

Novel Calix[4]arene Network Resin for Cr(VI) ions Remediation: A Response Surface Approach

Ali N. Siyal^{1*}, Saima Q. Memon²

¹ University of Sindh, M.A. Kazi Institute of Chemistry, Jamshoro, Pakistan

² University of Sindh, Institute of Advance Research Studies in Chemical Sciences, Jamshoro, Pakistan

* Corresponding author: e-mail: alinawazsiyal@yahoo.com

Novel Calix[4]arene Network (NCN) resin has been synthesized using Amberlite XAD-2 as the starting material. Hydroxyl groups have been introduced onto the para position of alkylated phenyl ring of Amberlite XAD-2 followed by the condensation to NCN by reacting it with formaldehyde. The NCN resin has been used for the remediation of Cr(VI) contaminated water using factorial design approach. A face-centered Draper-Lin composite design predicted ~100% removal efficiency at optimum variables (the initial concentration of Cr(VI) ion 10 mg/l sorbent dose 200 mg, agitation time 136 min and pH 2). The accuracy and the fitting of the model were evaluated by ANOVA and R^2 (0.9992) values. The 99.5% removal efficiency has been achieved experimentally at the optimum values of the variables. The Langmuir and D-R isotherm models were applicable to the sorption data with the value of R_L and the sorption free energy 0.0057–0.1 and 7.93 kJ/mol respectively, suggesting favorable and physical/ion-exchange nature of the sorption. The calculated sorption capacity was 176.1 ± 2.4 mg/g. The recycling studies of NCN resin showed that the multiple use of resin is feasible. Effect of concomitants has also been studied and proposed method was applied successfully for removal (98.7%) of Cr (VI) from electroplating wastewater.

Keywords: Modified Amberlite XAD-2, Calixarene, Cavities, Network, Optimization, Remediation, Removal, Chromium, Response Surface Methodology, Factorial design, Isotherms.

INTRODUCTION

Chromium which has been widely used by men for years, can be regarded as a longstanding environmental contaminant as a result of numerous industrial processes such as the leather tanning, electroplating, oxidative dyeing and manufacturing of steel paints and textiles¹. Cr(VI) ion species are strong oxidants, which act as carcinogens, mutagens and teratogens in biological systems^{2,3}. The structural similarity of Cr(VI) anions to the biologically important inorganic anions, such as SO_4^{2-} and PO_4^{3-} , is probably responsible for their ability to readily transverse cell membranes through the sulfate transport system⁴. The maximum permissible levels of Cr(VI) in potable water, inland surface water and industrial wastewater are 0.05, 0.1 and 0.25 mg/l respectively⁵. Beyond the permissible levels, it can cause health disorders, such as vomiting and hemorrhage⁶. Strong exposure to Cr(VI) ion causes cancer in digestive tract and lungs and may cause epigastric pain, nausea, vomiting, severe diarrhoea and hemorrhage. It has adverse impacts on aquatic species as it accumulates in fish tissues and causes reduction in fish production at higher concentration⁷. Reduction of the amount of such metal ions from such effluents to a permissible limit before discharging them into streams and rivers is very much important for human health and the environment⁸. Therefore, Cr(VI) ion must be properly treated before it is allowed for direct discharge to natural water streams⁹. For the treatment of wastewaters, various sorbents such as impregnated and chemically modified Amberlite XAD series with various organic ligands have been reported^{10–13}. In this study we focus on the synthesis of Novel Calix[4]arene Network (NCN) sorbent (7) from Amberlite XAD-2 (1) without using any organic ligand for the treatment of Cr(VI) contaminated water. XAD-2 (1) contains phenyl groups, these phenyl groups were

converted into para substituted phenols (5) and these para substituted phenols were converted into NCN resin (7). This paper reports on the synthesis of a NCN (7) resin and its application with a combined effect of four parameters, viz., adsorbent dose, pH, temperature and adsorbate concentration, a factorial design approach was adopted to optimize the removal efficiency and to study the interaction between effective variables.

MATERIALS AND METHODS

Adsorbate: Cr(VI) ion

A stock solution of Cr(VI) was prepared (1000 mg/l) by dissolving the required amount of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) in deionized water and was diluted with deionized water to obtain a series of solutions of concentration ranging from 10 to 100 mg/l. Amberlite XAD-2 resin beads of surface area 330 m^2/g , pore diameter 9 nm and bead size 20–60 mesh was obtained from Aldrich (Milwaukee, USA). HCl, acetate buffer and NaOH were used to maintain the pH 2.0, 5.5 and 9.0 respectively. CH_3COOH , CH_3COONa , SnCl_2 , NaOH, HCl, H_2SO_4 , HNO_3 , NaNO_2 and Iodide-Starch Paper were the products of Merck (Darmstadt, Germany).

Adsorbent: Synthesis of Novel Calix[4]arene Network Resin from Amberlite XAD-2

The Calix[4]arene resin has been synthesized by the conversion of Amberlite XAD-2 (1) into XAD-2 diazonium salt (4). The reaction scheme is illustrated in Fig. 1(1-4). Diazotization was performed by the reported procedure¹⁴, as concentrated nitric acid (10 ml) and sulphuric acid (25 ml) were added to Amberlite XAD-2 (5 g) and the mixture was stirred at 60°C for 1 h on a water bath. Thereafter, the reaction mixture was poured

into an ice-water mixture. The nitro derivative (2) was filtered off, washed repeatedly with deionized water until free from acid. The nitro derivative was then added to a reducing mixture of SnCl₂ (40 g), concentrated HCl (45 ml) and ethanol (50 ml). The mixture was refluxed for 12 h at 90°C. The amino derivative (3) was filtered off and washed with deionized water and 2.0 M NaOH and then with 2.0 M HCl and finally with deionized water to remove the excess of HCl. For diazotization, amino derivative (3) was suspended in 1.0 M hydrochloric acid (50 ml) solution at 0–5°C and 1.0 M sodium nitrite solution was added drop wise with stirred till the reaction mixture showed a permanent dark blue colour with Iodide-Starch Paper. The diazonium derivative (4) was filtered off and washed with ice-cold water. The diazonium derivative (4) was hydrolyzed to phenol derivative (5) by adding 100 ml of deionized water and 0.01 M of Acetic acid (10 ml) and reaction mixture was refluxed at 90°C till the disappearance of effervescences, formed due to release of molecular nitrogen from diazonium surface. The phenol derivative (5) was filtered off and washed with deionized water to remove excess acid. The phenol derivative (6) was converted into NCN resin (7) by refluxing with formaldehyde (50 ml) and 0.01 M NaOH (10 ml) at 60°C for 12 h. The resulting dark-brown resin was filtered off, washed with deionized water and air-dried.

