Study on adsorption and purification materials for ethylene in cold storage

Jiandong Yang, Xintang Shan, Xueping Huang, Hao Yang

China Satellite Maritime Tracking and Control Department, Jiangyin 214431, China

Abstract. In view of the lack of systematic quantitative and comparative studies on the purification effect of ethylene adsorbent in cold storage, starting from the selection of purification materials, this paper analyzed the purification effect of different zeolite materials on ethylene through a small test chamber, and screened out the best zeolite adsorbents used in self-made purification device. Combined with characterization analysis, purification efficiency evaluation and adsorption capacity of zeolite material, the removal performance of ethylene was investigated. The results showed that the zeolite samples with rough and porous surface showed better adsorption performance for ethylene. The larger the specific surface area and total pore volume, the stronger the adsorption capacity to ethylene. In addition, the presence of Na elements and mesoporous increased the exchange capacity and pore volume, which also played a certain role in the ethylene adsorption process. Experimental result demonstrates that clean air volume (CADR) of ethylene is 232 m^3/h, the ethylene removal rate at 30 min is 98.19%, and the purification energy efficiency is 1.39. At the same time, the adsorption capacity of the selected zeolite sample is 1380.5 μg/g by dynamic adsorption experiment, and the service life of the filter element of the self-made purification device is estimated to be 166 days. This study can provide a theoretical basis for ethylene purification in cold storage.

Keywords: Zeolite, Cold storage, Purification effect, Assessment.

1. Introduction

Ethylene is a colorless and flammable organic compound and an endogenous hormone of plants. Almost all plant tissues can produce ethylene. Ethylene is closely related to the maturity of fruits and vegetables (Dan et al., 2018; Sun et al., 2019). Ethylene is a double-edged sword in the ripening process of fruits and vegetables. While promoting the ripening of fruits and vegetables, it often leads to overripe or even rotten fruits, thus shortening the shelf life of fruits and vegetables. In the process of daily fruit and vegetable freshness preservation, the requirements for fresh fruits and vegetables cannot be met only by low temperature storage (Li et al., 2018). However, if ethylene in the storage environment can be controlled or removed, the freshness preservation period of fruits and vegetables will be more effectively extended (Liu et al., 2015; Hu et al., 2019). Therefore, it is particularly important to develop an ethylene removal material or equipment that can be used in cold storage and cold chain industries.

The purification of ethylene is mainly achieved through physical adsorption (activated carbon, silica gel and molecular sieve, etc.), oxidation reaction (potassium permanganate, ozone) and catalytic degradation (porous material loaded metal, TiO2) (Villa et al., 2022; Minas et al., 2014; Tirgar et al., 2018; Kim et al., 2019; Pathak et al., 2017). Among them, the purification technology with adsorbent as the core has the advantages of fast and simple, high adsorption efficiency, low cost and safety without secondary injury, and is now a more popular purification method.

Among various adsorption materials, zeolite is the most commonly used material because of its large space or cage, which can adsorb or adjust ethylene (Ichiura et al., 2003). Zeolite has a unique molecular sieve structure inside, which has cation exchange, selectivity and adsorption separation properties (Yildirim et al., 2018). However, most zeolites are not suitable for adsorption separation due to adsorption capacity, stability and other reasons, FAU (including X and Y type) and LTA (type A) zeolite (Sun Feng et al., 2021) are commonly used for adsorption and separation. The research shows that zeolite can have greater adsorption capacity and ion exchange capacity through high-temperature heating, acid and alkali immersion, metal and salt modification and other methods (Fu Jinxiang et al., 2021).

It is worth noting that despite the strong interest in food preservation technology, there is still little research on ethylene adsorption of fruits and vegetables under storage conditions. Most studies only evaluate the impact of adsorbent on a single product, without discussing the adsorption mechanism itself. In addition, the ethylene adsorption capacity of adsorbent is rarely reported. Due to the lack of systematic quantitative and comparative studies on ethylene adsorbents, the wide application of adsorption purification devices in the storage of fruits and vegetables has been greatly affected.

In this paper, the adsorption performance of different zeolites for ethylene is explored by comprehensively considering the cost and treatment effect. The best zeolite adsorbent is selected, and the sieved zeolite is further modified by potassium permanganate. The performance of modified zeolite for removing ethylene in cold storage is explored in combination with adsorption test, characterization analysis, purification efficiency evaluation of prototype and sewage capacity, so as to obtain zeolite adsorbent with good adsorption performance and high stability, It provides reference for ethylene purification design in cold storage in the future.

