Sorption of HCl from an Aromatic Hydrocarbon Mixture Using Modified Molecular Sieve Zeolite 13X
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ABSTRACT: In this study, the removal of chlorides, especially HCl, from an aromatic hydrocarbon mixture composed of benzene, toluene, xylenes, and ethylbenzene has been studied. Molecular sieve zeolite 13X as such and exchanged with different amounts of alkali and alkaline earth metal ions has been used as an adsorbent. Different techniques like inductively coupled plasma-optical emission spectroscopy, X-ray powder diffraction, N₂ adsorption–desorption for Brunauer–Emmett–Teller surface area and pore volume, and scanning electron microscopy were utilized to analyze all of the adsorbents. The effect of varying concentrations of alkali and alkaline earth metal cations and process parameters like temperature and flow rate on the removal of HCl has been studied by performing the adsorption breakthrough experiment. The main objective of this study is to determine the precise concentration of exchangeable ions and the optimum temperature, pressure, and feed flow rate at which the adsorbent exhibits the highest capacity toward the sorption of chloride species from an aromatic hydrocarbon stream. The maximum chloride sorption capacity was observed at \( T = 100 \, ^\circ\text{C}, \, P = 35 \, \text{kg/cm}^2 \), and a liquid hourly space velocity (flow rate) of 2 h\(^{-1}\) when the molecular sieve zeolite 13X (NaX) exchanged with 0.6 wt % Ca\(^2+\) and 1 wt % Mg\(^2+\) cations was used as an adsorbent.

1. INTRODUCTION
Contamination of refinery and petrochemical streams with chloride species is one of the major challenges faced in the hydrocarbon processing industries. Typically, halides are utilized to boost oil recovery\(^1\) and dewax crude oil that subsequently become a part of crude oil. The presence of these halides, especially chlorides, in naphtha from crude oil distillation could pose complications in hydrotreaters.\(^2\) Besides, the escape of chlorides from aged reforming catalysts has also been a problem and is one of the sources of chlorides in downstream hydrocarbons. These chlorides may cause serious operational issues if they are not removed from the hydrocarbon stream.\(^3\) The major issues associated with the occurrence of these chlorides in different hydrocarbon streams are as follows: (i) formation and deposition of ammonium chloride (NH₄Cl), (ii) corrosion of the processing equipment, (iii) poisoning of downstream costly catalysts and adsorbents, and (iv) product specification issues.\(^4\) Hence, it is imperative to remove these contaminants from hydrocarbon streams. Thus, in petrochemical plants and refineries, committed guard beds to trap chloride species are used at different locations. The precise locations and number of these guard beds rely on the nature and severity of contamination caused by the chloride species to the hydrocarbon stream. The life span of these guard beds is estimated based on their chloride sorption capacity, breakthrough time, pressure drop, and side product formation.

The most common and widely used approaches for removing chlorides from different hydrocarbon streams are pyrolysis,\(^5\) catalytic dechlorination,\(^6\)–\(^8\) and electrochemical dechlorination.\(^9\) Catalytic hydrodechlorination is one of the best approaches for removing both organic and inorganic chlorides. In this technique, a noble metal catalyst is used to convert organic chlorides to hydrogen chloride, which is subsequently removed by caustic treatment.\(^10\) However, this technique has a disadvantage of undesirable reduction of the hydrocarbons, such as unsaturated or oxygenated compounds.

Among the techniques used, adsorption is the preferred approach for removing chloride from different hydrocarbon streams. The most common and widely used adsorbents in this approach are alumina, activated alumina, promoted alumina, metal oxide/mixed metal oxides, and zeolites.\(^11\)–\(^20\) The literature studies have shown that activated and promoted

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alumina was the first kind of adsorbent used to capture the chlorides from hydrocarbon streams. Zeolite-based adsorbents are preferred materials over alumina and metal oxide-based adsorbents.

