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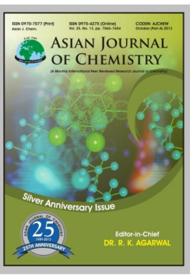

Study on Chlorine Adsorption Properties of NaY and NaY(H_4EDTA) Zeolites

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Commercially available NaY zeolite was modified by H_4EDTA to study its characterizations and adsorption properties on chlorine. The mechanisms of chlorine adsorption on NaY and modified NaY zeolites are entirely physical interactions. The modified NaY *i.e.*, [NaY(H_4EDTA)] zeolite had a significant enhancement on chlorine adsorption capacity. At 273 K and 0.19 MPa, the maximum chlorine adsorption capacity of the NaY and the NaY(H_4EDTA) zeolites were 30.09 and 35.43 %, respectively. The chlorine adsorption capacities and the physico-chemical properties of NaY(H_4EDTA) zeolite were studied after eight times adsorption-desorption, suggesting that the NaY(H_4EDTA) zeolite can be stably employed in the prolonged cyclic operation. The experimental data show that the chlorine adsorption capacity of the NaY(H_4EDTA) increases significantly, because the SiO_2/Al_2O_3 ratio of the NaY zeolite is improved after modified by H_4EDTA.

Key Words: NaY, Adsorption, Zeolites, Chlorine.

INTRODUCTION

Chlorine is used in the manufacture of various chemical products, which are essential in our daily life, such as plastics, pharmaceuticals and solvents. It has created great social wealth in the last 100 years. However, in the production and use of chlorine, plenty of waste gases which are rich in chlorine will be output. Chlorine is an extremely poisonous gas. It is harmful to human health and the growth of animals and plants (immediately dangerous to life or health when concentration value reaches 10 ppm)[1]. Therefore, people have paid more attention to the treatment of tail chlorine gas and hope to find a processing method which is efficient and environmentally friendly.

In order to design an adsorption and separation process of chlorine, searching for the adsorbents is the most crucial design consideration[2-4]. Zeolites with larger surface areas, uniform tunable pore volumes and pore sizes have been used as adsorbents for adsorption of most gases including chlorine. They are also low-cost with high separation efficiency and simple adsorption operating process. Therefore, zeolites are widely applied for adsorption and separation of chlorine. Young and Crowell[5] have used McBain Bakker balance to weight the zeolites before and after adsorption of chlorine in order to get the mass percentage of the zeolite s after adsorption of chlorine.

NaY zeolite has a higher stability and activity. It also has good hydrothermal stability, suitable micropore aperture and perfect ion-exchange properties[6]. Therefore, the subject of the adsorption performance of NaY zeolite has always been concerned. For example, Xue *et al.*[7] and others[8,9] have studied and compared chlorine adsorption properties of 13X, NaY zeolite and mordenite. It is proved that NaY zeolite has great advantages in adsorption of chlorine. In addition, the results also show that the skeleton structure, pore size, pore volume are main factors affecting the adsorption capacity. In recent years, Zarchy *et al.*[10] has pointed out that high-silicon zeolites had better chlorine adsorption capacity. Compared with the characters of NaY zeolite original sample, NaY zeolite modified by H_4EDTA can improve the SiO_2/Al_2O_3 ratio with a large number of secondary pore structures appearing, eventually leading to the changing of the adsorption capacity of NaY zeolite. This work focuses on the use of NaY zeolite and NaY zeolite modified by H_4EDTA as an alternative method to adsorb chlorine.

EXPERIMENTAL

NaY zeolite used in the work was industrial samples and EDTA used for modifying the NaY zeolite was analytical grade. The 99.9 % pure chlorine gas and 99.5 % pure nitrogen gas were industrial grade. Potassium iodide, sodium thiosulfate and soluble starch reagent used for titrating the residual chlorine content were all analytical grade.