2. Materials and methods

2.1. Test materials

Different zeolite samples were selected for the test, including sepiolite, 13x molecular sieve, marine molecular sieve, natural zeolite molecular sieve PD-01, natural zeolite molecular sieve PD-02, CC-SORB SE molecular sieve, etc. The specific conditions of zeolite samples used in this experiment are shown in Table 1.

Table 1. Different types of zeolite samples

Sample No	Sample name	product type
1	sepiolite	zeolite
2	13xmolecular sieve	zeolite
3	Marine molecular sieve	zeolite
4	Natural zeolite molecular sieve PD-01	zeolite
5	Natural zeolite molecular sieve PD-02	zeolite
6	CC-SORB SE	zeolite

2.2. Ethylene adsorption efficiency test

At $1m^3$ The ethylene removal efficiency of different types of zeolite in Table 1 was tested in the test chamber. Test method:

The sample was prepared as a molded filter screen and put into CZKJ-20F-001 vehicle mounted air purifier as a test module. Put the module into $1m^3$ The ethylene purification effect was measured in the test chamber. The test cabin is made of mirror stainless steel, and the air leakage rate is less than 0.05%/h. Inject ethylene gas into the experimental chamber and control the initial concentration of ethylene to 10.0 ± 2.0 μ L/L, turn on the mixing fan, and turn off the fan after the air in the test chamber is stirred evenly. After the initial concentration is stable, start the purification module and test the ethylene concentration in the cabin with a hand-held photoionization VOC detector (PGM-7340, Huarui, USA) every 2 minutes. The test time is 20 minutes.

2.3. Material characterization

After grinding, the samples are pasted on the sample test bench with conductive adhesive. Under vacuum conditions, gold is sprayed on the samples with an ion sputtering instrument to enhance their surface conductivity. The gold plated samples are placed on the sample bench. Under low vacuum conditions, the morphology and chemical composition of the particles are obtained with a field emission scanning electron microscope X-ray energy spectrometer (ESEM-EDS) (FEI, Quanta FEG 650). The probe collection area is 80 mm^2, the ESEM acceleration voltage is 15-30 kV, the beam current is 10-8-10-10 A, and the EDS data acquisition time is 30-45 s.

2.4. Efficiency evaluation method of purification device

Fill the prepared modified zeolite filter element material into the self-made integrated adsorption purification device, and then place the purification device to be inspected in the 30m^3 test chamber, avoiding the air inlet and outlet, 0.5m away from the wall, and 1m higher than the ground of the laboratory. Adjust the purification device to the rated state of the test, open the high efficiency air filter, and purify the air in the test chamber.

Connect the test gas pollutant generator to a pipe passing through the test bulkhead, and the pollutants generated can be drawn into the air vortex formed by the mixing fan. Shut down the generator when the transported gaseous pollutants reach a certain amount. The mixing fan shall be stirred for another 10min to make the gaseous pollutants uniformly mixed, and then the mixing fan shall be turned off. During the test, the circulating fan is kept on all the time, and the initial concentration of gaseous pollutants is measured when the mixing fan stops rotating.

The initial concentration of ethylene is (50.00 ± 5.00) μ L/L. Start the test after the initial sample collection in the test chamber is completed. During the test, collect once every 1.5~3min. The time when the second sampling starts is t=0min. The total sampling time is 60min. Ethylene is detected with a calibrated photoionization sensor (PID, RAE 7340). Record the relative humidity and temperature in the test chamber during the test. Repeat the above process for 3 times in parallel.

2.5. Evaluation method of pollutant capacity of modified materials

Accurately weigh 3.5g of modified zeolite material and fill it into small pieces of tooling for testing (ф= 12.2mm; L=42mm); Adjust the proportion of ethylene gas and synthetic air through mass flowmeter, and obtain about 30 μ Test ethylene gas with L/L concentration and flow rate of 3.0L/min; The small parts of the test tooling are connected to the ethylene gas source for test through the six way valve, and the outlet end is connected to the PGM-7340 tester; Turn the six way valve so that the gas does not pass through the small parts of the tooling to obtain the initial concentration; Rotate the six way valve to make the gas pass through the small parts of the tooling, and start to purify the ethylene gas. Record the purification curve hourly every minute. When the purification efficiency decreases to 30% of the initial efficiency, stop recording, and get the pollutant capacity of the material to ethylene.