The major reasons for the preference of zeolites over alumina and metal oxides are their high efficiency in the removal of chlorides and competency to work in both the gaseous and liquid phase flow conditions. Zeolite-based adsorbents work on the principle of chemisorption on the surfaces and physisorption within the structured pores. As a result, zeolite-based adsorbents tend to have higher chloride sorption capacities than those of alumina-based adsorbents. The pore aperture of 13X with 10 Å is known to pick up light hydrocarbons like CHCl₃ and CCl₄, which otherwise remain untreated by the adsorbents like metal oxides, mixed metal oxides, and alumina.²¹

Further, zeolite-based adsorbents have a negligible tendency to form green oil as compared to alumina-based adsorbents. Moreover, when zeolites are exchanged with basic metal ions, the acidic surfaces responsible for green oil formation are further minimized and added to the advantage of no green oil formation.²² Due to these added advantages, zeolite-based adsorbents have attracted the attention of researchers. Recently, many researchers have explored the feasibility of zeolite-based adsorbents for the sorption of chlorides, especially organic chlorides from a wide variety of hydrocarbon streams.

Kim et al.²³ have studied the potential of zeolite 13X to remove HCl. Sharma et al.²⁴ have performed a comparative analysis of different zeolite-based adsorbents for the sorption of HCl from H₂ streams and observed that zeolite 13X has a higher potential of HCl removal compared to other zeolite variants. Moreover, they have examined the effect of cation loading on HCl sorption capacity and found that cation loading on zeolites significantly impacts the HCl uptake.

Zhang et al.²⁵ have investigated the effect of impregnation of different metal ions on Hβ zeolites for the removal of organic chlorides from model naphtha. They found that when Hβ was modified with Zn, the chloride pickup capacity was enhanced drastically as compared to the parent Hβ zeolite. Additionally, they have regenerated the spent adsorbent and observed that the adsorbent was regenerated successfully.

Grisdanurak et al.²⁶ have investigated the impact of hydrocarbons on HCl removal from refinery off-gas using a NaY zeolite prepared from rice husk. They noticed that HCl adsorption was higher in the presence of alkenes as compared to the presence of light alkanes.

Torres et al.²⁷ have investigated the pyrolysis products of polyolefinic waste and the removal of HCl from this pyrolytic product using alumina and zeolite-based adsorbents. They found that zeolitic adsorbent was more efficient in removing HCl and had a higher capacity compared to alumina.

Despite the commercial relevance of chloride removal from the vapor and liquid phase, there is a scarcity of adsorption data on zeolitic adsorbents. Therefore, investigations on the utilization of zeolites for the removal of chlorides are desirable.

Thus, in this study, the removal of chlorides (HCl) from an aromatic hydrocarbon mixture comprising benzene, toluene, xylenes, and ethylbenzene has been studied over the molecular sieve zeolite 13X exchanged with varying amounts of Mg²⁺, Ca²⁺, and Cs⁺ ions. The adsorbent samples were analyzed by means of diverse techniques like X-ray powder diffraction.

**Figure 1.** Graphical presentation of the ion-exchange procedure.
and further, it was ion-exchanged with alkali (Cs+) and alkaline molecular sieve zeolite 13X (NaX) as a base case adsorbent, these cations by protons. In this study, we have utilized the exchanged zeolite for HCl will depend on the exchange of species (HCl) by performing the breakthrough experiment. The objective of this study is to improve the surface area and the specie concentration and process parameters, viz., temperature and flow rate has also been studied on the removal of chloride (HCl) removal capacity.

2. RESULTS AND DISCUSSION

HCl is polar and acidic in nature; thus, an adsorbent having basic properties will be a good choice for the selective adsorption of HCl from the hydrocarbon stream. Zeolites have extra-framework labile cations like Na+ or Ca2+ inside the zeolite pores, which are likely to chemically react with chloride ions to form a salt, and the negative charge on the zeolite framework gets compensated by exchange with the protons released from HCl. The effectiveness of the different cation-exchanged zeolite for HCl will depend on the exchange of these cations by protons. In this study, we have utilized the molecular sieve zeolite 13X (NaX) as a base case adsorbent, and further, it was ion-exchanged with alkali (Cs+) and alkaline earth metal cations (Ca2+ or Mg2+) as extra-framework cations. The schematic of the ion-exchange process is shown in Figure 1.

The effect of compensating cations on the chloride pickup capacity of molecular sieve zeolite 13X has been investigated. Moreover, the effect of process conditions like temperature and flow rate has also been studied on the removal of chloride species (HCl) by performing the breakthrough experiment. The objective of this study is to find the specific concentration of compensating cations and optimum operating conditions like temperature, pressure, and flow rate for the sorption of chloride from aromatic hydrocarbons, specifically from the BTX mixture.