The powder of NaY and NaY(H_4EDTA) zeolites were compressed by a single-punch tablet compression machine, which was FY-15 manual presses and these samples needed to be activated in a muffle SKW-240 furnace. In addition, SHZ-D III vacuum pump and the SKW-210 tow-way intelligent temperature controller were used in this experiment.

The pressure-composition-temperature (P-C-T) experimental setup for the adsorption process is shown in Fig. 1. Here, P_1 represents the indications for source pressure of the chlorine gas; P_2 represents the precision pressure gauge for the range 0-1.6 MPa (gauge pressure); P_3 represents the vacuum gauge range -0.1-0 MPa (vacuum); D represents the dry filter tube within the silica gel, anhydrous calcium chloride; F_1-F_6 are copper valves; G is the drying device composited by silica gel and NaA zeolite.

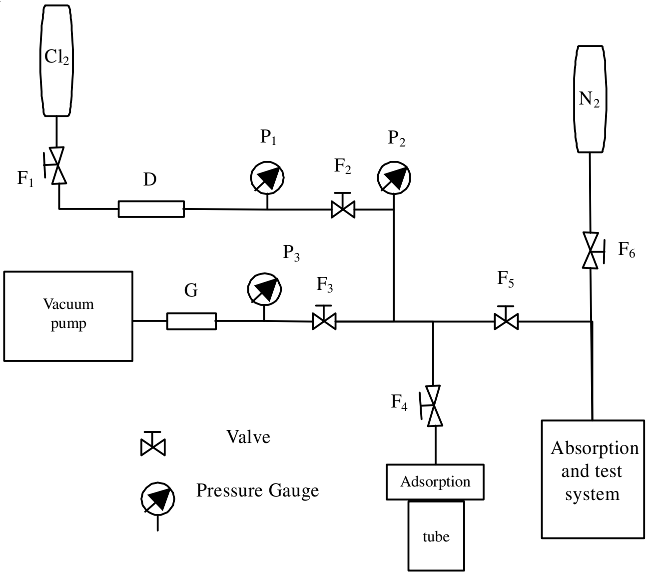

Fig. 1. P-C-T apparatus

General procedure: Take 10 g powder of NaY zeolite and 0.1127 g white crystalline powder of H_4EDTA accurately (the molar ratio of H_4EDTA and NaY zeolite is 0.675). After the water was removed under vacuum condition, the NaY zeolite was placed into a 250 mL round-bottom flask and 100 mL deionized water was added, then it was beating at room temperature. At the same time, H_4EDTA was dissolved with 20 mL deionized water and the solution was trickled into the round-bottom flask slowly, then they were stirred and refluxed for 0.5 h. In the end, they were cooled down to room temperature. After washed, filtrated and washed to neutrality with excess secondary deionized water, the samples were dried at 130 ºC. Then they were placed into a muffle furnace of 400 ºC and were activated for 2 h. In the end, the NaY(H_4EDTA) zeolite was obtained and placed into a desiccator. According to the testing of the SiO_2/Al_2O_3 ratio, the SiO_2/Al_2O_3 ratio of NaY original sample is 5.21, while the SiO_2/Al_2O_3 ratio of NaY modified by H_4EDTA is 5.79.

After the samples were activated for 4 h at 550 ºC in the muffle furnace and were cooled down to room temperature, they were put into the adsorption tube. The temperature of the adsorption tube was programmed to rise to 150 ºC. At this temperature, the samples should be activated for 3 h continuously maintaining a high-vacuum environment. After that, they were cooled down to room temperature again and were placed in a thermostatic container. At this temperature, the system device was filled with chlorine till the pressure reached the experimental pressure, then the test of chlorine adsorption properties started. When pressure gauge reading was stable and no longer changed, the adsorption of chlorine reached saturation, the data should be recorded. The chlorine pressure was reduced gradually, when the pressure gauge reading was no longer changed, the released amount of chlorine was titrated. Then the residual chlorine content was calculated at each balance pressure combined with the pressure gauge readings. Isothermal adsorption curves were drawn based on the pressures and the adsorption capacities. After the testing process, the samples which were saturated by chlorine adsorption were put into the muffle furnace again so that they could be desorpted and regenerated. Then the samples could be used to test adsorption life.