Batch Adsorption Experiments

All the experiments were performed in a thermostated shaker at controlled temperature of 30°C for a period of 10–180 min at 100 rpm using 250 ml Erlenmeyer flasks containing 10 ml of different Cr(VI) ion concentrations maintained at pH 2–9. The retention of Cr(VI) on NCN resin was conducted by agitating different weighted amount (50–200 mg) of the synthesized resin with 10 ml of Cr(VI) ion solution of different concentration (10–100 mg/l) at constant temperature of 30°C. The residual of Cr(VI) ion concentration was determined using the Perkin Elmer Atomic Absorption Spectrophotometer (AAS). The percent removal of Cr(VI) ion was calculated by eq. 1.

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

Where C_i and C_e are the initial and equilibrium concentration (mg/l) of Cr(VI) ion solutions respectively.

Experimental Design

Response Surface Methodology (RSM), an experimental technique was designed to find an optimal response. The Central Composite Design (CCD) was selected to study the combined effects of adsorbent dose (A, mg), pH of Cr(VI) ion solution (B), initial Cr(VI) ion concentration (C, mg/l) and agitation time (D, min) on percent removal. Each variable was studied at three different levels (low, medium and high, coded as -1, 0 and +1 respectively) as shown in Table 1. The design consisted of thirty runs, each run was performed twice to find the mean values for the CCD analysis under the response surface methodology. The design of the experiments was statistically analyzed by using Stat Graphics plus for Windows 5.1 (Stat-Point Technologies Inc. 2009)¹⁵.

Table 1. Levels of factors used in experimental design for removal of Cr(VI)

| Independent variables ranges | | Coded levels | | |
|------------------------------|-------------|--------------|-----|-----|
| | | - 1 | 0 | +1 |
| Amount (mg) | A(x_1) | 50 | 125 | 200 |
| Concentration (mg/l) | B (x_2) | 10 | 55 | 100 |
| pH | C (x_3) | 2 | 5.5 | 9 |
| Time (min.) | D (x_4) | 10 | 95 | 180 |

RESULTS AND DISCUSSION

The conventional batch sorption method require large number of experiments to find the optimal response. A major disadvantage of the conventional method is that it uses a variation of only one parameter at a time keeping the other parameters constant, and thus, the cumulative effect of all the affecting parameters at a time cannot be studied which could lead to unreliable results¹⁶. However, in RSM, the interactions of two or more variables can be studied simultaneously and the results are more reliable with the less process variability, less treatment time and minimum cost¹⁷. The CCD model was used to optimize the uptake of Cr(VI) ion by synthesized resin. The adsorption experiments, 1–25 (Table 2) were performed to optimize the sorption and 25–30 (Table 2) were performed to find the experimental error. The CCD model predicted the 100% removal of Cr(VI) ions while experimentally 99.5% of Cr(VI) ions have been removed successfully from aqueous media by synthesized resin at optimum values; adsorbent dose 200 mg, initial Cr(VI) ion concentration 10 mg/l, agitation time 136 min and pH 2. $R^2=99.92\%$ and $R^2_{\text{adj.}}=99.84\%$, indicating that the experimental and predicted values for Cr(VI) ion uptake are in close agreement as shown in Table 2. The accuracy and the fitting of the model were evaluated by the analysis of variance (ANOVA). The ANOVA results showed the lack of fit is not significant and regression is meaningful ($P=0.00352<0.05$) as shown in Table 3.

Characterization

The infrared spectra of Amberlite XAD-2 (1), NCN resin (7) and Cr(VI) loaded NCN resin were recorded using the Thermo Nicolet FT-IR spectrometer containing diamond accessory. Figure 2 (a-b) shows the FT-IR spectrum of XAD-2 (unmodified) and NCN resin, the additional peaks at; 3378.89 cm⁻¹ for OH and 1348.01 cm⁻¹ for CH₂ in the FT-IR spectrum-b, supported the formation of NCN resin. In order to confirm the formation of NCN resin (7), an elemental analysis of synthesized resin was performed and resulted C, 84.89; H, 5.68; O, 9.50%. Calculated for C₉₆H₇₆O₈; C, 84.93; H, 5.64; O, 9.43%. The elemental analysis result confirmed the formation of NCN resin (7), having the polymeric structure with both the m and n repeating units, the value for these both variables was approximately equal to 2, i.e. m=n. Figure 3 (a-b) shows the FT-IR spectrum of NCN resin (unloaded) and Cr(VI) loaded NCN resin; characteristic change in peak intensities 3378.89 cm⁻¹ (medium) to 3378.89 cm⁻¹ (weak), 1601.36 cm⁻¹ (medium) to 1601.36 cm⁻¹ (weak), 1527.81 cm⁻¹ (medium) to 1527.81 cm⁻¹ (weak), 1446.08 cm⁻¹ (medium) to 1446.08 cm⁻¹ (weak), 1348.01 cm⁻¹ (strong) to 1348.01 cm⁻¹ (medium) and disappearance of peak at 1041.54 cm⁻¹ have been observed which confirmed the involvement of hydroxyl groups in adsorption of Cr(VI) ions.

Table 2. Experimental design and results for percentage removal of Cr(VI) ion by NCN resin