2.1. Physicochemical Characterization. Molecular sieve zeolite 13X (NaX) and Ca2+, Mg2+, and Cs+ ion-exchanged zeolite 13X samples were characterized using XRD, inductively coupled plasma-optical emission spectrometry (ICP-OES), scanning electron microscopy (SEM), and BET surface area based on N2 adsorption–desorption using a surface area analyzer ASAP 2020 (Micromeritics).

To confirm the percentage loading of different metal ions on zeolite 13X and the reproducibility of the ion-exchange process, ICP-OES analysis of all of the final samples was done repeatedly and found that the results were reproducible without any divergence. ICP results are compiled and shown in Table 1.

Table 1 demonstrates that when the ion exchange of zeolite 13X (NaX) was done with Mg2+ ions, the concentrations of Na+ ions were decreased, indicating that Na+ has been exchanged with Mg2+ ions. Subsequently, when Ca2+ exchange was carried out in addition to Mg2+ ions, the concentrations of Na+ ions were further decreased. This data specifies that the ion exchange of the parent zeolite 13X occurred effectively. A similar trend was observed when the parent zeolite already exchanged with Ca2+ and Mg2+ was exchanged with Cs+ ions. The N2 adsorption–desorption isotherm technique was used to measure the BET surface area and textural properties, and the results are compiled in Table 2.

Table 2 shows that the surface area of zeolite 13X (NaX) was increased slightly and then decreased when it was ion-exchanged with other Ca2+ and Mg2+ ions; however, the micropore area and pore volume were drastically decreased when it was exchanged with Mg2+ (0.4 wt %) and Cs+ (3 wt %) metal ions.

Improvement in the surface area of zeolite 13X post exchanging it with Ca2+ and Mg2+ ions was mainly due to the replacement of Na+ 102 r(pm) by a smaller size Mg2+ 72 r(pm) and Ca2+ 100 r(pm) ions, respectively. However, the surface area and micropore volume of zeolite 13X decreased drastically after Cs+ ion exchange; it was mainly because of the bigger size and higher atomic mass of the cesium ion 167 r(pm) than that of the exchangeable Na+ cation.

This shows that when the Na+ ion is replaced by cations of a smaller size and lower molecular weight, the surface area and pore volume of zeolites increase. On the contrary, the surface area and micropore volume decreased when Na+ ions were exchanged with ions of higher molecular weight and bigger size. Another major reason for the lower surface area of the

Table 1. ICP-OES Analysis of As Such and Exchanged Molecular Sieve Zeolite 13X

| element | unit | a | b | c | d | e |
|---------|------|---|---|---|---|---|
| Na | % | 5.2 | 3.2 | 2.2 | 1.1 | 0.4 |
| Ca | % | nil | 0.4 | 0.2 | 0.4 | 1 |
| Mg | % | nil | 0.5 | 0.6 | 1 | 3 |
| Cs | % | nil | nil | nil | 1 | 2 |

Table 2. Physicochemical Properties of Zeolite 13X and Modified Zeolite 13X with the Chloride Pickup Capacity

| adsorbent | BET surface area (m2/g) | external surface area (m2/g) | micropore area (m2/g) | pore volume (cc/g) | average pore size (Å) | Cl pickup capacity (wt %) at an LHSV of 2 h−1 and T = 40 °C |
|-----------|------------------------|-----------------------------|----------------------|-------------------|---------------------|--------------------------------------------------|
| Na (5.2 wt %) zeolite 13X | 592 | 41 | 551 | 0.33 | 24 | 0.016 |
| Ca (0.4 wt %), (Mg 0.5 wt %), zeolite 13X | 590 | 40 | 550 | 0.26 | 22 | 0.020 |
| Ca (0.6 wt %), Mg (1 wt %), zeolite 13X | 637 | 52 | 585 | 0.27 | 21 | 0.024 |
| Ca (0.3 wt %), (Mg 0.6 wt %), Cs (1 wt %), zeolite 13X | 547 | 39 | 508 | 0.24 | 25 | 0.010 |
| Ca (0.2 wt %), Mg (0.4 wt %), Cs (3 wt %), zeolite 13X | 252 | 5 | 247 | 0.11 | 19 | 0.006 |
Cs⁺-exchanged sample was the decay in the crystallinity of the adsorbent after the Cs⁺ cation exchange. Our findings are in line with the study of Sethia et al.²⁸

The XRD of all of the samples is shown in Figure 2. The crystallinity was assessed from the XRD pattern by taking into account the intensity of the main ten peaks ranging from 5 to 35° at 2θ. The highest intensity peaks at 6.10, 11.69, 15.39, 30.85, and 33.49°, respectively, corresponded to the distinguishing crystal planes at (111), (333), (331), (555), and (664) of zeolite 13X (NaX) JCPDS card 38-0237.

