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Biological and Chemical Research, 93-102 | Science Signpost Publishing

Recovery of Zeolite 4A for the Depollution of Water of Rejections

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Received: April 30, 2018 / Accepted: May 29, 2018 / Published: September 25, 2018

Abstract:

The zeolites constitute a large family of inorganic compounds and have a remarkable molecular sieve effect thanks to the regular size of their pores, which thus excludes any molecule whose diameter is greater than that of the pores. 4Å zeolites are materials used in the gas industry in Algeria but this material becomes waste at the industry level. The latter generates an additional cost to the complexes of the gas industry, which must, by force of law, take in charge of their waste either by their own means or through the intermediary of qualified services. The zeolites used in the dehydration section for liquefied natural gas become waste as soon as they are saturated and after several regeneration.

The purpose of this work is to recover these industrial wastes (zeolites 4A), which are subjected to various analyzes and experiments, with a view to recovering industrial waste in order to give it a second life, Adsorption of organic compounds (methanol and ethanol). The experiments are carried out in discontinuous system (batch). The influence of several parameters such as the contact time, the granulometry and the mass of the adsorbent on the adsorption rate will be presented.

Key words: Depollution, Zeolite, Organic compounds, Methanol, Ethanol.

1. Introduction

The importance that is now increasingly attached to the protection of natural environments and to the improvement of water quality is constantly increasing. In this connection, numerous wastewater treatment processes have been developed. Among these techniques, the adsorption which is the subject of this study has shown a treatment of wastewater of large capacity, particularly industrial. For example, it has been very simple and effective for the disposal of certain organic compounds transported by certain industrial effluents.

Our work consists in studying the molecular sieves used in the dryers of the GL1/Z complex. Molecular sieves are aluminosilicates of crystalline hydrated metals with a certain number of unusual properties. The important commercial types of molecular sieves are made of synthetic material but their structures are relatively similar to some natural minerals to be classified as zeolites.

There are several chemists who have worked on the zeolites namely Kenji Ikrda and his colaborators who have demonstrated fixed bed adsorption for a favorable isotherm, [1]
There are J. Patarin and his collaborators who have studied nanoporals, as well as the study of the adsorption of a solution of the red congo in ca-bentonite ect. [2]

As part of our work, we have been particularly interested in the removal of methanol and ethanol often present in industrial discharges by the use of a recovered 4A zeolite.

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We will start with the characterization of the zeolites before and after use by the methods of analysis: DRX, IR.

An experimental study has been carried out for the removal of methanol and ethanol often present in industrial discharges by this recovered molecular sieve (powder and grain). The experiments are carried out in a batch system. The influence of several parameters such as the contact time, the granulometry and the mass of the adsorbent on the adsorption rate will be presented, which will lead us to make an interpretation and give results that will solve our problem.

2. Materials and Methods

The purpose of the experimental part is the evaluation of the removal of methanol and ethanol, from synthetic solutions having a concentration of 281mg/L, by the spent zeolite 4A. The process is conducted in batch system.

Equipment

- X-ray diffractometer
- Infrared spectroscopy
- Gas Chromatography (GPC)

Zeolite used

The zeolite examined in this work is a molecular sieve of type 4A. This zeolite is of trilobic geometrical form (Rods), with a particle diameter equal to 3.2 mm, and the nominal diameter of the pore 4A°. [3]

3. Results and Discussion

Characterization of zeolite

X-ray diffraction

The aim of the X-ray diffraction technique is to determine the state of crystallization of the materials and their state of amorphization after treatment thermal.[4]