Detection method: The phase and crystallization framework structures of the samples were analyzed by Japanese Rigaku motor X-ray diffractometer (Rigaku D/2500 X-Ray diffractometer). The skeleton structure and surface functional groups of the samples were analyzed by Germany BRUKER Company VERTEX70 series Fourier transform infrared spectrometer. The morphological characteristics of the samples were characterized by the JSM-35C scanning electron microscope of Japanese JEMOL Company.

RESULTS AND DISCUSSION

SEM images: The SEM images of NaY and NaY(H_4EDTA) zeolites are shown in Fig. 2. According to the images, there were microporous and pore channels, whose sizes were regular, existed in sieve lattice before and after modified with H_4EDTA. The crystal caves and pore channels of these microporous materials arranged in the whole structures periodically. Granularity distribution of the grains was very evenly with a better degree of dispersion and its morphology was basically ordered hexagonal structure.

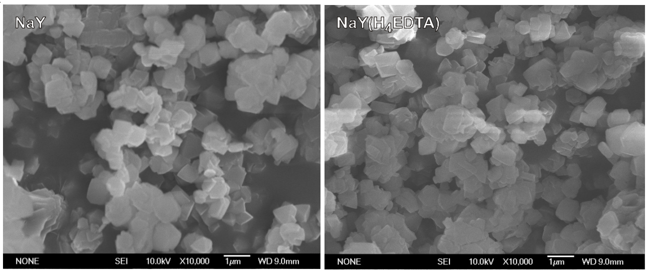

Fig. 2. SEM images of NaY and NaY(H_4EDTA)

XRD patterns: The XRD pattern of NaY zeolite original sample is shown in Fig. 3(a). Comparing it with the standard XRD pattern of NaY zeolite original sample, the peak position and relative peak intensity were consistent with the standard pattern[11], which showed the selected samples met the experimental requirements. The XRD pattern of NaY(H_4EDTA) zeolite is shown in Fig. 3(b). Comparing it with the XRD pattern of the NaY zeolite original sample, the peak position did not change and the intensity of 6.0-6.5º Y zeolite characteristic diffraction peaks remained basically unchanged, but several other peaks became higher in different degree, which due to the increasing of the mole number of Si in unit mass of

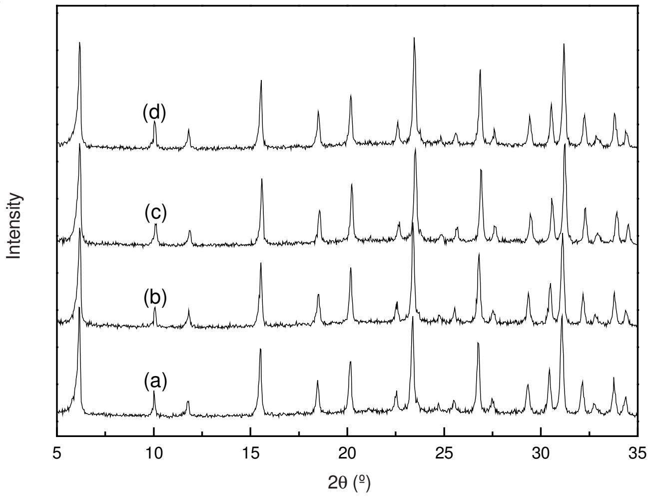

Fig. 3. XRD patterns of NaY and NaY(H_4EDTA), (a) NaY, (b) NaY(H_4EDTA), (c) NaY(H_4EDTA) adsorbing chlorine for once, (d) NaY(H_4EDTA) adsorbing chlorine for eight times