The XRD pattern reveals that all of the adsorbents were crystalline, and the crystallinity of the zeolite 13X framework was well-preserved even post ion exchange. However, in the case of Cs⁺ ion exchange, the crystallinity of zeolite 13X reduced with an augmenting degree of ion exchange. The root cause of this anomalous behavior was the manifestation of Cs⁺ cations on the zeolite framework rather than the breakdown of the crystalline architecture. The Cs⁺ cations being bigger in size than that of Na⁺ ion affect the structure of the zeolite.

The N₂ adsorption and desorption isotherm is shown in Figure 3. Figure 3 shows that a hysteresis at \( \frac{P}{P_0} \approx 1.0 \) was spotted, revealing the presence of a minor volume of mesopores. However, the isotherm is of type-I (with H4), indicating that the majority of the pores were micropores with a slit type geometry due to the presence of clay as a binder. Only a minor change in the porosity of zeolite 13X (NaX) was noticed after exchanging NaX with a lower amount of alkali and alkaline earth metal ions; however, a drastic change in the porosity of NaX was noticed when it was exchanged with a higher concentration of Mg²⁺ and Cs⁺ ions.

To investigate the alteration in the morphology of zeolite 13X after its exchange with different metal ions, the SEM images of all of the samples were recorded and are shown in Figure 4.

These images specify that zeolite 13X (NaX) has a uniform particle morphology; however, when it was exchanged with Cs⁺, Ca²⁺, and Mg²⁺ metal ions, the morphology of the native material changed. Different particle species were spotted on the surfaces of the adsorbents: smaller spherical aggregates seem to be zeolite NaX particles, while larger particles with a more angular and striated morphology were also present, indicating the presence of Cs⁺, Ca²⁺, and Mg²⁺ metal ions.

Further, the images indicate that the external morphology of ion-exchanged zeolite 13X has changed drastically. The root cause behind the change in the morphologies of Ca²⁺ and Mg²⁺ ion-exchanged zeolite 13X as compared to the parent zeolite 13X (NaX) might have been the higher polarizing power of Ca²⁺ and Mg²⁺ ions. The direct impact of change in the morphologies on the BET hysteresis loop and porosity was observed. It was noticed that with the increasing population of the angular and strained particle on the surfaces of the adsorbent, the BET surface area and pore volume decreased drastically and the hysteresis loop narrowed down. Precisely, the shape of the hysteresis loop of the Cs⁺ ion-exchanged sample changed drastically, indicating that the surface morphology and pore architecture have changed. Thus, the morphology of zeolite 13X is critically affected after ion exchange with Cs⁺, Ca²⁺, and Mg²⁺, and as a result, the BET surface area and pore volumes were decreased drastically. This shows that the larger the size of the particle, the lesser will be the number of particles in a fixed volume section, and thus, in turn, a decrease in the BET surface area. Hence, the BET surface area of Cs⁺-exchanged NaX was drastically lowered as compared to the parent NaX.

Overall, the XRD, BET surface area, and SEM data reveal that even though the crystallinity and structure of the ion-
exchanged zeolite 13X were retained, the textural properties were changed.

2.2. Breakthrough Adsorption Study. To study the effect of compensating ions, temperature, and the feed flow rate on chloride removal, a dynamic adsorption breakthrough study was conducted at $T = 40 - 100 \, ^\circ C$, $P = 35 \, \text{kg/cm}^2$, and LHSV = 2 and 6 h$^{-1}$. The aromatic hydrocarbon feed having 5 ppmw chloride (HCl) was passed through a fixed bed packed with an adsorbent, as shown in Figure 5. The concentration of Cl at the outlet of the adsorber was checked at regular intervals using a chloride analyzer (M/S Mitsubishi Analytics, Japan).