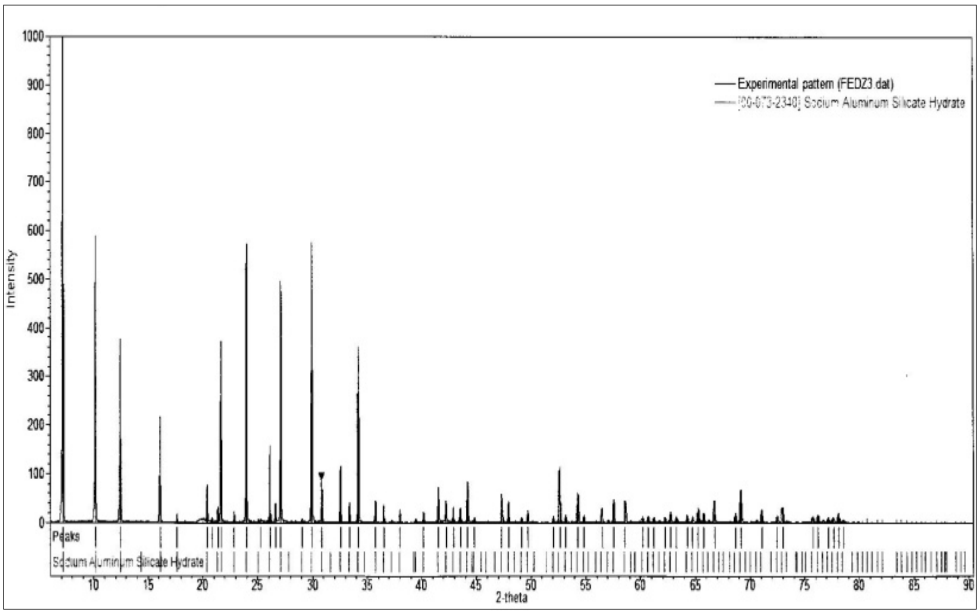

Fig.1: X-ray diffraction patterns of a molecular sieve used

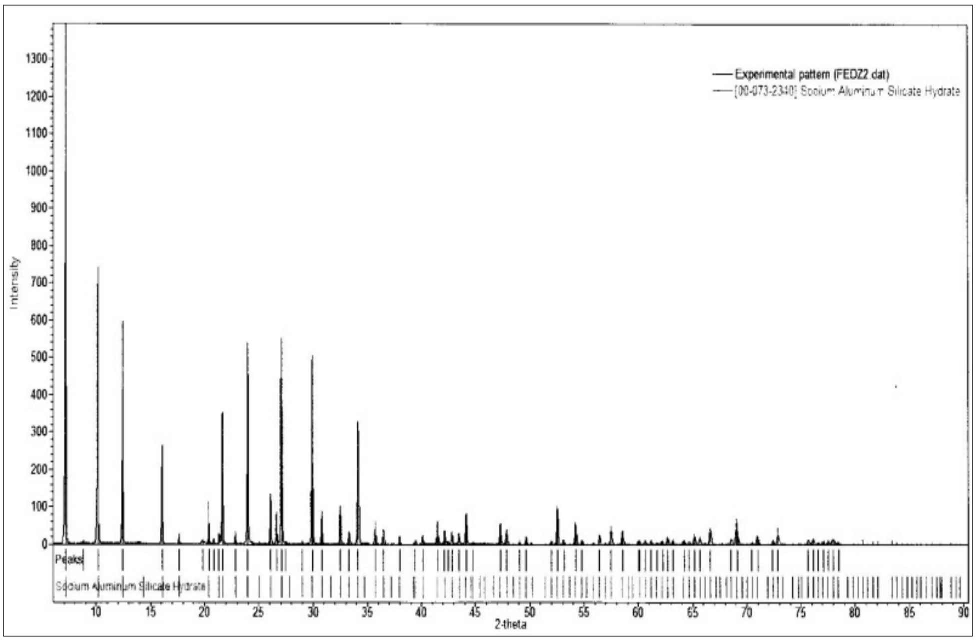

Fig.2: X-ray diffraction patterns of an unused 4A molecular sieve

Analytical Discussion

We have studied the molecular sieves used by comparing them with unused molecular sieves, after studying our materials and after passing them through the X-ray machine. See figure 1.

We have noticed that our molecular sieve is a zeolite of type A see Fig.2. It is noted that our molecular sieve identifies with a structural formula $Na_{12}Al_{12}Si_{12}O_{48}$. The molecular sieve diffraction spectrum extends over a 2∂ bande band between 5° and 60°.

X-ray diffraction analyzes allow to characterize the nature of the crystallized mineral phases present in the zeolite. For the unused zeolite the crystallinity is visible, the spectra are well defined, there are 12 molecular sieve peaks which are clearly legible, for the Molecular sieves used already the crystallinity is not so readable the peaks are not well defined and one sees dark black lines owed to the impurities. It is a method used for quantitative analysis.

