequate because the residuals are very close to the diagonal line. Figure 3 shows the normal probability plot of studentized residuals for Ni(II) removal by AESB/HZO. A normal probability plot suggests that if the residual follows the normal distribution, the points will lie on a straight line. Figure 3 shows that few data points are scattered from the straight line. Now it is assumed that the data are normally distributed as no transformation is required. In this study, independent variables such as contact time ($X_1$), pH ($X_2$), adsorbent dose ($X_3$), and Ni(II) concentration ($X_4$) are highly significant parameters with $p < 0.0001$. Moreover, the second order effects such as contact time ($X_1^2$), pH ($X_2^2$), adsorbent dose ($X_3^2$), and Ni(II) concentration ($X_4^2$) are also significant as $p < 0.0001$. In addition, the interaction between factors such as $X_1X_2$, $X_1X_3$, $X_1X_4$, $X_2X_3$, $X_2X_4$, and $X_3X_4$ are significant as the value of $p < 0.0001$. The negative coefficient of quadratic term in the polynomial expression pointed toward negative effect on the removal efficiency. Adequate precision, measure of the signal to noise ratio, was found to be 147.84. The adequate precision values greater than 4.0 pointed toward the adequacy of signal and also confirmed the good prediction by the model designed by CCD.

**Effect of Parameters on Responses.** The 3D plots for removal of Ni(II) versus two variables were obtained while keeping other variables constant at the center level. The combined effect of pH and contact time on percent removal of Ni(II) is shown in Figure 4a, which revealed that at any fixed pH, removal efficiency increases with contact time. The maximum removal (99.35%) was obtained at a contact time of 85 min. The interactive effect of contact time and adsorbent dose, keeping pH 6 and initial concentration of 20 mg L$^{-1}$ constant, on percent removal is shown in Figure 4b. The increase in adsorbent dose and contact time causes increase in removal efficiency, which is due to the increase in surface area and binding sites provided by greater amounts of AESB/HZO.

### Table 3. ANOVA for Quadratic Model for Removal of Ni(II) by AESB/HZO$^a$

| source     | sum of squares | df | mean square | $F$-value | p-value |
|------------|----------------|----|-------------|-----------|---------|
| model      | 15537.69       | 14 | 1109.83     | 1770.61   | <0.0001 |
| $X_1$      | 740.04         | 1  | 740.04      | 1180.64   | <0.0001 |
| $X_2$      | 4316.14        | 1  | 4316.14     | 6885.88   | <0.0001 |
| $X_3$      | 285.45         | 1  | 285.45      | 455.41    | <0.0001 |
| $X_4$      | 997.04         | 1  | 997.04      | 1590.66   | <0.0001 |
| $X_1X_2$   | 249.25         | 1  | 249.25      | 397.64    | <0.0001 |
| $X_1X_3$   | 72.46          | 1  | 72.46       | 115.61    | <0.0001 |
| $X_1X_4$   | 41.51          | 1  | 41.51       | 66.22     | <0.0001 |
| $X_2X_3$   | 21.93          | 1  | 21.93       | 34.98     | <0.0001 |
| $X_2X_4$   | 435.87         | 1  | 435.87      | 695.38    | <0.0001 |
| $X_3X_4$   | 55.47          | 1  | 55.47       | 88.49     | <0.0001 |
| $X_1^2$    | 205.00         | 1  | 205.00      | 327.05    | <0.0001 |
| $X_2^2$    | 53.32          | 1  | 53.32       | 8506.57   | <0.0001 |
| $X_3^2$    | 2446.90        | 1  | 2446.90     | 3903.74   | <0.0001 |
| $X_4^2$    | 2720.33        | 1  | 2720.33     | 4339.96   | <0.0001 |
| residual   | 9.40           | 15 | 0.6268      |           |         |
| lack of fit| 9.40           | 10 | 0.9402      |           | insignificant |
| pure error | 0.0000         | 5  | 0.0000      |           |         |
| cor total  | 15547.09       | 29 |             |           |         |

$^a$ $R^2 = 0.994$, adjusted $R^2 = 0.9988$, and predicted $R^2 = 0.9965$. 

