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ORIGINAL ARTICLE

# Evaluation of perchlorate sorption behavior of calix[4]arene appended resin

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**Abstract** In the present work, perchlorate sorption ability of calix[4]arene appended resin was investigated to develop a new efficient method for the removal of perchlorate from aqueous media. The column sorption process was performed at a wide range of pH (1–7) and perchlorate content in the effluent was determined through ion chromatography. From the results, it has been concluded that maximum sorption (97 %) of perchlorate is taking place at pH 3. The breakthrough curves were obtained as a function of time to get clear picture of sorption process and the data obtained was tested by applying two kinetic sorption models, i.e. Yoon-Nelson and BDST. The data obtained through experiments were compared with the theoretically calculated values and it has been found that both have close agreement with each other.

**Keywords** Perchlorate · Calix[4]arene · Fixed-bed column · Ion chromatography

## Introduction

Perchlorate is an emerging contaminant in the environment. Perchlorate salts are highly persistent in water for decades and their exposure in humans includes ingestion of contamination through drinking water and food. Due to potential toxicity perchlorate has become serious threat to human health. Perchlorate salts are most widely used in solid rocket fuel, fireworks, explosive materials, flares, dyes, household electronic appliances and pharmaceutical products [1]. These can disrupt thyroid hormone production by preventing iodide uptake into thyroid gland and result in a reduced production of hormones [2]. In 1990 US EPA considered perchlorate as toxic material and in 1998 US EPA included perchlorate in contaminant candidate list (CCL) with a drinking water level up to 24.5 ppb [3].

Although perchlorate is a strong oxidizing agent but kinetically it is inert in many redox reactions and shows non-complexing behavior with metals typically found in the environment [4]. Thus, due to inert nature perchlorate ion is very difficult to remove from water. Various perchlorate treatment technologies have been developed such as microbial reduction [5], electrochemical reduction [6], and membrane-based techniques [7]. Moreover, ion exchange technologies have also been used for the removal of perchlorate from contaminated water. These ion exchange resins are divided into two types, first type includes strong-base anion exchange resins that are selective but non-regenerable and second type is non-selective or low-selective resins, which are re-generable [8]. Many synthetic and natural resins have been used for the removal of perchlorate form aqueous media. Gu et al. [9] have used bifunctional Purolite A530E resin for the removal of perchlorate. Yoon et al. [10] have reported activated carbon and SR-7 ion exchange resin for the removal of perchlorate and mechanism of sorption of perchlorate has been studied.

In addition, calixarenes have been proved as an excellent class of building blocks for the synthesis of ionophores with almost unlimited derivatization possibilities [11]. To improve the ionophoric ability of calixarenes toward the target species, various groups are incorporated at their lower/upper rim and then appended within a polymeric backbone. Beside this, for definite functions such as the separation of ions from aqueous environment, etc., it is very important to have an insoluble form of calixarenes.

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Consequently, these macrocycles need to be modified in order to reduce their solubility by holding them into a polymeric matrix. The preparation of such insoluble polymeric calixarenes is done either by covalently linking the calixarene to the polymeric framework or by connecting two calixarene by some spacer or functionality to give to resin like substance [12, 13].

Various studies have been carried out by many research groups for the removal of anions, for example, Selahattin et al. silica gel-immobilized calix[4]arenes dichromate anion [14]. I.B Solangi et al. [15] appended Merrifield resin on lower rim of calix[4]arene derivative and used for the removal of fluoride from aqueous environment. I. Qureshi coworkers [16] used *p-tert* butylcalix[8]arene impregnated on XAD-4 for the removal of chromium(VI). Thus, ionophoric polymers have just received great importance may be due to their utility and stability in materials suitable for applications in separation sciences, etc. [17–20].

In the present study, a calix[4]arene based resin was synthesized according to previously reported method [21] and its ability towards removal of perchlorate from aqueous media through sorption process was assessed.