3. Results and discussion

3.1. Selection of materials

In this study, the adsorption properties of different zeolites for ethylene without modification were investigated. Zeolite with the best ethylene adsorption effect is proposed to be selected as the modified carrier to improve the operation efficiency of the ethylene purification device developed. See Figure 1 for the results.

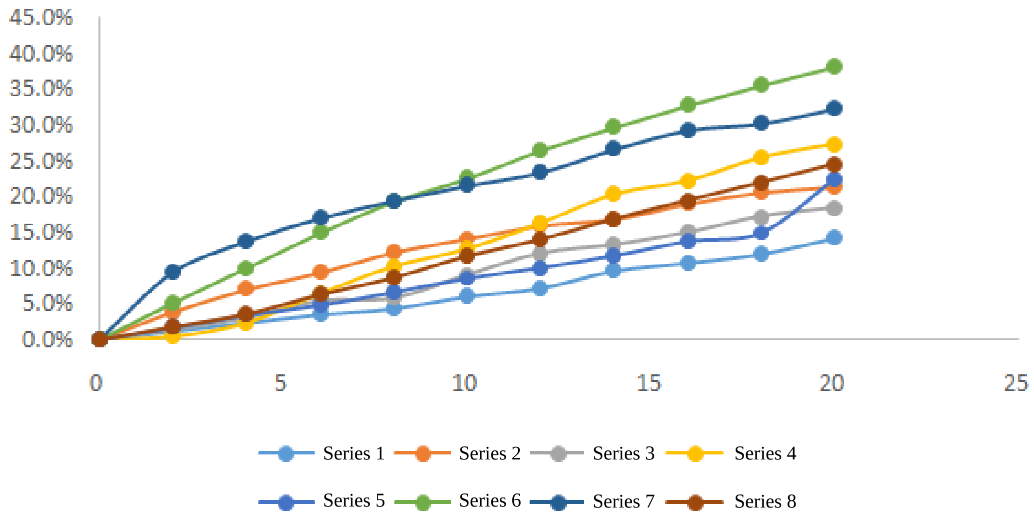

Figure 1. Adsorption effect of ethylene by different zeolite

Series 1-Natural Attenuation, Series 2-Sepiolite, Series 3-13x Molecular Sieve, Series 4-Marine Molecular Sieve, Series 5-natural zeolite molecular sieve PD-01, Series 6-natural zeolite molecular sieve PD-02, Series 7-CC-SORB SE molecular sieve, series 8-GP4060 activated carbon

It can be seen from Fig. 1 that compared with molecular sieves and activated carbon, the adsorption effect of zeolite on ethylene is relatively rapid, especially the adsorption equilibrium of natural zeolite molecular sieves PD-01 and PD-02 can be reached in 20 minutes, and the final removal rate of ethylene can reach 38.2% and 32.3%. Therefore, natural zeolite is used as modified carrier in this study.

3.2. Physicochemical characterization of materials

Using natural zeolite as raw material, potassium permanganate was modified. S1 is the original zeolite, S2 and S3 are modified zeolite, and S4 is the companion sample of activated carbon. The morphological characteristics of different samples were analyzed by scanning electron microscopy (SEM). At the same time, the composition and content of inorganic elements were analyzed by using the X-ray energy spectrum analyzer (EDX) connected with the scanning electron microscopy (SEM). The results are shown in Figure 2 and Table 2.