2.2.1. Effect of Compensating Ions on the Chloride Pickup Capacity. To study the effect of compensating ions on chloride removal, a breakthrough study was carried out at $T = 40 \, ^\circ C$, $P = 35 \, \text{kg/cm}^2$, and LHSV = 2 h$^{-1}$. The breakthrough curves for all the adsorbents are shown in Figure 6. It is known that the breakthrough curve shapes depend on the adsorption equilibrium, whereas the broadness of the curve is because of fluid mixing and transfer resistances in the porous media.29 Figure 6 shows that in the case of NaX, the breakthrough occurs after 20 h of study, while in the case of Mg$^2+$ and Ca$^{2+}$ ion-exchanged zeolite 13X, the breakthrough time was

Figure 3. N$_2$ adsorption and desorption isotherm of (a) zeolite 13X (NaX), (b) Ca (0.4 wt %) and Mg (0.5 wt %) ion-exchanged zeolite 13X, (c) Ca (0.6 wt %) and Mg (1 wt %) ion-exchanged zeolite 13X, (d) Ca (0.3 wt %), Mg (0.6 wt %), and Cs (1 wt %) ion-exchanged zeolite 13X, (e) Ca (0.2 wt %), Mg (0.4 wt %), and Cs (3 wt %) ion-exchanged zeolite 13X.
extended to 30 h. Conversely, when zeolite 13X was exchanged with an excess amount of Mg$^{2+}$ and Cs$^+$ ions, the breakthrough time was decreased to even less than that of NaX. Enhancement in the life of the impregnated molecular sieve zeolite 13X with respect to zeolite 13X (NaX) was mainly because of the interaction of alkali and alkaline earth metal ions with chloride species (HCl), thereby forming respective metal chlorides. For instance, alkali metal ions (Na$^+$) interact with chloride species and form a salt molecule of type M-Cl (M is a cation atom) within the material pores. For Mg$^{2+}$ and Ca$^{2+}$, around two HCl molecules interact per metal cation. This shows that each doubly charged cation will interact with two HCl molecules, thereby leading to the formation of an M-Cl$_2$ type salt (MgCl$_2$ or CaCl$_2$).

Figure 4. Scanning electron microscopy images of (a) zeolite 13X (NaX), (b) Ca (0.4 wt %) and (Mg 0.5 wt %) ion-exchanged zeolite 13X, (c) Ca (0.6 wt %) and Mg (1 wt %) ion-exchanged zeolite 13X, (d) Ca (0.3 wt %), Mg (0.6 wt %), and Cs (1 wt %) ion-exchanged zeolite 13X, and (e) Ca (0.2 wt %), Mg (0.4 wt %), and Cs (3 wt %) ion-exchanged zeolite 13X at 50 μm.

Figure 5. Experimental setup for dynamic adsorption study.

Figure 5 reveals that all of the cations (viz., Na$^+$, Cs$^+$, Mg$^{2+}$, Ca$^{2+}$) contribute to the HCl uptake; however, uptake varies with the percentage of ion exchange. Finally, the pore volumes (micro and total) seem to highly influence HCl adsorption. As long as the cations are accessible, interaction with HCl will take place. Overall, a complex relationship of various parameters is expected to affect the HCl uptake capacities of the ion-exchanged zeolite 13X materials.

However, when the NaX was exchanged with a higher percentage of Mg$^{2+}$ and Cs$^+$ ions, the breakthrough occurred too early as compared to zeolite 13X (NaX). This shows that in addition to the surface area, a specific cation ratio is required for improving the overall adsorption capacity. A three-atomic salt molecule is expected to be formed with doubly charged cations, and simultaneously two HCl molecules will interact
with the cation. In this case, the size of the cation will be smaller compared to two HCl molecules, contrary to a single HCl molecule interacting with a single charge cation, thereby offering a less stabilizing atmosphere. Similarly, when NaX is exchanged with the Cs⁺ ion, the chloride pickup capacity is much lower than that of Ca²⁺- and Mg²⁺-doped zeolite. This shows that when Cs⁺ resides along with high amounts of Na⁺, Ca²⁺, and Mg²⁺ ions on the surfaces and pores of zeolite, a less favorable system for HCl uptake takes place, with a competitive interaction of HCl with multiple ions together. Additionally, the bigger size of Cs⁺ ions leads to cation flocking in the supercage and threshing of Na⁺ and other cations to relocate inside the less accessible β-cages, thereby making them less-accessible to interact with HCl. Our findings are in good agreement with the studies reported in the literature.²⁴