## Experimental

### Apparatus

Ion-chromatograph (Metrohm, Switzerland) instrument model 861 Advance Compact with 833 IC liquid handling unit equipped with self regenerating suppressor, which consists a double gradient peristaltic pump along with conductivity detector has been used. The IC anion column (4.0 × 250-mm) METROSEP A SUPP 4–250 (6.1006.430) was used to quantitate the perchlorate in the aqueous media. Standard method, with sodium hydrogen carbonate and sodium carbonate buffer as mobile phase at flow rate 1.5 ml/min, was applied. Peristaltic pump (Gilson, France) model M312 was used to control column flow rate. For pH measurements pH meter (781-pH/Ion meter, Metrohm, Herisau, Switzerland) with glass electrode and internal reference electrode was used.

### Standard solutions and reagents

All chemicals, except Merrifield Resin, were purchased from Merck (Darmstadt, Germany) and used without further purification. Merrifield resin 1 % cross-linked (200 × 400 mesh size) 1.0 × 1.3 mmol/g purchased from Alfa Aesar (Germany). High purity $KClO_4$ was used to prepare 1 g/L stock solution. Calibration standards were prepared using stock solution. All glassware and polyethylene bottles were thoroughly washed and soaked overnight in 5 M $HNO_3$, and rinsed with de-ionized water before use. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli-Q Plus water purification system (ELGA Model CLASSIC UVF, UK).

### Synthesis

Compounds **1–3** and resin **4** were synthesized according to previously reported methods [21–23] (Scheme 1).

### Sorption experiment

Fixed-bed column experiment has been carried out for the sorption of perchlorate on synthesized resin. The glass column of 0.8-mm diameter and 60-mm of length was used. Different bed depths were taken 3.5, 4.5, and 5.7-mm. 5 mg/L of perchlorate delivered downflow to column through peristaltic pump and volumetric flow rate was adjusted at 2 ml/min. Samples concentration was then determined by using Ion Chromatography.

### Analysis of fixed-bed column data

Time for breakthrough to occur and shape of the breakthrough curve are important parameters to determine the process operation and dynamic response of column adsorption process. The loading behavior of perchlorate on resin is expressed in term of $C_{eff}/C_o$ as a function of time or volume of the effluent for a given bed height, giving a breakthrough curve [24].