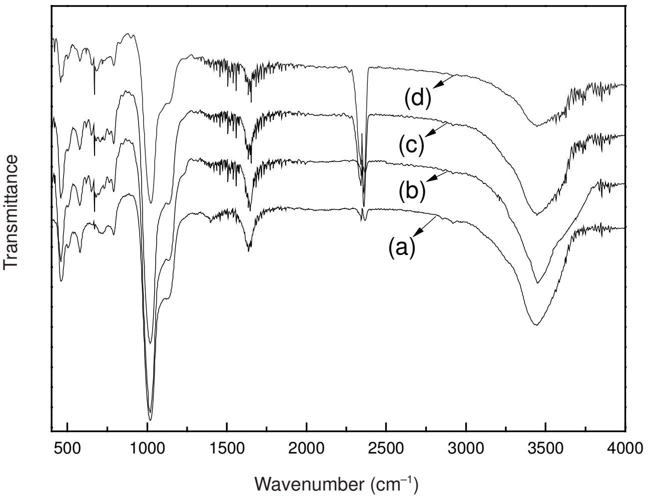

Fig. 4. Infrared spectras of NaY and NaY(H_4EDTA). (a) NaY; (b) NaY(H_4EDTA); (c) NaY(H_4EDTA) adsorbing chlorine for once; (d) NaY(H_4EDTA) adsorbing chlorine for eight times

dealuminated zeolite. Therefore, after modified by H_4EDTA, washed by distilled water and dried by muffle furnace, the skeleton of the zeolite has not been damaged.

According to the Fig. 3, characteristic diffraction peaks of the zeolites adsorbing chlorine for once and eight times still existed and the diffraction peak intensity did not change significantly. As the increasing of the adsorption times, the effect of adsorbing chlorine on the zeolites was very little. Therefore, NaY(H_4EDTA) zeolite is stable and it can be used and recycled for many times and it can also meet the requirements of industrial applications.

Infrared spectra: According to Fig. 4(a), NaY zeolite included several characteristic absorption peaks as followed: 1020, 1635 and 3446 cm^{-1}, which were respectively caused by asymmetric stretching vibration of Si-O-Si bonds, stretching vibration of H-O-H bonds and stretching vibration of hydrogen bonds and these hydrogen bonds existed in the silicon alcohol component[12,13]. The absorption peak, caused by the bending vibration of internal tetrahedral T-O (T = Si or Al) bonds whose structure was less sensitive, was at 459 cm^{-1}. The absorption peak, caused by the vibration of internal double six-member ring, was at 578 cm^{-1}. Between 650 and 720 cm^{-1}, there were two characteristic peaks, which were respectively caused by the symmetric stretching vibration of internal tetrahedral and external links. These characteristic peaks of skeleton vibration were consistent with the results reported in the literature[14]. The FT-IR spectrum of NaY(H_4EDTA) zeolite is shown in Fig. 4(b), which showed that the basic skeleton structure of the modified NaY zeolite had not changed, only the intensity of the skeleton vibration changed a little. The vibration intensity of NaY(H_4EDTA) zeolite characteristic peaks had increased at 1020 and 3446 cm^{-1}, that is because the SiO_2/Al_2O_3 ratio has greatly increased after dealuminated, resulting in both the asymmetric stretching vibration of Si-O-Si bonds and the stretching vibration of hydrogen bonds, which exist in the silicon alcohol component, become stronger.

According to Fig. 4, the main characteristic peaks of the samples before and after adsorbing chlorine were basically consistent. With the increasing of adsorption times, absorption peak intensity of the zeolites gradually increased at 2366 cm^{-1}, which is due to the chlorine weak adsorptionof chlorine on the zeolites; with the increasing of adsorption times. Several other characteristic peaks became lower in different degree, which is due to the trace acid existing in the chlorine has a certain effect on the zeolites.

Effects of temperature on the adsorption capacity: According to Figs. 5 and 6, the curves of chlorine adsorption of NaY and NaY(H_4EDTA) zeolites conformed to the Langmuir adsorption isotherm basically, which are typically physical adsorption curves. When the pressure was at 0.19 MPa and the temperatures were at 0, 30 and 50 ºC, chlorine adsorption capacities of NaY zeolite were 30.09, 24.936 and 18.82 %, respectively; chlorine adsorption capacities of NaY(H_4EDTA) zeolite were 35.43, 31.01 and 28.99 %, respectively. Therefore, at different temperatures, chlorine adsorption capacities of NaY and NaY(H4EDTA) zeolites increase with the temperature decreasing.