| Trail | Coded values | | | | % Removal (Experimental) | % Removal (Predicted) |
|-------|--------------|----|----|----|-----------------------------|--------------------------|
| | A | B | C | D | | |
| 1 | -1 | -1 | -1 | -1 | 35.50 | 36.25 |
| 2 | +1 | -1 | -1 | -1 | 79.18 | 78.96 |
| 3 | -1 | +1 | -1 | -1 | 21.11 | 21.44 |
| 4 | +1 | +1 | -1 | -1 | 69.97 | 69.92 |
| 5 | -1 | -1 | +1 | -1 | 24.58 | 24.09 |
| 6 | +1 | -1 | +1 | -1 | 59.97 | 60.29 |
| 7 | -1 | +1 | +1 | -1 | 10.91 | 10.68 |
| 8 | +1 | +1 | +1 | -1 | 52.11 | 52.65 |
| 9 | -1 | -1 | -1 | +1 | 35.73 | 34.98 |
| 10 | +1 | -1 | -1 | +1 | 98.89 | 99.74 |
| 11 | -1 | +1 | -1 | +1 | 26.77 | 27.06 |
| 12 | +1 | +1 | -1 | +1 | 97.32 | 97.59 |
| 13 | -1 | -1 | +1 | +1 | 21.22 | 21.88 |
| 14 | +1 | -1 | +1 | +1 | 80.67 | 80.13 |
| 15 | -1 | +1 | +1 | +1 | 15.33 | 15.34 |
| 16 | +1 | +1 | +1 | +1 | 79.50 | 79.37 |
| 17 | -1 | 0 | 0 | 0 | 23.15 | 22.57 |
| 18 | +1 | 0 | 0 | 0 | 76.99 | 75.94 |
| 19 | 0 | -1 | 0 | 0 | 75.21 | 74.62 |
| 20 | 0 | +1 | 0 | 0 | 67.88 | 66.84 |
| 21 | 0 | 0 | -1 | 0 | 55.62 | 54.15 |
| 22 | 0 | 0 | +1 | 0 | 39.11 | 38.96 |
| 23 | 0 | 0 | 0 | -1 | 17.70 | 16.75 |
| 24 | 0 | 0 | 0 | +1 | 30.15 | 29.48 |
| 25 | 0 | 0 | 0 | 0 | 45.51 | 46.33 |
| 26 | 0 | 0 | 0 | 0 | 45.52 | 46.33 |
| 27 | 0 | 0 | 0 | 0 | 45.52 | 46.33 |
| 28 | 0 | 0 | 0 | 0 | 45.51 | 46.33 |
| 29 | 0 | 0 | 0 | 0 | 45.53 | 46.33 |
| 30 | 0 | 0 | 0 | 0 | 45.52 | 46.33 |

Table 3. ANOVA and estimated regression coefficients for Cr(VI) ion removal by NCN resin

| Source | Sum of Squares | Df | Mean Square | F-Ratio | P-Value | Regression coeff. |
|---------------|----------------|----|-------------|---------|---------|-------------------|
| Constant | | | | | | 63.922 |
| A:Amount | 3195.57 | 1 | 3195.57 | 3423.53 | 0.0000 | 0.140 |
| B:pH | 305.73 | 1 | 305.74 | 327.55 | 0.0000 | -24.377 |
| C:con | 825.23 | 1 | 825.23 | 884.10 | 0.0000 | -0.126 |
| D:time | 362.51 | 1 | 362.51 | 388.38 | 0.0000 | 0.549 |
| AA | 22.11 | 1 | 22.12 | 23.69 | 0.0002 | 0.000 |
| AB | 33.33 | 1 | 33.34 | 35.72 | 0.0000 | 0.005 |
| AC | 42.37 | 1 | 42.37 | 45.39 | 0.0000 | 0.000 |
| AD | 486.16 | 1 | 486.16 | 520.84 | 0.0000 | 0.000 |
| BB | 1542.04 | 1 | 1542.04 | 1652.05 | 0.0000 | 1.991 |
| BC | 1.9155 | 1 | 1.92 | 2.05 | 0.1725 | 0.002 |
| BD | 47.42 | 1 | 47.41 | 50.80 | 0.0000 | 0.006 |
| CC | 0.12 | 1 | 0.12 | 0.13 | 0.7237 | 0.000 |
| CD | 0.90 | 1 | 0.90 | 0.97 | 0.3406 | -0.000 |
| DD | 1396.79 | 1 | 1396.79 | 1496.44 | 0.0000 | -0.003 |
| Total error | 14.00 | 15 | 0.93 | — | — | — |
| Total (corr.) | 17864.30 | 29 | — | — | — | — |

Statistical Analysis

The verification of the model adequacy is an important part of the data analysis procedure, as the approximating model would give poor or misleading results if it is an inadequate fit. The residual plots were examined to approximate the model¹⁸.

Interpretation of Residual Graphs

The residual is the difference between the observed and the predicted values from the regression to obtain the normal distribution. The Durbin-Watson statistic test is a powerful statistical mean that generates normal prob-

ability plot and performs a hypothesis test to examine whether the observations follow the normal distribution. The P value ($0.00352 < 0.05$) showed that the null hypothesis could not be rejected so it was concluded that residuals followed the normal distribution. It could be seen that the experimental points were reasonably aligned, suggesting normal distribution.

The normality of the data can be checked by plotting the normal probability plot (NPP) of the residuals. Fig. 4a, plots the normal probability versus residuals for the removal of Cr(VI) ion. The residuals show, how well the