## Results and discussion

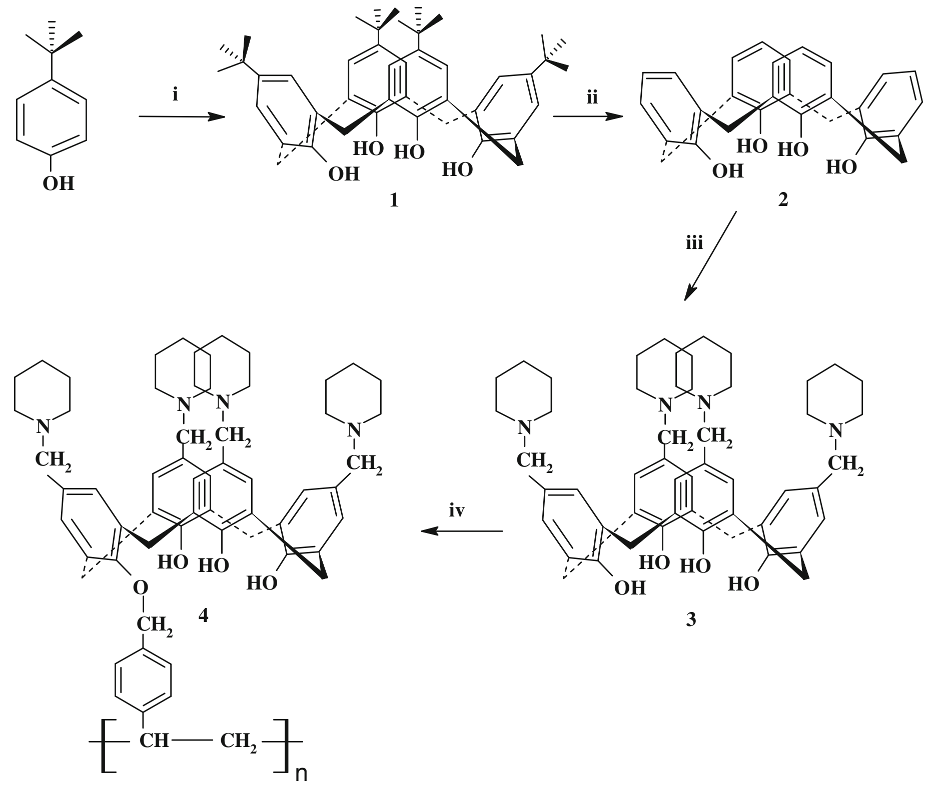
### Effect of pH on sorption

The perchlorate removal efficiency of the resin was studied in the pH range of 1–7. From the study it has been observed that maximum sorption occurs in acidic conditions i.e., at pH 3 (Fig. 1). These interactions can be attributed to the hydrogen bonding between perchlorate and the resin [21]. Possible interaction mechanism is shown in Fig. 2 which shows that at higher hydrogen ion concentration, amino group on resin gets protonated and attracts negatively charged perchlorate ion.

### Breakthrough curves

Breakthrough curves were plotted using different bed heights as shown in Fig. 3. Breakthrough curves show similar trend and the capacity of the column increases with increase in bed height. The service time and the bed depth are related to each other, when the sorption operation

**Scheme1** i HCHO/NaOH, ii $C_6H_6O/AlCl_3$, iii $C_6H_{10}N/$ HCHO, iv NaH/Merrifield Resin



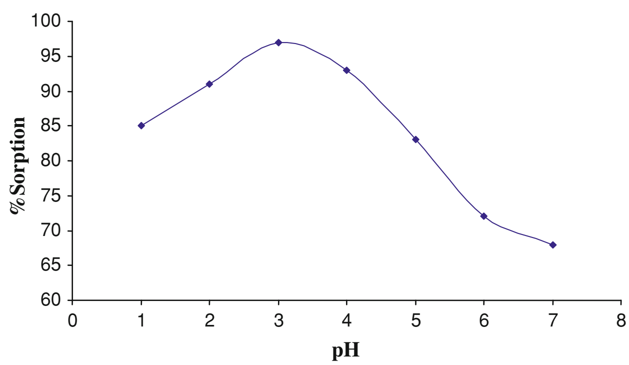




**Fig. 1** Effect of pH on sorption of perchlorate on calix[4]arene based resin

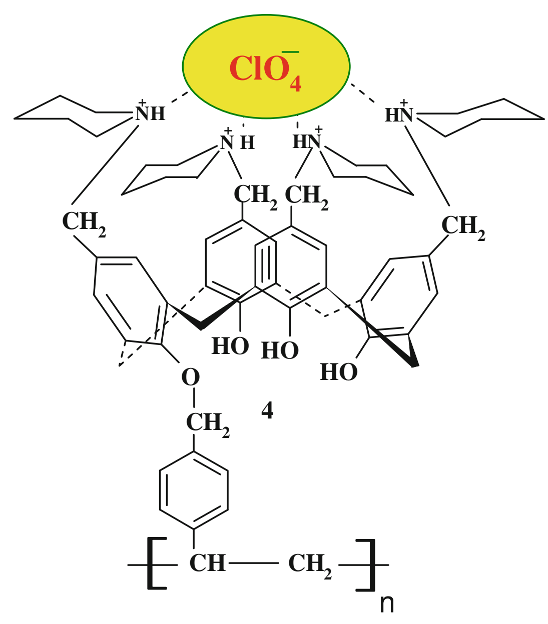



**Fig. 2** Representation of proposed interaction through hydrogen bonding between Resin **4** and perchlorate at low pH

begin, the concentration of perchlorate is lower, as the sorption proceeds and the sorbent material is being gradually saturated, the effluent concentration increases and reaches so-called breakthrough point.

## Modeling of breakthrough curves

### Yoon-Nelson model

The Yoon-Nelson model [25] is simple to use and less complicated than other models. It does not require any detailed data concerning the characteristic of adsorbate. The model is based on the assumption that the rate of decrease in the probability of sorption for each adsorbate molecule is proportional to the probability of adsorbate sorption and the probability of adsorbate breakthrough on the adsorbent [26].