Infrared spectroscopy

Infrared spectroscopy in the fundamental vibration range between 200 and 1300cm^{-1}.[5] provides information on the structural characteristics of zeolites, In particular Tetrahedra TO_4 (T = Si or Al). It makes it possible to identify the crystalline phases and to follow the advancement of the crystallization. It also has the advantage of being able to study amorphous phases. [6]

Table 1 Interpretation of peaks

peaks	Interpretation
566.93 cm^{-1}	Al-OH
667.25 cm^{-1}	Al-O
1006.66 cm^{-1}	Si-O
1659.45 cm^{-1}	Diffraction de l’eau adsorbée
3435.56 cm-1	Elongation d’eau

The infrared spectra of the molecular sieves show two classes of vibrations see figure (3,4)

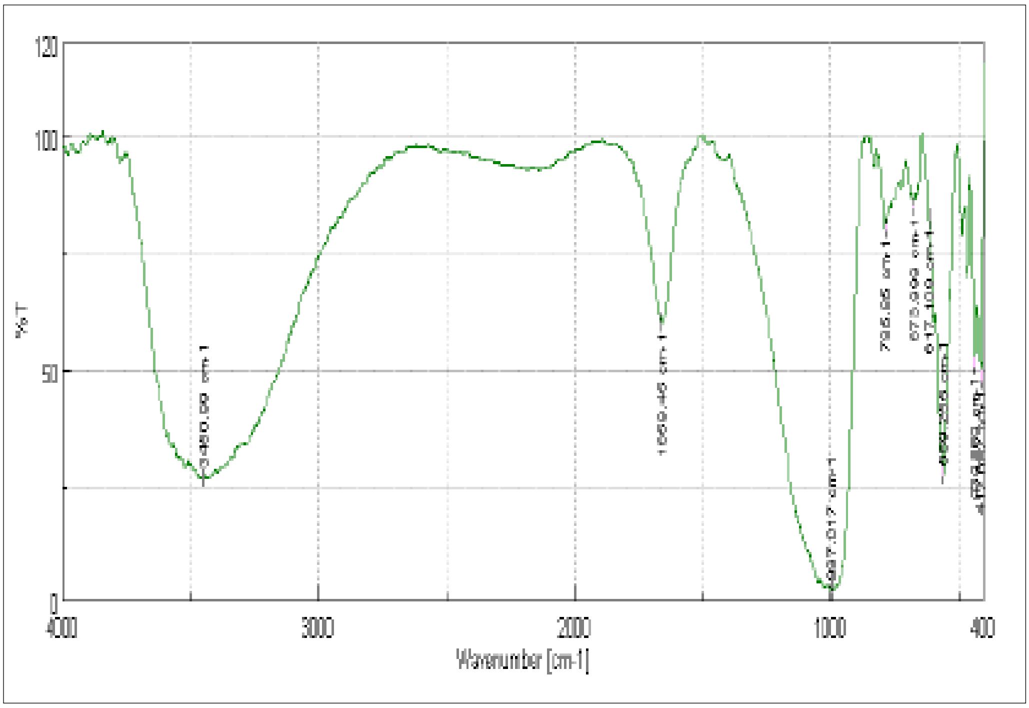

Fig. 3: IR spectrum of unused 4A molecular sieve

Table 2 Of IR Analysis Results

peaks	Interpretation
673.99 cm^{-1}	Al-OH
785.85 cm^{-1}	Al-O
997.017 cm^{-1}	Si-O
1659.45 cm^{-1}	Diffraction of adsorbed water
3450.99 cm^{-1}	Elongation of adsorbed water

The vibrations internal to the tetrahedra of the aluminosilicic framework are common to all molecular sieves.

They are represented by three bands of adsorption, the most intense of which are between 950-1250 cm^{-1} [7,8] and the others between 650-7200 cm^{-1} and 420-500 cm^{-1} . [9,10,11]