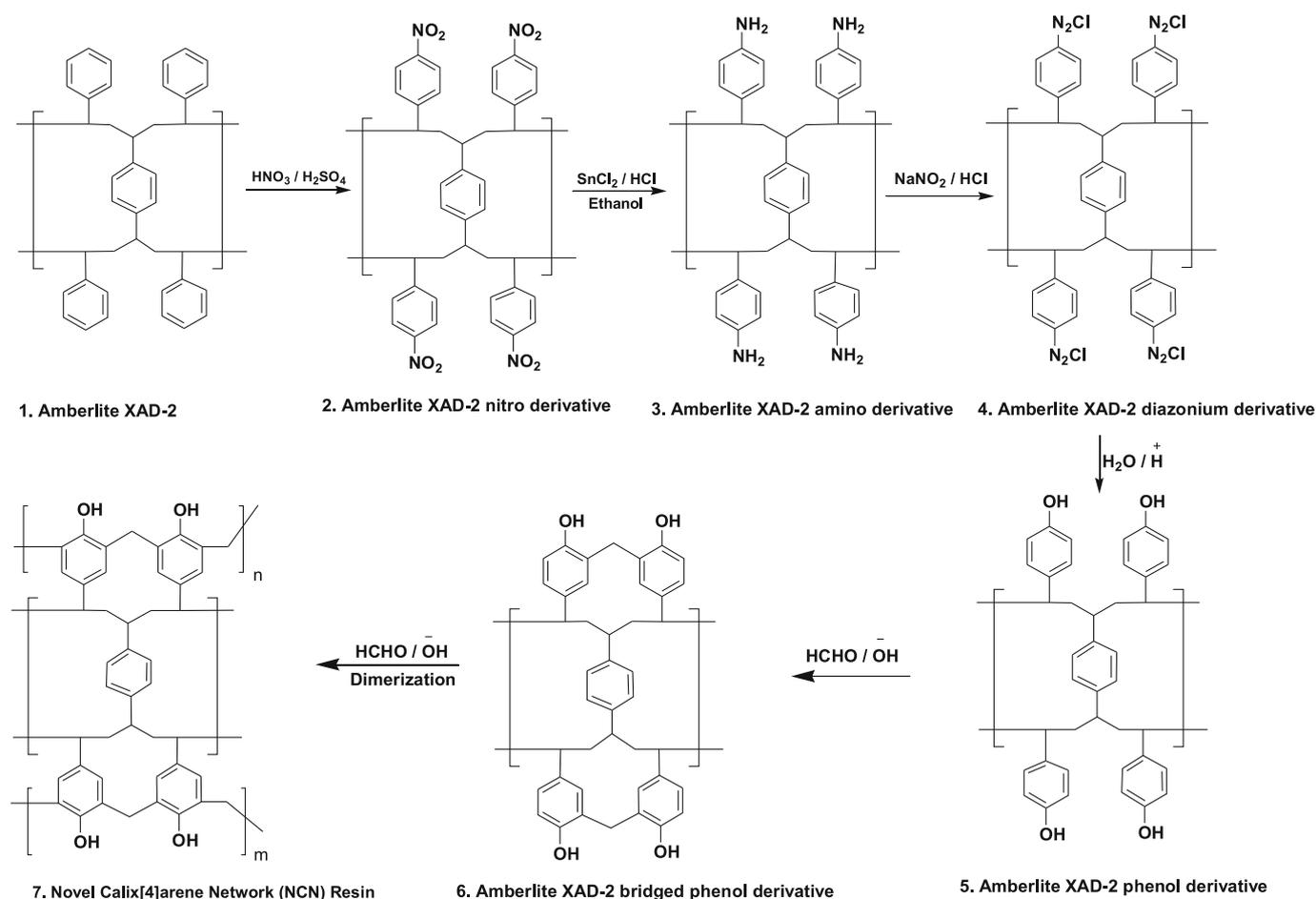


Figure 1. Synthesis of Novel Calix[4]arene-Network (NCN) Resin from Amberlite XAD-2

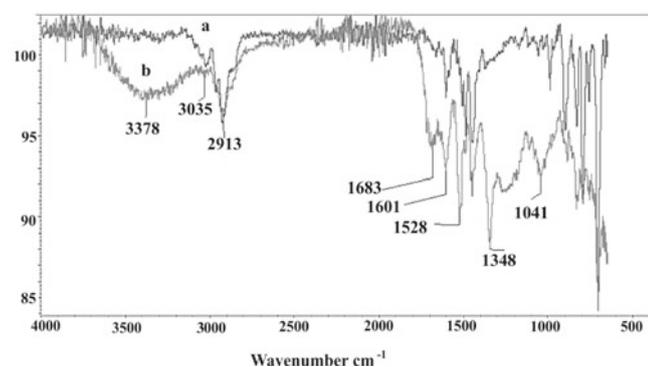


Figure 2. FT-IR Spectrum; Amberlite XAD-2 plain (a) and NCN Resin (b)

model satisfies the assumptions of ANOVA. The residuals measure the number of standard deviations separating the actual and predicted values that indicate, neither the response transformation was needed nor there was any apparent problem with normality. Fig. 4b plots the residuals versus the predicted values (fitted); the residuals were scattered randomly around zero, showing that the errors have a constant variance. The general impression was that the plot should be a random scatter, suggesting the variance of original observations is constant for all values of the response. This plot also indicates the possible existence of the outliers if a point lies far from the majority of points. It is important to identify the outliers, because they can significantly influence the model, providing the potentially misleading or incorrect results. All points were found in the range of +1.5 to -1.5, which confirmed that the model did not violate the

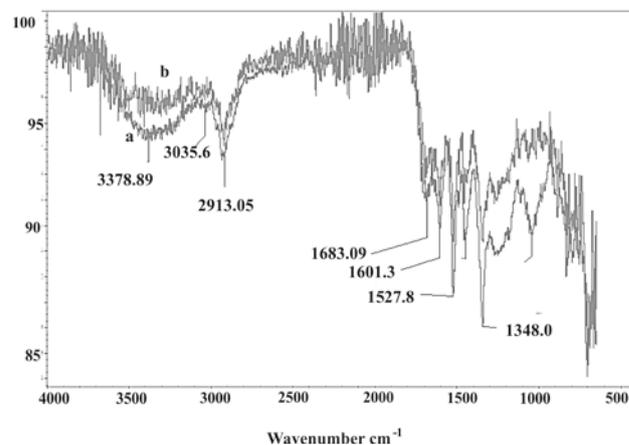


Figure 3. FT-IR Spectrum; NCN Resin (a) and Cr(VI) loaded NCN Resin (b)

regression assumptions. Fig. 4c shows the plot for the observed versus the predicted adsorption of Cr(VI) ions onto NCN resin. The actual values measure the percent removal data for a particular run and the predicted values are evaluated from the CCD model and are generated by using the approximating functions. The plot showed a good agreement between the experimental and the predicted values of sorption.

Interpretation of Response Surface Plots

The 3D response surface plots (Fig. 5a–5c) are the graphical representations of the regression equation. The main goal of response surface is an efficient search for the optimum values of variable when the response is maximized. Each graph represents an infinite number

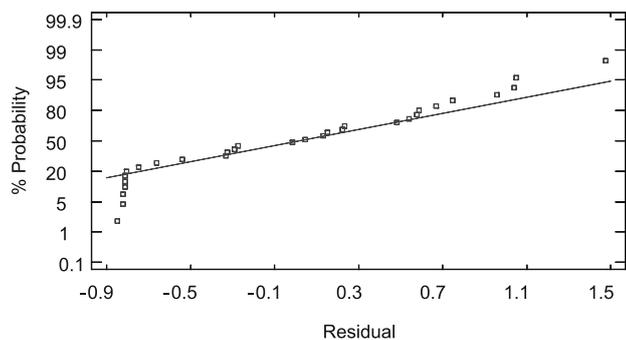


Figure 4a. The Studentized residuals and normal percentage probability plot of adsorption of Cr(VI)