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Figure 2. Regression plot of experimental data against the predicted values from the response surface model.

Figure 3. Normal probability plot of the residuals.
Figure 4c shows the interactive effect of contact time and initial Ni(II) concentration (constant pH and adsorbent dose). It can be seen that the removal efficiency increases with increasing initial concentration at any given contact time. The combined effect of pH and adsorbent dose (Figure 4d) revealed that the removal efficiency increases with increasing adsorbent dose at any fixed pH value. The removal efficiency decreases at pH less than 6 which may be due to protonation of $-\text{NH}$ group in AESB and formation of Zr$\text{OOH}^+$. The interactive effect of pH and initial Ni(II) concentration (Figure 4e) revealed that the
removal efficiency increases with increase in pH up to 6 at an initial concentration of 20 mg L\(^{-1}\). Further increase in initial concentration causes a decrease in removal efficiency which is due to the non-availability of sufficient number of binding sites for Ni(II). The combined effect of adsorbent dose and initial concentration on the removal of Ni(II) (Figure 4f) suggested a decrease in removal efficiency at lower amounts of adsorbent dose which is due to non-availability of binding sites for Ni(II).

**Effect of pH and Ionic Strength.** Figure 5 shows the effect of pH on Ni(II) sorption in 0.001, 0.01, and 0.1 mol L\(^{-1}\) NaCl solutions. The sorption increases with increasing pH and attaining the maximum sorption in the pH range 6.0–7.5. At pH > 7.5, the decreasing trend in sorption was observed. Sorption of Ni(II) in 0.1 mol L\(^{-1}\) NaCl solution is slightly higher as compared to 0.001 mol L\(^{-1}\) NaCl solution at pH < 6.0. The maximum sorption was found in the pH range 6.0–7.5 which was independent of NaCl solution. At pH > 7.5, no difference was observed in the sorption curves in three different solutions. At pH < 6.0, the sorption of Ni(II) on AESB/HZO depends on the ionic strength and pH of medium. At lower pH, the –NH and –NH\(_2\) groups present in the adsorbent are protonated, whereas the –SO\(_4\)\(^2-\) group is available for binding with Ni(II). This resulted in decrease in sorption efficiency. Moreover, this finding revealed that the sorption of Ni(II) on AESB/HZO is mainly governed by outer sphere surface complexation. In pH range 6.0–7.5, ionic strength did not affect the sorption of Ni(II) on AESB/HZO and the functional groups such as –NH, –NH\(_2\), and –SO\(_4\)\(^2-\) are available for binding with Ni(II). This suggested that sorption of Ni(II) is governed mainly by inner sphere surface complexation.\(^{56,57}\)

**Optimization of Variables.** The numerical optimization was carried out by assigning a minimum and maximum level to each input variables, whereas the response was designed to achieve the maximum. Figure 6 shows the range of input variables obtained from the model. RSM with desirability function has assigned the optimum values to each variable as follows: contact time: 85 min, pH: 6, adsorbent dose: 10 mg/20 mL, and initial Ni(II) concentration: 20 mg L\(^{-1}\). Experiments were also performed under optimization conditions. The results agreed well with the predicted value.

**Isotherm Models.** Adsorption data were analyzed by using Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models. The linear form of Langmuir, Freundlich,

**CONCLUSIONS**

In this study, the AESB/HZO composite material was prepared, which showed excellent potential for the removal of Ni(II) from aqueous solutions. The result showed that AESBH/ZO has high Ni(II) removal efficiency (99.35%) from

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**Figure 5.** Sorption of Ni(II) on AESB/HZO as a function of pH in different NaCl solutions.

**Figure 6.** Profiles for the predicted response and desirability functions for the percent removal of Ni(II) onto AESB/HZO.

**Table 4** shows the isotherm parameters for each model, which were calculated from the corresponding isotherm plots. On the basis of \(R^2\) values, the order of best fit was Langmuir > Temkin > Dubinin–Radushkevich > Freundlich model at all temperatures (303, 313, and 323K). The error functions such as \(\chi^2\) and APE were calculated with respect to the experimental adsorption capacity. In case of the Langmuir isotherm model, the values of \(\chi^2\) and APE are the lowest, and hence, this model explained the adsorption of Ni(II) onto AESB/HZO more accurately as compared to the other model.