Another probable reason behind the low HCl sorption capacity of Cs⁺-exchanged zeolite 13X might have been the eclipsing of the pore opening of zeolite 13X by Cs⁺ as it has bigger ionic radii (1.67 Å) compared to Na⁺ (1.02 Å), Ca²⁺ (1.0 Å), and Mg²⁺ (0.72 Å) ions, thereby restricting the HCl molecule from entering inside the pores. However, in all of the cases, the rate of HCl adsorption decreases with time, and it is mainly because of an increase in the diffusive resistances with the HCl uptake in the pores of the adsorbent. Dynamic adsorption capacities for all of the breakthrough curves were calculated via eq 1 and are reported in Table 1.

\[ q_e = \frac{(M_{\text{feed}}(C_{\text{feed}} - C_p))\times100}{M_{\text{ads}}} \]  

\[ (1) \]

2.2.2. Effect of the Residence Time/Flow Rate on Chloride Pickup Capacity. To explore the effect of erratic feed flow rate on chloride pickup capacity, the studies were performed at an LHSV of 2 and 6 h⁻¹ separately, while other parameters such as temperature (T = 40 °C), pressure (P = 35 kg/cm²), bed height, and inlet feed composition were static. The results of varying volumetric flow rates are shown in Figure 7.

Figure 7 shows that at a higher flow rate (LHSV 6 h⁻¹), a slightly sharp breakthrough curve is obtained compared to that at a low flow rate. At higher flow rates, chloride removal efficiency is diminished. This is mainly because of competing effects. With an increase in the flow rate, the degree of contact
between HCl and the adsorbent increases, thereby resulting in enhanced diffusion. However, at elevated flow, the normal interaction period between HCl and the adsorbent decreases, leading to lower adsorption proficiency. The chloride adsorption capacity of zeolite 13X has been calculated using eq 1 at different LHSVs, and it was observed that at higher LHSV, the chloride pickup capacity is reduced to around 38%.

2.2.3. Effect of Temperature on Chloride Pickup Capacity. To understand the effect of temperature on the chloride adsorption capacity of zeolite 13X species, the breakthrough study was carried at diverse temperatures ($T=40$–$100^\circ C$); however, other parameters like flow rate (LHSV of 6 h$^{-1}$) and pressure ($P=35$ kg/cm$^2$) were kept constant. The idea to study the effect of temperature up to 100 °C was that most of the hydrocarbon processing streams are operated below 100 °C. The results of varying temperature on Cl adsorption capacity are shown in Figure 8.

Figure 8 shows that with an increase in temperature, the chloride uptake increases, indicating enhanced adsorbate–adsorbent interaction, i.e., the interaction of HCl with the adsorbent. This may be attributed to (i) the activation of the adsorbent surface, (ii) the intermolecular forces between the adsorbate and adsorbent being much stronger than those between the adsorbate and solvent, (iii) increases in the mobility of chloride species, and (iv) increasing number of chloride species (adsorbate) to acquire enough energy to undergo interactions with the active site at the adsorbent surface.

Our findings are in accordance with the study carried out by Singh et al.$^{30}$ They studied the interactions of organic chloride (methylene chloride) and found that the interaction between the chloride species and aromatic hydrocarbons (BTX) is weak at a higher temperature, i.e., the solute–solvent interaction at a higher temperature is weak. Moreover, it has been noticed that the profiles of the breakthrough curves have changed with augmenting temperature, indicating that mass transfer at higher temperatures ($T=100^\circ C$) is better than that at lower temperatures ($T=40^\circ C$). The chloride adsorption capacity of zeolite 13X was calculated using eq 1 at different temperatures, and it was observed that the chloride sorption efficiency of zeolite 13X increased drastically with an increase in temperature almost 12 times at $T=100^\circ C$ as compared to $T=40^\circ C$.

3. CONCLUSIONS

It has been observed that molecular sieve zeolite 13X with and without ion exchange is capable enough to eliminate the chloride species from an aromatic hydrocarbon mixture, and 97% chloride removal was seen. However, the chloride uptake capacity of NaX decreased when it was exchanged with a considerable amount of Cs+, indicating that the bigger sized Cs+ ions result in the accumulation of cations in the supercage, whereas Na+ and other cations get relocated inside less-accessible $\beta$-cages.

The adsorption capacity of zeolite 13X (NaX) was observed to improve substantially with an increase in temperature, demonstrating the enhanced interaction of HCl with the adsorbent and minimal mass transfer resistance. It has been noticed that the chloride sorption capability of zeolite 13X was augmented considerably with an increase in temperature of almost about 25 times at $T=100^\circ C$ as compared to $T=40^\circ C$.