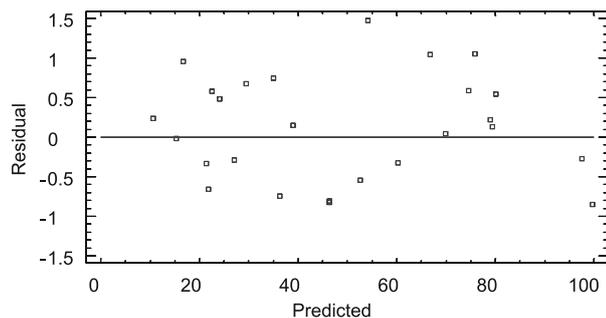


Figure 4b. Residual plot for % Removal of Cr(VI) by NCN resin

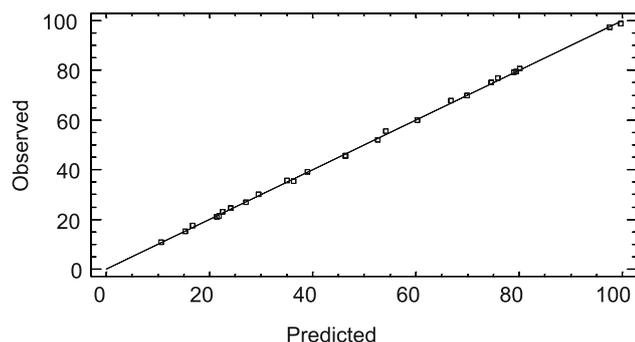


Figure 4c. plot of observed versus predicted values for % Removal of Cr(VI) by NCN resin

of combinations of two test variables with the other two maintained at their respective optimum value. Fig. 5a shows an interactive effect of pH (2–9) and initial Cr(VI) ion concentration (10–100 mg/l) at the optimum adsorbent dose (200 mg) and the agitation time (136 min) on Cr(VI) ions uptake. The cavities and hydroxyl groups of NCN resin played a vital role in the adsorption of Cr(VI) ion. About 60% of Cr(VI) removal was achieved due to the adsorption in the cavities that was not effected by pH ranging 6–9, while Cr(VI) removal further increased to 99.5% due to functioning of pH ranging 6–2 and can be explained on the basis of the participation of hydroxyl groups of the resin. In the acidic medium, the protonation of hydroxyl groups occurred, the extent of protonation increased as pH decreased (6–2). The positively charged hydronium ions associated with the negatively charged CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ existing in the acidic medium, resulting in an adequate increase in percent sorption¹⁹. While percent removal slightly decreased with increasing initial Cr(VI) ion concentration. Fig. 5b shows the interactive effect of adsorbent dose (50–200 mg) and the agitation time (10–180 min) at the optimum initial Cr(VI) ion concentration (10 mg/l) and pH (2) on uptake of Cr(VI) ion. The Cr(VI) ion uptake was increased with increasing adsorbent dose

due to the increase of active sites, while metal uptake increased with an increase of agitation time, a decline was observed with a further increase of the agitation time might be due to the desorption process. With the increase of the adsorbent dose, the extent of the effect of agitation was increased, within 136 min, about 99.5% removal of Cr(VI) ion was achieved. Fig. 5c shows the combined effect of agitation time (10–180 min) and initial Cr(VI) ion concentration (10–100 mg/l) on the uptake of Cr(VI) ions at optimum pH (2) and adsorbent dose (200 mg). The initial Cr(VI) ion concentration has inverse effect on percent removal of Cr(VI) ion, the extent of the effect of the agitation time decreased with the increase of initial Cr(VI) ion concentration, indicated the adsorption equilibrium because of the limited adsorption sites available for Cr(VI) ions²⁰.

Adsorption Isotherms

The equilibrium relationship between the adsorbent and adsorbate was described by the adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. In order to evaluate the sorption capacity and the

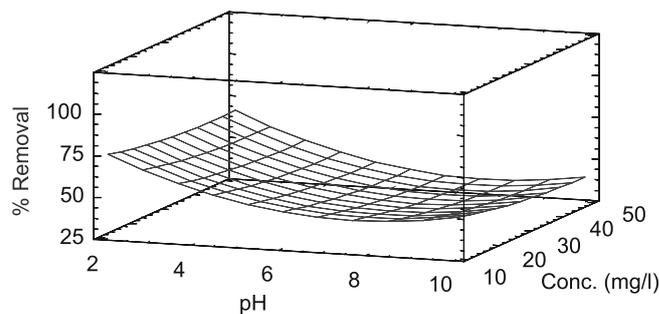


Figure 5a. Combined effect of pH and concentration for % Removal of Cr(VI) by NCN resin

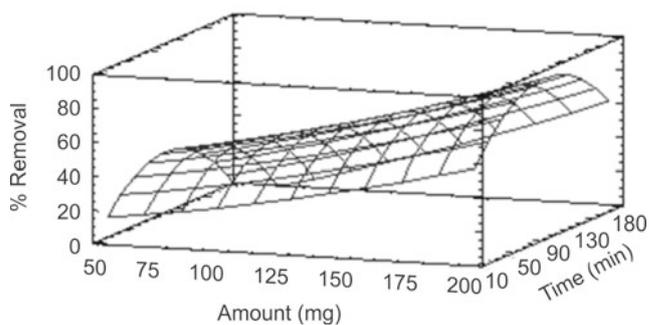


Figure 5b. Combined effect of Amount of resin and agitation time for % Removal of Cr(VI) by NCN resin

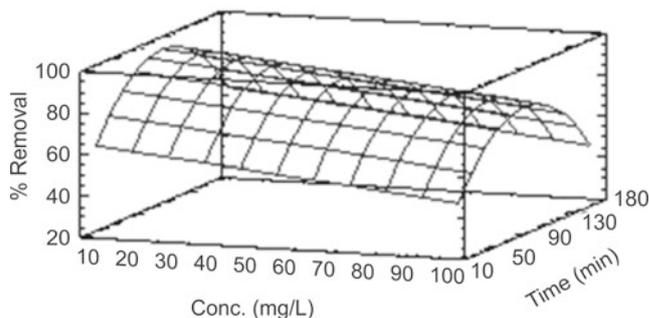


Figure 5c. Combined effect of concentration and agitation time for % Removal of Cr(VI) by NCN resin

nature of sorption of Cr(VI) ions onto the surface of NCN resin. The Langmuir and Dubinin-Radushkevich (D-R) isotherms were investigated.