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water. The oxygen and nitrogen-containing functional groups present in the adsorbent could form strong surface complexes with Ni(II). The characterization of the composite material was performed through FTIR, SEM with EDX, and TGA−DTA. The experimental parameters for the removal of Ni(II) were optimized using CCD. The experimental data were analyzed by Langmuir, Freundlich, Temkin, and Dubinin−Radushkevich isotherm models. On the basis of error analysis, it was found that the Langmuir isotherm model is able to explain the adsorption of Ni(II) more accurately.

EXPERIMENTAL SECTION

Materials. Zirconium(IV) oxychloride octahydrate (Otto Chemie Pvt. Ltd., India), ammonia solution (25%; Merck Life Science, India), triethylenetetramine (Merck Life Science, India), carboxybenzene sulfonamide (Himedia Laboratories Pvt. Ltd. India), and benzene boronic acid (Merck Life Science, India) were used for the synthesis of the adsorbent. Nickel chloride hexahydrate (Extrapure; Loba Chemie Pvt. Ltd., India) was used to prepare standard solution.

Preparation of AESB/HZO. The synthesis of the adsorbent (AESB/HZO) was carried out in three steps. First, hydrous zirconium(IV) oxide (HZO) gel was prepared by mixing equal volumes of 0.10 M zirconium(IV) oxychloride octahydrate and 6% ammonium hydroxide. Second, triethylenetetramine was added to the HZO gel and stirred on a magnetic stirrer for 4 h at room temperature. Lastly, HZO gel treated with triethylenetetramine was mixed with 4-carboxybenzene sulfonamide and benzene boronic acid (5 mol %) and refluxed for 1 h. The gel was filtered, washed with distilled water, followed by ethanol, and then dried in an oven at 40 °C. The dried material was immersed in distilled water to get small granules and then sieved to obtain granules of uniform size (50−100 μm). Scheme 1 shows the synthesis of AESB/HZO.

Characterization. FTIR spectra were recorded over the range 4000−400 cm−1 on an FTIR spectrophotometer (PerkinElmer Inc., spectrum 2, USA) using the KBr pellet approach. The surface morphology of the material was characterized by SEM images, which were obtained using a scanning electron microscope (JEOL JSM-6510 LV, Japan), and elemental composition was measured with EDX mappings. TGA and DTA were performed using a DTG-60H thermal analyzer (Shimadzu, Japan). A water bath shaker (NSW Pvt. Ltd., India) was employed to monitor the temperature and shaking speed.

Experimental Design and Optimization by RSM. RSM, a combination of statistical and mathematical approaches, is used for modeling and optimization of process variables to obtain the best response.58,59 In this study, RSM based on CCD was applied to optimize the adsorption of Ni(II) onto AESB/HZO. The independent factors such as contact time (X1), pH (X2), adsorbent dose (X3), and initial concentration of Ni(II) (X4) were selected on the basis of initial experiments. Each factor was studied at five levels namely −α1, 0, +1, and...
α as lowest, low, center, high, and highest, respectively. Table 5 shows the range and levels of each factor. CCD consists of $2^k$ factorial runs, 8 axial runs, and 6 at the center point. The total number of experimental runs required to build CCD matrix can be obtained from the following equation

$$N = kC + 2k + np$$

where $N$, $k$, and $C_p$ are the total number of experimental runs, number of variables, and number of replicate at the center point, respectively. In this study, 30 experimental runs are required for four independent variables. The matrix of CCD and experimental results are given in Table 1. The optimization of variables of adsorption process involves three steps

(i) First, the statistically designed experiments were performed.
(ii) Second, the coefficients of the mathematical model were determined.
(iii) Lastly, the response was predicted from mathematical model and confirming the adequacy of the model.

The experimental values of adsorption capacity ($q_e$) for Ni(II) are 96.20, 102.18, and 104.84 mg g$^{-1}$ at 303, 313, and 323 K, respectively.