It was observed that at higher flow rates, chloride removal efficiency decreased. This was primarily due to the competing effects. With an increase in the flow rate, the degree of contact between HCl and the adsorbent increases, thereby leading to enhanced diffusion. However, at elevated flow rates, the typical interaction period between HCl and the sorbent decreases, thereby leading to low adsorption proficiency.

Overall, it can be concluded that zeolite 13X (NaX) as such, as well as exchanged with different alkali and alkaline earth metal ions, are proficient enough to remove chlorides from aromatic hydrocarbons at an optimized flow rate and temperature. The best performance of the adsorbent zeolite 13X (NaX) was observed when it was exchanged simultaneously with Ca$^{2+}$ and Mg$^{2+}$ ions in the range of 0.5–1 wt % in the absence of Cs+ ions, as the larger size of Cs+ ions results in cation assembly in the supercage and threshing of the Na+ and other cations to the less-accessible $\beta$-cages. The maximum chloride (HCl) removal was achieved when the temperature,
pressure, and flow rate were 100 °C, 35 kg/cm², and 2 LHSV h⁻¹, respectively.

4. EXPERIMENTAL SECTION

4.1. Materials. In this section, the selection of chemicals required for ion exchange of the adsorbent and the procedure of ion exchange to modify the adsorbent zeolite 13X have been explained. In the last part of this section, the method of aromatic feedstock preparation has been described.

4.1.1. Chemicals. Benzene (Fluka, 98% purity), toluene (Fluka, 98% purity), α-, m-, and p-xylene (Fluka, 98% purity), ethylbenzene (Fluka, 98% purity), anhydrous MgCl₂ (Fluka, 99%), anhydrous CaCl₂ (Fluka, 99%), CsCl (Sigma-Aldrich, 99%), and anhydrous HCl (Sigma-Aldrich, 99%) were used as such, and no further purification was done. The reagents used in this investigation were of high-purity AR grade.

4.1.2. Adsorbents. Molecular sieve zeolite 13X (NaX, having a Si/Al ratio of 1.5, spherical shape, and a particle diameter of 1.6 mm) having 20 wt % of kaolin as a binder was obtained from the CATAD division of formerly Indian Petrochemicals Corporation Ltd. Further, molecular sieve zeolite 13X was exchanged with different alkali and alkaline earth metal ions following the method reported in the literature. Molecular sieve zeolite 13X (unmodified zeolite, known as NaX) has been used as the starting material for ion exchange. For Mg²⁺ ion exchange, the sample was refluxed with a 10% aqueous mixture of magnesium chloride (MgCl₂), keeping the solid-to-liquid ratio (S/L) as 1:4, at T = 80 °C until 5 h. All of the samples were washed with distilled water after each exchange. This process was repeated at least four times to obtain a molecular sieve 13X having varied concentrations of Mg²⁺ ions. After four Mg²⁺ exchanges, the adsorbent sample was cleaned completely with lukewarm distilled water (5–6 times) to ensure the adsorbent was free from chloride ions as tested with a AgNO₃ solution. An aliquot of the sample was taken and dried and used for analyzing the degree of Mg²⁺ exchange attained.

Subsequently, the remaining Mg²⁺-exchanged sample was kept for calcium exchange, with 10% of an aqueous solution of calcium chloride (CaCl₂), keeping the S/L ratio as 1:80. To obtain a high degree of Ca²⁺ exchange, the same procedure was followed at least four times to attain a varying amount of Ca²⁺. Then, the adsorbent sample was washed with warm water, followed by drying at 80 °C in an oven.

Afterward, the residual Ca²⁺-exchanged adsorbent sample was kept for Cs exchange using 10% of an aqueous solution of cesium chloride (CsCl), keeping the S/L ratio as 1:80. To obtain a high degree of Cs exchange, the same procedure was followed four times. Further, the adsorbent sample was washed with lukewarm water, followed by drying at 80 °C in an oven. Finally, the sample was heated at 400 °C up to 5 h. An aliquot of the sample was used for analyzing the degree of ion exchange. The degree of exchange of the sample was determined by ICP-OES (inductively coupled plasma-optical emission spectrometer). Before use, all of the adsorbents were activated at 350 °C for 3 h in a muffle furnace.