Langmuir Isotherm

The Langmuir isotherm model is based on the assumption that there are finite numbers of active sites which are homogeneously distributed over the surface of the adsorbent and there is no interaction between the adsorbed molecules. The study of isotherm was carried out by varying the initial Cr(VI) ion concentrations ranging 10–100 mg/l while pH was kept constant at 2. The amount of the sorbent used was 200 mg and the mixture was agitated for 136 min at 30°C. The linear form of the Langmuir equation is represented by eq. 2.

$$\frac{C_e}{C_{ads}} = \frac{1}{Q} C_e + \frac{1}{Qb_L} \quad (2)$$

Where C_e is the equilibrium concentration of Cr(VI) ions in solution (mg/l) and C_{ads} is the adsorbed amount of Cr(VI) ion onto NCN resin surface (mg/g), Q and b_L are the Langmuir constants related to the monolayer sorption capacity (ml/g) and free sorption energy (l/g) respectively. Experimental data fitted eq. 2 very well with correlation coefficient equal to 0.982. An important characteristic of the Langmuir isotherm can be expressed by a dimensionless factor, R_L , mathematically represented by eq. 3.

$$R_L = \frac{1}{1 + (b_L C_e)} \quad (3)$$

The R_L values indicate the type of adsorption as either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$)²¹. The R_L values calculated for the sorption of Cr(VI) ions on NCN resin surface were in the range of 0.0057–0.1 through the investigated range of concentrations indicating the favorable nature of sorption. The Langmuir sorption capacity was calculated from slope of the plot and was found to be 176.1 ± 2.4 mg/g.

D-R Isotherm

D-R sorption isotherm was chosen to estimate the characteristic apparent free energy of adsorption. The linear equation of D-R model is represented by eq. 4.

$$\ln C_{ads} = \ln K_{D-R} - \beta \varepsilon^2 \quad (4)$$

Where, ε is Polanyi potential and is equal to $RT \ln(1 + 1/C_e)$, T is temperature and R is general gas constant; β is related to the mean free energy of adsorption per mole of the adsorbent when it is transferred from infinite distance in the solution to the surface of the solid. C_{ads} and C_e are as previously described, a linear relationship was obtained as a plot of $\ln C_{ads}$ versus C_e with correlation coefficient equal to 0.973. Magnitude of adsorption energy was calculated from the slope of the plot using eq. 5 and was found to be 7.93 kJ/mol, suggesting the sorption process may be physical and/or partially ion-exchange²².

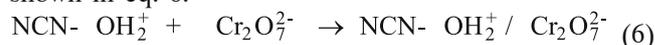
$$E = \frac{1}{\sqrt{-2\beta}} \quad (5)$$

Table 4. Model validation for Cr(VI) ion removal by NCN resin

| Amount of adsorbent A (mg) | pH B | Initial Concentration C (mg/l) | Time D (min) | % Removal | |
|----------------------------|------|--------------------------------|--------------|-----------|--------------|
| | | | | Predicted | Experimental |
| 200 | 2.0 | 10 | 136 | 100 | 99.5 |

POSSIBLE SORPTION MECHANISM

Based on the FT-IR study, pH dependent sorption observations and mean free energy of the sorption calculated from D-R isotherm following mechanism of the process could be proposed. The cavities and hydroxyl groups of NCN resin participated in the sorption process. Hydroxyl groups undergo protonation to form positively charged hydronium ions which associated with the negatively charged chromate ions resulting in the adsorption, as shown in eq. 6.



MODEL VALIDATION

The optimum adsorption conditions determined from CCD model were used to validate the model. The model was proved to be valid due to its good predictability. Maximum percent removal (99.5%) of Cr(VI) ions was achieved at optimum conditions predicted by CCD model and comparable experimental and predicted removal values. Table 4 shows a good agreement between experimental and predicted values for Cr(VI) ions removal. This shows that the model has high prediction ability.

DESORPTION AND RECYCLING OF NCN RESIN

Desorption of the adsorbed Cr(VI) ion from the NCN resin was also studied in a batch experimental system. Various factors are probably involved in determining the rates of Cr(VI) ion desorption, such as the extent structure of the sorbent desorbing the medium and the nature of binding between adsorbent and adsorbate. However, an important factor appears to be binding strength. When 1.0 N NaOH was used as a desorption agent, the coordination sphere of chelated Cr(VI) anions was disrupted and subsequently Cr(VI) anions were released from the Cr(VI)-templates into desorption medium. In order to show the recycling of the NCN resin, adsorption-desorption cycles were repeated 6 times using the same NCN resin. NCN resin was reused and successfully adsorbed Cr(VI) ion without significant decrease in the sorption capacity.

INTERFERENCE OF OTHER IONS

The interfering effect due to Cd^{2+} , Cu^+ , Cu^{2+} , Al^{3+} , Pb^{2+} , Mg^{2+} , Ca^{2+} , Na^+ and K^+ at 10-fold excess was also studied at optimum conditions. It was found that under these conditions, there is no significant adverse effect on percent removal of Cr(VI) ions.

APPLICATION OF METHOD

The applicability of the proposed method was tested for the removal of Cr(VI) ions from an electroplating wastewater sample that was obtained from a small scale electroplating unit in Karachi, Pakistan. The sample was stored in polythene bottle. Cr(III) ions present in

the electroplating wastewater sample was oxidized to Cr(VI) ions with alkaline peroxide. The total chromium concentration was determined spectrophotometrically. The wastewater sample was treated with NCN resin in the batch process at optimum variables. Overall 98.7% of Cr(VI) ions have been adsorbed onto NCN resin. By applying 1.0 N NaOH, 100% desorption was achieved. NCN resin was reused six times successfully without a significant decrease in its performance.

COMPARISON OF SORPTION CAPACITIES

Various modified resins have been reported for the uptake of Cr(VI) ions from aqueous media. The capacity of NCN for Cr(VI) ions uptake is comparatively better than the other modified resin as shown in Table 5. This is due to the participation of hydroxyl groups and cavities for the adsorption of Cr(VI) ions.

CONCLUSIONS

The FT-IR and elemental analysis showed successful conversion of Amberlite XAD-2 into NCN resin. The synthesized NCN resin has been effectively used for Cr(VI) ions remediation using factorial design approach ($R=0.9992$) to predict the optimum variables. 98.7% of Cr(VI) ions have been removed successfully from electroplating wastewater, confirmed the practical applicability of the synthesized resin.

ACKNOWLEDGEMENT

Authors are thankful to Pakistan Science Foundation (PSF) for financial support.