According to Figs. 7-9, compared with NaY zeolite, chlorine adsorption capacity of NaY(H_4EDTA) zeolite largely improved. The reason is that the SiO_2/Al_2O_3 ratio of the NaY zeolite is improved significantly after the NaY zeolite is

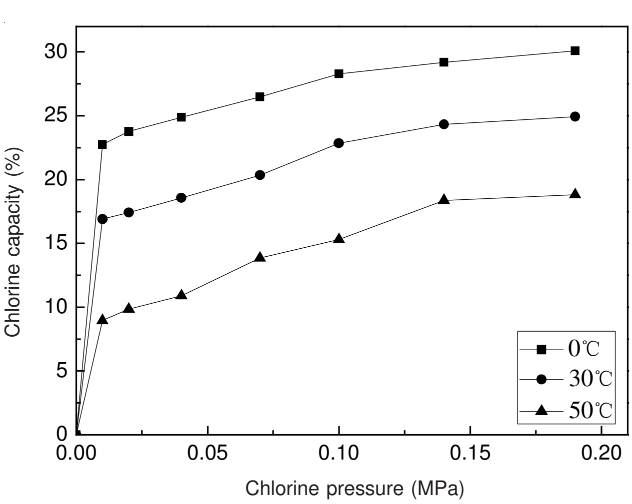

Fig. 5. Chlorine adsorption isotherms of NaY at 0, 30 and 50 ºC

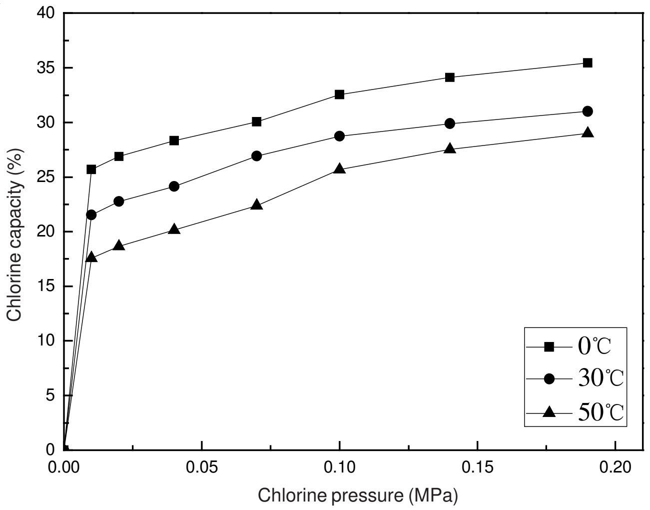

Fig. 6. Chlorine adsorption isotherms of NaY(H_4EDTA) at 0, 30 and 50 ºC

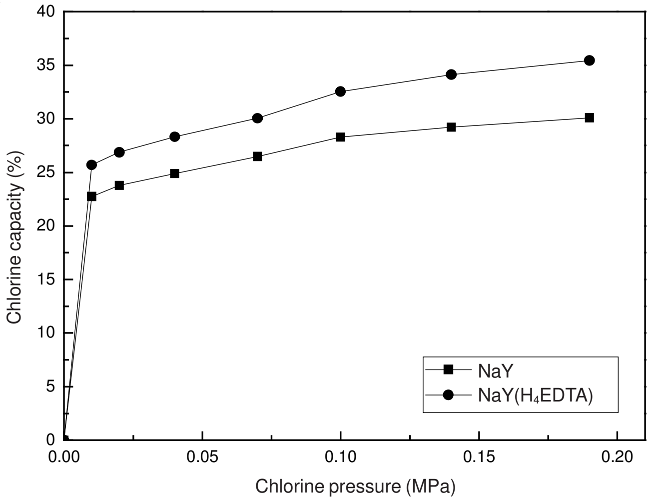

Fig. 7. Chlorine adsorption isotherms of NaY and NaY(H_4EDTA) at 0 ºC

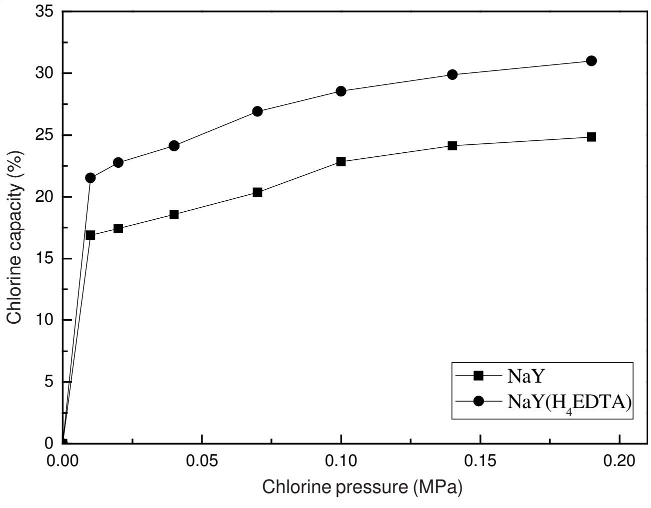

Fig. 8. Chlorine adsorption isotherms of NaY and NaY(H_4EDTA) at 30 ºC

dealuminated by H_4EDTA. The higher SiO_2/Al_2O_3 ratio is, the lower the polarity will be[15]. Chlorine is non-polar molecules, so the lower the polarity of the zeolite is, the greater the chlorine adsorption capacity will be.