Table 4. Parameters of Different Isotherms Obtained by Linear Fitting for Adsorption of Ni(II) ions onto AESB/HZO

| Isotherm       | Temperature (K) | Parameters | Error Function |
|----------------|-----------------|------------|----------------|
| Langmuir       | 303             | 96.03      | 2.427          |
|                | 313             | 102.04     | 3.636          |
|                | 323             | 104.16     | 6.000          |
| Freundlich     | 303             | 117.21     | 3.179          |
|                | 313             | 116.41     | 3.408          |
|                | 323             | 122.46     | 4.510          |
| Temkin         | 303             | 97.49      | 88.058         |
|                | 313             | 99.04      | 171.228        |
|                | 323             | 99.95      | 2705.38        |
| Dubinin–Radushkevich | 303       | 81.10      | 3              |
|                  | 313             | 86.14      | 2              |
|                  | 323             | 89.59      | 1              |

The experimental values of adsorption capacity ($q_e$) for Ni(II) are 96.20, 102.18, and 104.84 mg g$^{-1}$ at 303, 313, and 323 K, respectively.

Scheme 1. (a): Synthesis of Triethylentetramine Hydrous Zirconium Oxide (TTHZO). (b): Synthesis of AESB/HZO

Table 5. Experimental Range and Levels of the Independent Variables

| Variables          | Range and level | factor | $-\alpha$ | $-1$ | 0 | $+1$ | $+\alpha$ |
|--------------------|-----------------|--------|-----------|------|---|-----|---------|
| time (min)         | $X_1$           | 15.00  | 50.00     | 85.00| 120.00 | 155.00 |
| pH                 | $X_2$           | 2.00   | 4.00      | 6.00 | 8.00   | 10.00  |
| dosage (mg)        | $X_3$           | 2.00   | 6.00      | 10.00| 14.00  | 18.00  |
| concentration (mg L$^{-1}$) | $X_4$   | 4.00   | 12.00     | 20.00| 28.00  | 36.00  |

The experimental data from CCD were subjected to multiregression analysis and the predicted percent removal can be calculated by the second order (quadratic) polynomial equation in terms of coded factors as

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} B_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j + \epsilon$$

where $Y$ and $\beta_0$ are the predicted response [% removal of Ni(II)] and model constant, respectively. $\beta_i, B_{ii}, \beta_{ij}$ are the
linear, quadratic, and interaction coefficients, respectively. $\chi_i$ and $X_i$ represents the coded variables of experiments and $\epsilon$ is the error of prediction.

All data were processed by Design Expert (free trial 11.1.0.1 version). Analysis of variance was used to evaluate the significant and insignificant terms in the equation fitted. The robustness of the model was assessed based on $R^2$, adjusted $R^2$, and predicted $R^2$. The optimum values of the variables were estimated by showing the regression equation and examining the response surface plots.

**Adsorption Experiments.** The adsorption of Ni(II) onto ASES/HZO was carried out in 100 mL Erlenmeyer flasks according to CCD using batch experiments. The required amount of adsorbent was added to 20 mL of Ni(II) solution (4–36 mg L$^{-1}$). The pH was adjusted from 2–10 with dilute solution of HCl or NaOH. The resulting solutions were agitated at 160 rpm for the required time in a water bath shaker. For determination of maximum adsorption capacity, 10 mg of the adsorbent was added to 20 mL of Ni(II) solution (20 mg L$^{-1}$) adjusted to pH 6 and the resulting mixture was agitated in a water bath shaker (160 rpm) for 85 min. The samples were filtered and the concentration of Ni(II) in the filtrate was determined by AAS. All experiments were performed in triplicate and the average values were reported. The amount of Ni(II) adsorbed at equilibrium, $q_e$ (mg g$^{-1}$) and percentage removal of Ni(II) were calculated using the following equations

$$q_e = \frac{(C_i - C_e)V}{M}$$

(9)

Removal efficiency (%) $= \frac{C_i - C_e}{C_i} \times 100$  

(10)

where $C_i$ and $C_e$ are the initial and equilibrium concentration of Ni(II) in mg L$^{-1}$, respectively; $V$ is the volume of solution (L); and $M$ is the mass of the adsorbent (g).

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**Notes**

The authors declare no competing financial interest.

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