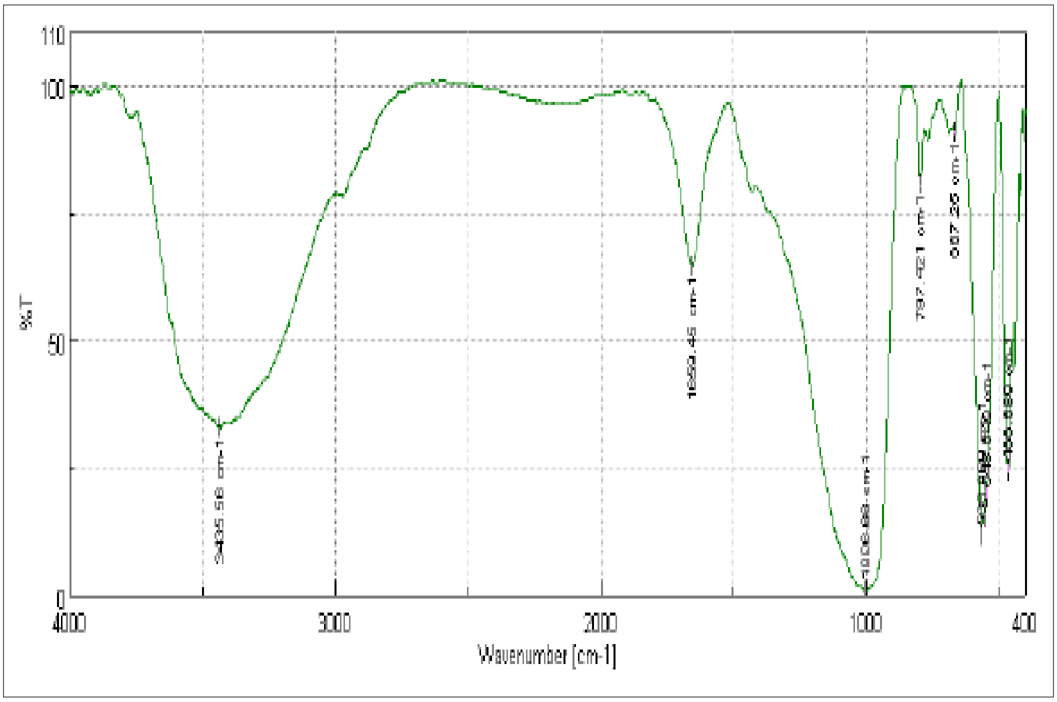

Fig. 4: IR Spectrum of a Molecular Sieve 4A used

Application of zeolite A in Methanol and Ethanol elimination discontinuous system

In order to determine the equilibrium time of adsorption, the methanol and ethanol removal experiments were carried out for an initial content of 281 mg/L for a mass of zeolite of 1g. Samples of methanol and ethanol were analyzed using Gas Phase Chromatography (CPG).The whole is stirred for periods ranging from half an hour to 8 hours. The efficiency of the process is determined by evaluating the residual methanol and ethanol content (mg/L) and calculating the elimination efficiency of the process.

$$\mathbf{R\ (\%)} = \left(\mathbf{1-}\ \frac{C}{C_0}\right)\times\mathbf{100}$$

Where C_0: is the initial concentration (mg/L).

C: is the residual concentration (mg/L).

Effect of contact time on the removal of Methanol and Ethanol Methanol

Table 3 Amount of methanol adsorbed on zeolite 4A powder and grain in batch system (C_0 = 281mg/L)

Time (h)	The 4A powder		The 4A grain	
	C (mg/L)	R (%)	C (mg/L)	R (%)
0	281	-	281	-
0.30	265.56	5.49	274.28	2.39
1	239.05	14.93	262.4	6.62
2	220.89	21.39	239.05	14.93
3	197.74	29.63	234.28	16.63
4	197.4	29.63	235.45	16.21
6	197.32	29.68	236.41	15.87
8	198.72	29.28	234.58	15.72