Table 5. Comparison of sorption capacities for Cr(VI) sorption using different sorbent materials

| Adsorbent | Capacity (mg/g) | Ref. |
|---|-----------------|------|
| Iron oxide modified polyglycidyl methacrylate graft copolymer (PGMA) and hybrid adsorbent (PGMAFe) | 132.5 and 162.9 | 23 |
| Chitosan CCTS-ECH-DH Salophen | 238 | 24 |
| Chitosan CCTS-ECH-DH Salophen | 75.93 | 25 |
| Glycidyl methacrylate-based polymer (GMD) and (GMDFe) | 109.54 and 157 | 26 |
| Ion-imprinted polymer (IIP) and control polymer | 37.58 and 25.44 | 27 |
| Triethylamine impregnated Amberlite XAD-1180 | 171.82 | 28 |
| Iron oxide based gelatin nanoparticles (FeOGel) | 120 | 29 |
| Polysulfone microcapsules containing Cyanex 923 | 22.36 | 30 |
| Magnetic poly(GMA-EGDMA) beads | 137.7 | 31 |
| Chitosan based polymeric surfactants (CBPSs) | 180 | 32 |
| Methylene crosslinking of calix[6]arene hexacarboxylic acid | 67.6 | 33 |
| Immobilization of novel the semicarbazone derivatives of calix[4]arene onto magnetite nanoparticles | 15.5 | 34 |
| A Calix[4]arene-Containing Polysiloxane Resin | 50.4 | 35 |
| Immobilization of calix[6]arene bearing carboxylic acid and amide groups on aminopropyl silica gel | 37.66 | 36 |

LITERATURE CITED

- Cronje, K.J., Chetty, K., Carsky, M., Sahu, J.N. & Meikap, B.C. (2011). Optimization of chromium(VI) sorption potential using developed activated carbon from sugarcane bagasse with chemical activation by zinc chloride. *Desalination* 275(1-3), 276–284. DOI: 10.1016/j.desal.2011.03.019.
- Arica, M.Y. & Bayramoglu, G. (2005). Cr(VI) biosorption from aqueous solution using free and immobilized biomass of *Lentinussajor-caju*: preparation and kinetic characterization. *Colloid.Surf.A.* 253(1-3), 203–211. DOI: org/10.1016/j.colsurfa.2004.11.012.
- Bayramoglu, G., Celik, G., Yalcin, E., Yilmaz, M. & Arica, M.Y. (2005). Modification of surface properties of *Lentinus sajor-caju* mycelia by physical and chemical methods: evaluation of their Cr⁶⁺ removal efficiencies from aqueous medium. *J. Hazard. Mater.* 119(1-3) 219–229. DOI: 10.1016/j.jhazmat.2004.12.022.
- Bayramoglu, G. & Arica, M.Y. (2011). Synthesis of Cr(VI)-imprinted poly(4-vinyl pyridine-co-hydroxyethyl methacrylate) particles: Its adsorption propensity to Cr(VI). *J. Hazard. Mater.* 187(1-3), 213–221. DOI: 10.1016/j.jhazmat.2011.01.022.
- Ahmad, H.B., Mohammad, S.H.i, Masoud, S.G., Somayye, Z. & Hosseini, E.H.H.B. (2010). Kinetics, equilibrium and thermodynamic study of Cr(VI) sorption into toluidine blue o-impregnated XAD-7 resin beads and its application for the treatment of wastewaters containing Cr(VI). *Chem. Eng. J.* 160(1), 190–198. DOI: 10.1016/j.cej.2010.03.040.
- Uluozlucua, O.D., Tuzen, M., Mendil, D., Kahveci, B. & Soylak, M. (2009). 3-Ethyl-4-(p-chlorobenzylideneamino-4,5-dihydro-1H-1,2,4-triazol-5-one (EPHBAT) as precipitant for carrier element free coprecipitation and speciation of chromium(III) and chromium(VI). *J. Hazard. Mater.* 172(1), 395–399. DOI: 10.1016/j.jhazmat.2009.07.021.
- Suhong, C., Qinyan, Y., Baoyu, G., Qian, L. & Xing, X. (2011). Removal of Cr(VI) from aqueous solution using modified corn stalks: Characteristic, equilibrium, kinetic and thermodynamic study. *Chem.Eng.J.*168, 909–917. DOI: 10.1016/j.cej.2011.01.063.
- Korngold, E., Belayev, N. & Aronov, L. (2003). Removal of chromates from drinking water by anion exchangers. *Sep. Purif. Technol.* 33(2), 179–187. DOI: 10.1016/S1383-5866(03)00006-6.
- Serpil, E. & Erol, P. (2010). Evaluation of Amberlite IRA96 and Dowex 1×8 ion-exchange resins for the removal of Cr(VI) from aqueous solution. *Chem. Eng. J.* 161(1-2), 161–166. DOI: 10.1016/j.cej.2010.04.059.
- Narin, I., Kars, A. & Soylak, M. (2008). A novel solid phase extraction procedure on Amberlite XAD-1180 for speciation of Cr(III), Cr(VI) and total chromium in environmental and pharmaceutical samples. *J. Hazard. Mater.* 150(2), 453–458. DOI: 10.1016/j.jhazmat.2007.04.125.
- Manjusha, K. & Reeta, V.R. (2007). Amberlite XAD-2 Impregnated with Cyanex302 for Separation of Traces of Thorium(IV) *Sep. Sci. Technol.* 42(10), 2255–2273. DOI: 10.1080/01496390701310439.
- Gonzalez, M.E.L. & Arribas, L.V.P. (2000). Chemically modified polymeric sorbents for sample Preconcentration; *J. Chromatogr. A* 902(1) 3–16. DOI: 10.1016/S0021-9673(00)00942-0.
- Katheline, O.V.F., Alcino, P.D.A., Monica, R.M.P.D.A. & Luiz, C.D.S.M. (2007). Microwave assisted Friedel-Crafts acylation reactions of Amberlite XAD-4TM resin, *Mater. Lett.* 61(4-5) 1190–1196. DOI: 10.1016/j.matlet.2006.06.081.
- Saima Q. M., Bhanger, M.I., Hasany, S.M., & Khuhawar, M.Y. (2007). The efficacy of nitrosonaphthol functionalized XAD-16 resin for the preconcentration/sorption of Ni(II) and Cu(II) ions. *Talanta* 72, 1738–1745. DOI: http://dx.doi.org/10.1016/j.talanta.2006.12.017.
- Siyal, A.N., Memon, S.Q. & Khaskheli, M.I. (2012). Optimization and equilibrium studies of Pb(II) removal by

grewia asiatica seed: A factorial design approach. *Polish J. Chem. Tech.* 14(1), 17–77. DOI: 10.2478/v10026-012-0062-9.