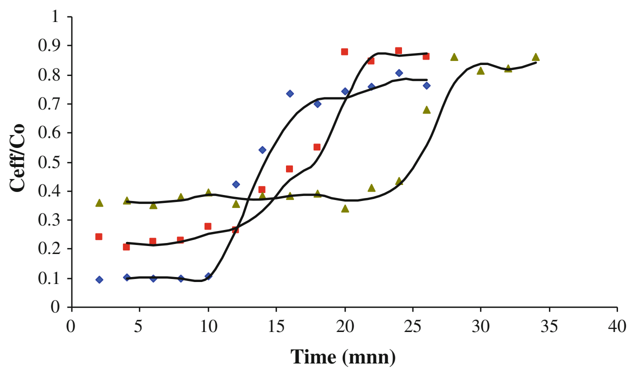



**Fig. 3** Breakthrough curves at different bed heights. At 3.5-mm (*filled diamond*), at 4.5-mm (*filled square*), at 5.7-mm (*filled triangle*)

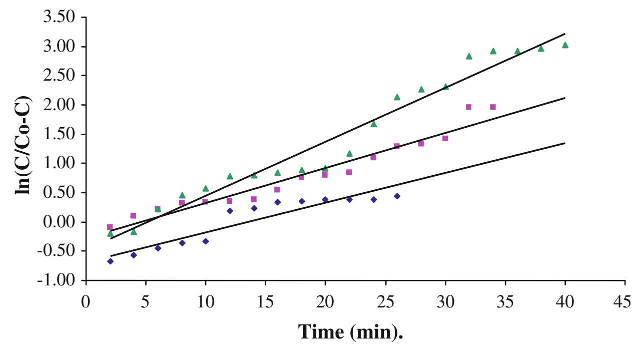



**Fig. 4** Application of Yoon and Nelson model to the experimental data. At 3.5-mm bed height (*filled diamond*), at 4.5-mm bed height (*filled square*), at 5.7-mm bed height (*filled triangle*)

$$\ln\frac{C}{C_o - C} = k_{YN}t - \tau k_{YN} \tag{1}$$

where $C$ is the concentration at any time, $C_o$ is the initial concentration, $t$ is the sampling time, $\tau$ is the 50 % breakthrough time and $k_{\mathrm{YN}}$ is the rate constant. The value of $k_{\mathrm{YN}}$ and $\tau$ can be obtained from plot of $\ln\frac{C}{C_o-C}$ versus $t$.

The value of maximum sorption capacity can be calculated from the model using equation [27].

$$q_o = \frac{1}{2}C_oQ(2\tau) = C_oQ\tau \tag{2}$$

where $q_{\mathrm{o}}$ is sorption capacity, $C_{\mathrm{o}}$ is inlet concentration; $\tau$ is the 50 % breakthrough time.

The simple theoretical model applied to explore the breakthrough behavior of perchlorate. From Yoon-Nelson plots the correlation coefficients ($R^2$), rate constant ($k_{\mathrm{YN}}$), and breakthrough time ($\tau$) were determined at different bed heights varied between 3.5, 4.5, and 5.7-mm. As shown in Table 1 $k_{\mathrm{YN}}$ decreased and $\tau$ increased with increasing bed heights. The linear regression coefficient shows good fit of data to theoretical data (Fig. 4).

## Bed depth service time model

The BDST model [28] is based on the assumption that the sorption rate is controlled by the surface reaction between adsorbate and the unused capacity of the adsorbent [29]. BDST model only describe the initial part of the breakthrough curve i.e., up to the breakpoint or 10–50 % of the saturation points [30]. This model explores the two characteristic parameters such as maximum sorption capacity and sorption rate constant. Original BDST model was proposed by Bohart and Adams as expressed by Eq. 3: [31].