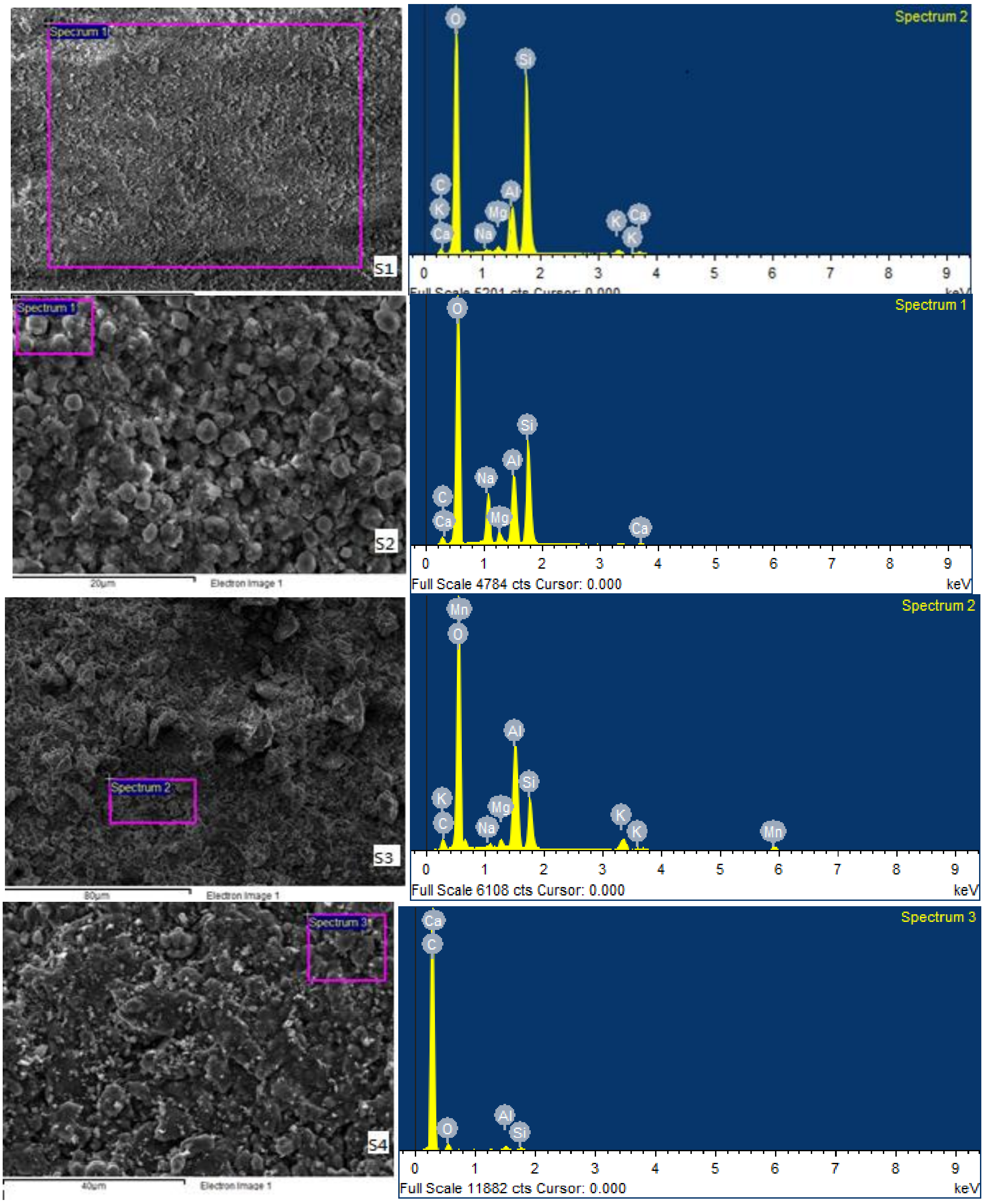

Figure 2. SEM image and EDS patterns of different zeolite

Table 2. Results of surface spectrum analysis of different zeolite

sample	EDS data/(wt.%)									
	C	O	Mn	Na	Si	S	Ca	Mg	K	Al	Fe
S1	3.91	53.39	—	—	30.00	—	1.20	0.59	1.60	5.91	3.40
S2	4.55	55.00	—	7.53	19.85	—	1.06	1.41	—	10.60	—
S3	4.09	50.42	14.87	0.55	9.12	—	—	0.98	4.94	15.04	—
S4	91.10	5.81	—	—	1.13	0.31	0.63	—	—	1.02	—

Specific surface area and pore volume are one of the important indicators to characterize the microstructure of adsorption materials, and to some extent, are also the main indicators of the adsorption capacity of reactive adsorption materials. The specific surface area and pore distribution results before and after zeolite modification are shown in Table 3.