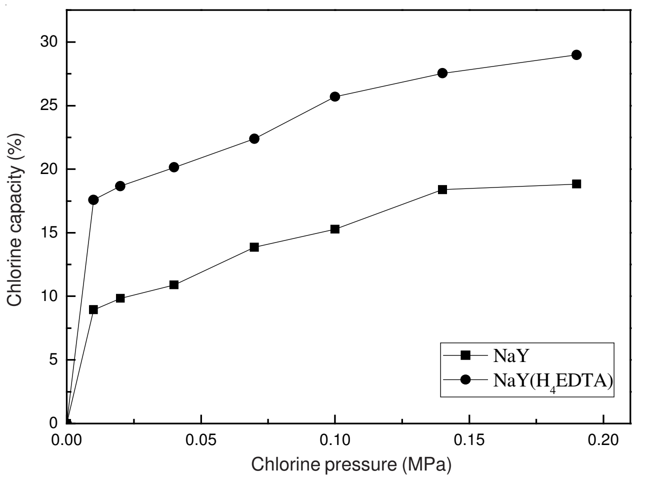

Fig. 9. Chlorine adsorption isotherms of NaY and NaY(H_4EDTA) at 50 ºC

Effects of pressure on the adsorption capacity: According to Figs. 5 and 6, chlorine adsorption capacity of NaY and NaY(H_4EDTA) zeolites increased with the pressure increasing. When the pressures ranged from 0 to 0.1 Mpa, the adsorption capacity increased significantly, the reason is that the pore volume of the zeolites is larger at the beginning, so the chlorine molecules can easily enter. When the pressure was greater than 0.10 MPa, the remaining pore volume of the zeolites was very small, the adsorption capacity increased slowly, but it did not reach saturation immediately. This may because the pressure of chlorine is far less than its critical pressure. As the chlorine pressure increased in the experiment, the adsorption capacity tended to saturation gradually.