16. Tan, I.A.W., Ahmad, A.L., & Hameed, B.H. (2008). Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology. *Chem. Eng. J.* 137(3), 462–470. DOI: 10.1016/j.cej.2007.04.031.

17. Sanchez-Martin, J., J. Beltrán-Heredia, J. & Carmona-Murillo, C. (2011). Adsorbents from *Schinopsis balansae*: Optimization of significant variables. *Ind. Crop. Prod.* 33(2) 409–417. DOI:10.1016/j.indcrop.2010.10.038.

18. Box, G.E.P. & Hunter, W.G. (1987) *Statistics for Experiments: An Introduction to Design, Data Analysis and Model Building*. Wiley Interscience, New York.

19. Luis, K.C., Ramelito, C.A., Johannes, L.L.R., Marcel, O. & Van- der-Wielen, L.A.M. (2001). Potential of biosorption for the recovery of chromate in industrial wastewaters. *Ind. Eng. Chem. Res.* 40(10), 2302–2309. DOI: 10.1021/ie0008575.

20. Saban, M.T. (2011). Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by peanut hull. *Chem. Eng. J.* 168(3), 1234–1240. DOI: 10.1016/j.cej.2011.02.021.

21. Saima, Q.M., Hasany, S.M., Bhangar, M.I. & Khuhawar, M.Y. (2005). Enrichment of Pb(II) ions using phthalic acid functionalized XAD-16 resin as a sorbent. *J. Colloid Interf. Sci.* 291(1), 84–91. DOI: 10.1016/j.jcis.2005.04.112.

22. Saeed, M.M. (2003). Adsorption profile and thermodynamic parameters of the preconcentration of Eu(III) on 2-thenoyltrifluoroacetone loaded polyurethane (PUR) foam. *J. Radioana. Nucl. Chem.* 256(1), 73–80. DOI: 0236-5731/2003/USD 20.00.

23. Duranoğlu, D., Buyruklardan Kaya, T.G., Beker, U. & Şenkal, B.F. (2012). Synthesis and adsorption properties of polymeric and polymer-based hybrid adsorbent for hexavalent chromium removal. *Chem. Eng. J.* (181–182), 103–112. DOI: org/10.1016/j.cej.2011.11.028.

24. Nuriye, K., Mustafa, S., Gulsin A. & Ismet, H.U. (2012). Synthesis of crosslinked chitosan possessing schiff base and its use in metal removal. *J. Inorg. Organomet. Polym.* 22, 166–177. DOI: 10.1007/s10904-011-9509-3.

25. Kumar, A.S., Rajesh, N., Kalidhasan, S. & Rajesh, V. (2011). An enhanced adsorption methodology for the detoxification of chromium using n-octylamine impregnated Amberlite XAD-4 polymeric sorbent. *J. Environ. Sci. Health., Part A* 46 (13), 1598–1610. DOI: 10.1080/10934529.2011.609460.

26. Kaya, I.G.B., Duranoğlu, D., Beker, U. & Senkal, B.F. (2011). Development of polymeric and polymer-based hybrid adsorbents for chromium removal from aqueous solution. *Clean – Soil, Air, Water* 39 (11), 980–988. DOI: 10.1002/clen.201000552.

27. Pakade, V., Cukrowska, E., Darkwa, J., Torto, N. & Chimuka, L. (2011). Selective removal of chromium (VI) from sulphates and other metal anions using an ion-imprinted polymer. *Water SA* 37 (4), 529–538. DOI: org/10.4314/wsa.v37i4.11.

28. Rajesh, N., Kumar, A.S.K., Kalidhasan, S. & Vildya, R. (2011). Trialkylamine impregnated macroporous polymeric sorbent for the effective removal of chromium from industrial wastewater. *J. Chem. Eng. Data* 56 (5), 2295–2304. DOI: 10.1021/je1012873.

29. Agrawal, P. & Bajpai, A.K. (2011). Synthesis of iron oxide based gelatin nanocomposites and their applications in removal of Cr (VI) ions from aqueous solutions. *J. Macromol. Sci. Part A Pure Appl. Chem.* 48 (1), 47–56. DOI: org/10.1080/10601325.2011.528308.

30. Ozcan, S., Tor, A. & Aydin, M.E. (2010). Removal of Cr(VI) from aqueous solution by polysulfone microcapsules containing Cyanex 923 as extraction reagent. *Desalination* 259 (1-3), 179–186. DOI: org/10.1016/j.desal.2010.04.009.

31. Bayramoğlu, G. & Yakup, A.M. (2008). Adsorption of Cr(VI) onto PEI immobilized acrylate-based magnetic beads: Isotherms, kinetics and thermodynamics study. *Chem. Eng. J.* 139 (1), 20–28. DOI: org/10.1016/j.cej.2007.07.068.

32. Lee, M.-Y., Hong, K.-J., Shin-Ya, Y. & Kajiuchi, T.

(2005). Adsorption of hexavalent chromium by chitosan-based polymeric surfactants. *J. Appl. Polym. Sci.* 96 (1) 44–50. DOI: 10.1002/app.21356.

33. Adhikari, B.B., Gurung, M., Kawakita, H., Jumina & Ohto, K. (2011). Methylene cross linked calix[6]arene hexacarboxylic acid resin: A highly efficient solid phase extractant for decontamination of lead bearing effluents. *J. Hazard. Mater.* 193, 200–208. DOI: org/10.1016/j.jhazmat.2011.07.051.

34. Enise, A., Serkan, E. & Mustafa, Y. (2011). Immobilization of novel the semicarbazone derivatives of calix[4]arene onto magnetite nanoparticles for removal of Cr(VI) ion. *J. Incl. Phenom. Macrocycl. Chem.* (1-10). DOI: 10.1007/s10847-011-0083-7.

35. Mustafa, T., Mustafa, E. & Mustafa, Y. (2006). A calix[4]arene-containing polysiloxane resin for removal of heavy metals and dichromate anion. *J. Macromol. Sci. Part A Pure Appl. Chem.* 43, 57–69. DOI: 10.1080/1060132050040590.

36. Mustafa, T. (2008). Immobilization of calix[6]arene bearing carboxylic acid and amide groups on aminopropyl silica gel and its sorption properties for Cr(VI). *J. Incl. Phenom. Macrocycl. Chem.* 61, 53–60. DOI: 10.1007/s10847-007-9392-2.