The reproducibility of the percentage metal ion-exchange process was checked by repeating the ion-exchange process and subsequently analyzing the ion-exchanged samples in terms of Na⁺, Ca²⁺, Mg²⁺, and Cs⁺ ions using ICP-OES.

4.1.3. Aromatic Hydrocarbon Feed Stock Preparation. An aromatic hydrocarbon mixture was prepared by mixing benzene (14 wt %), toluene (39 wt %), o-xylene (9 wt %), m-xylene (30%), p-xylene (1 wt %), and ethylbenzene (7 wt %). This mixture was prepared to mimic the BTX aromatic stream. Dry HCl was obtained from Sigma-Aldrich with 99% purity. To prepare a final aromatic hydrocarbon mixture feedstock having 5 ppmw HCl, a calculated amount of dry HCl was introduced to the aromatic hydrocarbon mixture.

To confirm the exact 5 ppmw HCl in the aromatic hydrocarbon feedstock, the Cl analysis of this feedstock was done using a total chloride analyzer (model: NSX 2100 H; ASTM D4929, D5808, D6721, D7457; M/S Mitsubishi Analytics, Japan).

4.2. Methods. In this subsection, all of the techniques utilized for the complete characterization of the adsorbent and the method of chloride measurement are reported. Finally, the breakthrough evaluation of parent and ion-exchanged zeolites is explained.

4.2.1. Adsorbent Characterization. XRD measurement of all of the adsorbents was done using a Philips X-ray diffractometer (model: PW 1729) using Cu Kα radiation and PC-APD diffraction software. The XRD pattern of each sample was measured using 10% α-Al₂O₃ as the internal standard. Major crystallinity changes were monitored using a Bruker D-8 advance X-ray powder diffractometer without using any internal standard or specific sample pretreatment method.

The BET surface area, pore volume, and textural properties of molecular sieve zeolite 13X (NaX) and ion-exchanged zeolite 13X were determined by N₂ adsorption−desorption isotherms at 77 K using a surface area analyzer ASAP 2020 (M/S Micromeritics). The adsorbents were degassed at 573 K using vacuum atmosphere for >12 h prior to generating adsorption isotherms. To estimate the percentage loading of different metal ions, metal analysis of the parent zeolite 13X and ion-exchanged zeolite 13X was done using an inductively coupled plasma-optical emission spectrometer (ICP-OES).

4.2.2. Chloride Content Measurement. Chlorine content analysis of the hydrocarbon mixture before and after passing through the adsorber (packed with the adsorbent) was performed using a total chloride analyzer (model: NSX 2100 H; ASTM D4929, D5808, D6721, D7457; M/S Mitsubishi Analytics, Japan). In this technique, the hydrocarbon sample is injected with a microsyringe into a flowing stream of argon and oxygen. The samples are burned in an argon/oxygen atmosphere in a pyrolysis tube. The chloride species generated in this process are subsequently driven to a titration cell where these chlorides are titrated against the silver ions produced coulometrically. The chlorine concentration is then estimated from the amount of electricity obligatory for the titration.

\[ \text{HCl} + \text{Ag} \rightarrow \text{AgCl} + \text{H}^{+} + \text{Ag}^{+} \quad \text{(titration)} \]

\[ \text{Ag} \rightarrow \text{Ag}^{+} + e^{-} \quad \text{(electrolysis)} \]

4.2.3. Breakthrough Adsorption Study. A dynamic adsorption study was carried out to find the chloride pickup capacity of all of the adsorbents using the experimental setup shown in Figure 5. The internal diameter and height of the packed bed used in this study were 1.57 and 20.9 cm, respectively. Prior to loading the adsorbent on the adsorber, it was activated at 350 °C and placed in the middle portion of the reactor, and the remaining space was filled with silicon carbide (20–40 μm). The adsorption study was carried at T = 40–100 °C, P = 35 kg/cm², and LHSV of 2 and 6.
h⁻¹ separately. The aromatic hydrocarbon feedstock containing 5 ppmw HCl (prepared in the subsection 4.1.3) was passed through the packed bed at T = 40–100 °C, P = 35 kg/cm², and LHSV of 2 and 6 h⁻¹ separately. The chloride content of the hydrocarbon mixture at the outlet of the adsorber was measured at regular intervals using a chloride analyzer (M/S Mitsubishi Analytics, Japan).

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**Notes**
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