Table 3. Structure parameters of different zeolites

Sample No	Test items	detection result
S1	Specific surface area (BET method)	25.93 m^2/g
	Total pore volume (when P/P0=0.99)	0.086 m^3/g
	Average aperture	13.60 nm
S2	Specific surface area	516.33 m^2/g
	Total pore volume (when P/P0=0.99)	0.296 m^3/g
	Average aperture	10.48 nm
S3	Specific surface area	75.99 m^2/g
	Total pore volume (when P/P0=0.99)	0.117 m^3/g
	Average aperture	7.01 nm
S4	Specific surface area	1048.26 m^2/g
	Total pore volume (when P/P0=0.99)	0.468 m^3/g
	Average aperture	2.84 nm

Based on the above test results, the surface of modified zeolite S_2 sample has relatively rich tunnels; EDS analysis indicated that more C elements were introduced and some Al elements were doped in the modification process, forming a zeolite carbon composite; Its specific surface area is the largest among the three test samples, reaching 516.33 m^2/g, and its pore volume is 0.296 m^3/g, which is 49.2% and 63.2% of the equivalent quality of activated carbon companion samples respectively. S_2 sample is an ideal modified zeolite filter element material.

3.3. Treatment effect of purification unit on ethylene

According to the evaluation scheme designed above, the ethylene treatment effect of the self-made purification device was investigated, and the results are shown in Table 4.

Table 4. Test results of ethylene purification efficiency

	Device OFF		Device ON	
Time/ min	Concentration/μL/L	lnC	Concentration/μL/L	lnC
0	47.68	3.8645	46.4	3.8373
3	47.6	3.8628	27.45	3.3124
6	47.59	3.8626	20.2	3.0057
9	47.54	3.8616	13.91	2.6326
12	47.5	3.8607	10.23	2.3253
15	47.45	3.8597	6.99	1.9445
18	47.41	3.8588	4.87	1.5831
21	47.36	3.8578	3.27	1.1848
24	47.32	3.8569	2.23	0.8020
27	47.27	3.8559	1.24	0.2151
30	47.23	3.8550	0.84	-0.1744
50	47.06	/	0.086	/
60	46.93	/	0.022	/

3.4. Measurement of the sewage capacity of modified zeolite

According to the test plan designed above, the sewage capacity of the modified zeolite was evaluated, and the test results are shown in Table 5.

Table 5. Test results of adsorption capacity

Time/ min	Outlet concentration/μL/L	Purification efficiency/ %	Efficiency attenuation/ %	Contaminant capacity/ μg/g
-15	31.38	-	-	-
0	12.92	58.5	0%	-
12	14.76	52.6	10%	222.5
79	22.02	29.3	50%	912.0
147	25.69	17.6	70%	1380.5

In order to reduce the adsorption equilibrium time before penetration, the adsorption capacity of high concentration ethylene was tested in this experiment. The experiment is divided into two steps. First, do the blank experiment of gas without quartz glass tube, measure the initial concentration of ethylene gas, and keep it stable for 15 minutes. Then switch the six way valve to make the gas pass through the quartz glass tube filled with adsorbent. As the concentration of ethylene gas is excessive, it can be seen from Table 5 that the gas is penetrated at the beginning of flowing through the adsorbent, and the ethylene concentration at the gas outlet gradually increases with time. In this experiment, the starting time of the second step is defined as t=0 min, which is regarded as the beginning of efficiency decay. When the purification efficiency decays to 30% of the initial efficiency, it is defined as the adsorption saturation of ethylene adsorbed by the adsorbent. At this time, the ratio of ethylene outlet concentration to initial concentration is 81.9%, and the experiment is over.

4. Conclusion

(a) Use 1 m^3 The removal effect of different zeolite samples on ethylene was analyzed in the small test chamber, and the best zeolite sample S2 was selected, which was used to evaluate the purification efficiency of the self-made adsorption purification device and determine the adsorption capacity.

(b) The scanning electron microscope (SEM-EDX) equipped with energy dispersive X-ray spectrometer was used to characterize the surface characteristics of zeolite samples. It was found that the rough and porous structure of the sample surface had certain advantages for ethylene adsorption. EDS analysis showed that there was more Na in the sample and there was greater exchange capacity in the process of ethylene adsorption. BET characterization shows that the larger the specific surface area and total pore volume are, the more active sites and pore volumes can be provided, and the stronger the corresponding adsorption capacity for ethylene. In addition, mesopores also play a role in ethylene adsorption.

(c) The 30 m^3 test chamber was used to evaluate the ethylene purification efficiency of the self-made adsorption purification device. It was found that the clean air volume (CADR) of the purification device for ethylene was 232 m3/h, the ethylene removal rate was 98.19% in 30 minutes, and the purification energy efficiency was 1.39. At the same time, the adsorption capacity of the selected zeolite sample is 1380.5 according to the dynamic adsorption experiment μ G/g, and on this basis, it is estimated that the service life of the filter element of the self-made adsorption purification device is 166 days.

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