Effects of cyclic adsorption times on the chlorine adsorption capacity of NaY(H_4EDTA): Eight curves for chlorine adsorption of NaY(H_4EDTA) zeolite at 30 ºC are shown in Fig. 10 repeatedly. The curves (1), (2), (3), (4), (5), (6), (7), (8) respectively show the chlorine adsorption isotherms of the dealuminated zeolite for once, twice, three times, four times, five times, six times, seven times and eight times and specific adsorption capacities of the eight times adsorptions are shown in Table-1. According to the eight adsorption curves, with the increasing of the adsorption times, chlorine adsorption capacity of dealuminated zeolite decreased, but the magnitude of decreasing was very little. According to the characterizations which have been done in this work, the XRD characteristic diffraction peaks of the NaY zeolite which was dealuminated and the XRD characteristic diffraction peaks of these samples that had adsorbed chlorine for once and eight times all conformed to the XRD characteristic diffraction peaks of the NaY zeolite original samples. The intensity of characteristic diffraction peaks was essentially unchanged. The absorption peaks of the infrared spectrum changed a little. According to the data obtained and the results of the characterizations, the stability of the dealuminated zeolite is perfect and it can be recycled.

Conclusion

In this work, chlorine adsorption properties of NaY zeolite modified by H_4EDTA were studied. The effects of cycle adsorption times on the chlorine adsorption capacity of modified zeolites were also discussed. The experimental results show that:

TABLE-1
EFFECTS OF CYCLIC ADSORPTION TIMES ON THE CHLORINE ADSORPTION CAPACITY OF NaY(H_4EDTA)

Pressure (Mpa)	Adsorption capacities (%)							
	1	2	3	4	5	6	7	8
0.19	31.01	30.96	30.75	30.50	30.25	29.99	29.56	29.01
0.14	29.89	29.42	29.28	29.08	29.01	28.90	28.54	27.99
0.10	28.54	27.98	27.68	27.48	27.25	27.15	26.66	26.43
0.07	26.93	26.54	26.43	26.12	26.01	25.97	25.32	25.02
0.04	24.13	24.01	23.99	23.87	24.10	24.01	23.86	23.54
0.02	22.77	22.69	21.88	21.66	22.09	21.96	21.77	21.37
0.01	22.03	21.13	21.01	20.99	21.01	21.12	20.78	20.19

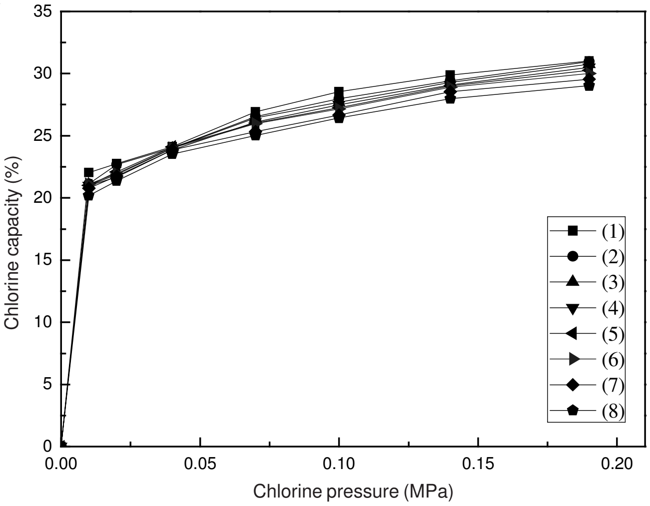

Fig. 10. Eight times chlorine adsorption isotherm of NaY(H_4EDTA) at 30 ºC

(1) The chlorine adsorption curves of NaY zeolite before and after modified conform to the Langmuir adsorption isotherm. The adsorption capacity decreases with the temperature increasing, while increases with the pressure rising and they all belong to physical adsorption.

(2) Under the same experimental conditions, compared with NaY zeolite, the chlorine adsorption capacity of NaY(H_4EDTA) zeolite increases significantly, which is due to the increasing of the SiO_2/Al_2O_3 ratio.

(3) With the increasing of cycle times of adsorption, chlorine adsorption capacity of the NaY(H_4EDTA) zeolite changes a little, so the modified zeolite is very stable and it can be recycled and it is suitable for wide application for processing of exhaust rich in chlorine in industry.

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