**Table 1** Parameters predicted from the Yoon-Nelson Model

| $X$ (mm) | $k_{\mathrm{YN}}$ (1/min) | $\tau$ (min) | $R^2$ | $q_{\mathrm{o}}$ (mg/g) |
|---|---|---|---|---|
| 3.5 | 0.09 | 5.07 | 0.88 | 0.06 |
| 4.5 | 0.07 | 11.24 | 0.95 | 0.14 |
| 5.7 | 0.06 | 29.2 | 0.96 | 0.36 |

$$\ln\left[\frac{C_o}{C} - 1\right] = \ln\left[\exp\left(\frac{\mathrm{KN_oX}}{\mathrm{V}}\right) - 1\right] - \mathrm{KC_ot} \tag{3}$$

Hutchins [28] modified the Bohart and Adams model and proposed a linear relationship between the bed depth and service time by rearranging Eq. 3;

$$\mathrm{t} = \frac{\mathrm{N_oX}}{\mathrm{C_oV}} - \frac{1}{\mathrm{kC_o}}\ln\left[\frac{\mathrm{C_o}}{\mathrm{C}} - 1\right] \tag{4}$$

where $C_{\mathrm{o}}$ is the initial concentration, $C$ is effluent concentration, $X$ is the bed height, $N_{\mathrm{o}}$ is sorption capacity, $k$ is sorption rate constant, $V$ is applied flow rate and $t$ is the service time. Simplified form of Eq. 4 can be elaborated as shown in Eqs. 5–7:

$$t = b + mX \tag{5}$$

$$b = -\frac{1}{kC_o}\ln\left[\frac{C_o}{C} - 1\right] \tag{6}$$

$$m = \frac{\mathrm{N_o}}{\mathrm{C_oV}} \tag{7}$$

A plot of breakthrough time versus bed height will produce a straight line passing through origin, however, it does not pass through origin that results the sorption occurs through complex mechanism and more than one rate limiting steps are involved. Figure 5 represents a plot of breakthrough time versus bed height; from the slope of the respective line the sorption capacity per unit volume of bed ($N_{\mathrm{o}}$), and from the intercept the rate constant of sorption can be calculated.

Table 2 shows results obtain from the slope and intercept BDST model. The sorption capacity of column was obtained as 55 mmol/g with rate constant equals to 0.054 g/mmol/min. Correlation coefficient calculated by

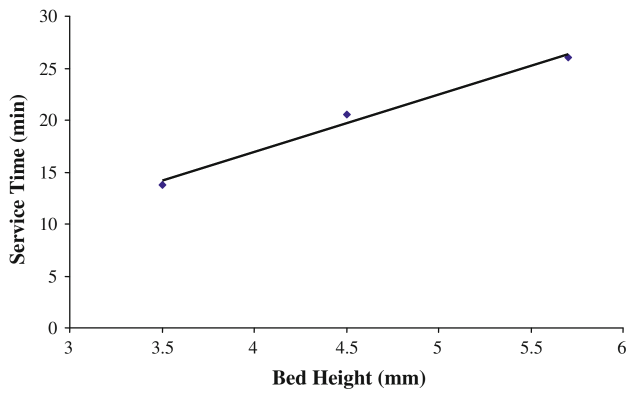



**Fig. 5** Prediction of the BDST model for experimental data at 50 % breakthrough

**Table 2** Parameters predicted from BDST Model

| $N_o \times 10^{-3}$ (mg/L) | $K$ (L/mg/min) | $R^2$ |
|---|---|---|
| 55.13 | 0.054 | 0.99 |

linearization of experimental data suggests that sorption data fit the BDST model very well.

### Interference study

The interference study has been performed in the presence of other ions such as $F^-$, $Cl^-$, $Br^-$, $NO_3^-$, $NO_2^-$, $PO_4^{3-}$, and $SO_4^{2-}$. It has been observed that there is no significant effect of $F^-$, $Cl^-$, $Br^-$, $NO_3^-$, $NO_2^-$, except $PO_4^{3-}$, and $SO_4^{2-}$, which showed 10–15 % decrease in the extraction efficiency of the resin may be due to the same nature of these oxyanions**.**

## Conclusion

In the present study, calix[4]arene based Merrifield resin has been found as an effective sorbent for the removal of perchlorate from aqueous media. Maximum perchlorate removal achieved at pH 3. The Yoon-Nelson and BDST models show that experimental data is in good agreement with theoretical data. Column capacity value (55 mmol/g) was obtained through graphical integration. The study hopefully will find its applicability in the remediation of perchlorate polluted sites.

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