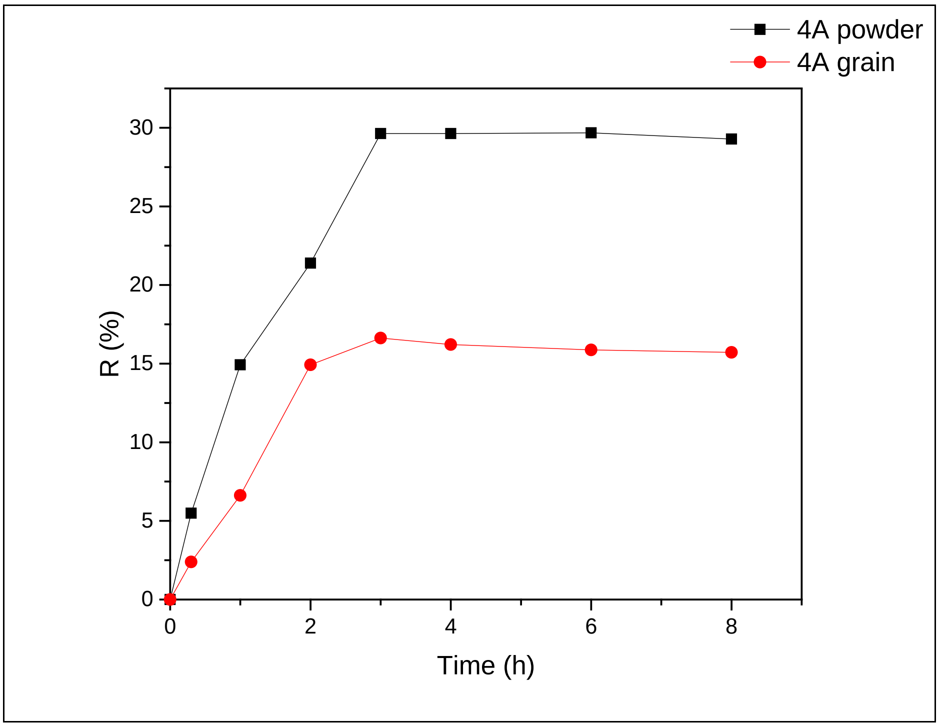

Fig. 5: Effect of time on the adsorption of methanol by zeolite 4A powder and grain (C_0 = 281mg/L).

Ethanol

Table 4 Amount of ethanol adsorbed on zeolite 4A powder and grain (C_0 = 281mg/L)

Time (h)	The 4A powder		The 4A grain	
	C (mg/L)	R (%)	C (mg/L)	R (%)
0	281	-	281	-
0.30	269.28	4.17	274.93	2.16
1	254.28	9.51	262.99	6.41
2	244.3	11.76	257.14	8.49
3	243.77	13.06	255.82	8.96
4	244.83	13.24	251.66	10.44
6	243.82	13.23	252.31	10.21
8	245.06	13.20	252.84	10.20

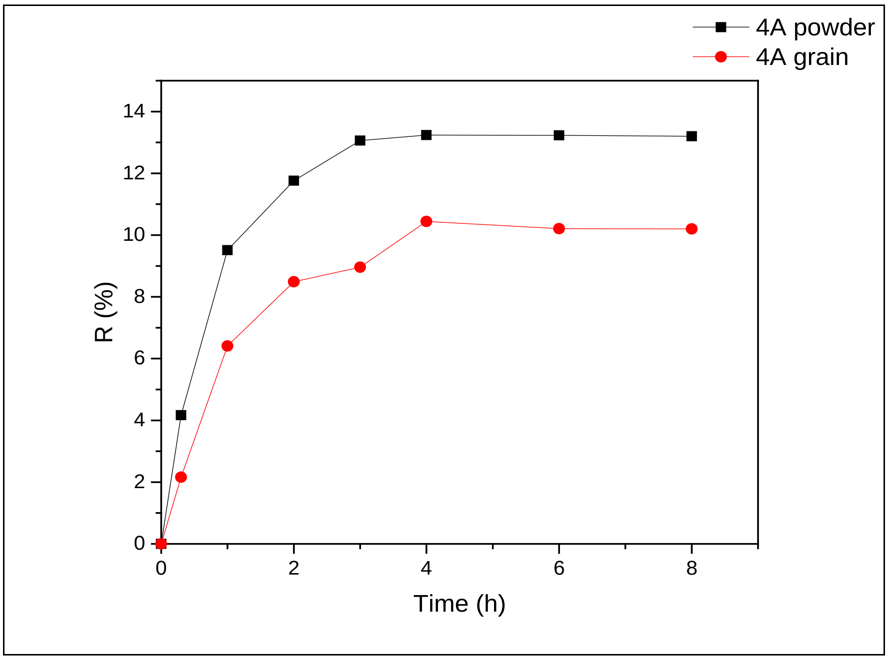

Fig. 6: Effect of time on the adsorption of ethanol by zeolite 4A powder and grain (C_0 = 281mg/L).

The results obtained show the evolution of the residual content of methanol and of ethanol as a function of the contact time. They show that the zeolite/solution contact time significantly affects the elimination efficiencies of ethanol.

It can be seen from Figs (5,6) that the rate of removal of methanol by the zeolite 4A increases with the contact time until a saturation stage is obtained from 3h, with removal rates of 29.63% for 4A powder and 16.63% for 4A grain.

For ethanol, the removal rate by zeolite 4A increases with the contact time until a saturation level is obtained from 3 hours elimination of 13.06% for the 4A powder, and at a time of 4 hours with a removal rate of 10.44% for the 4A grain, these percentages hardly change, showing that the adsorbent-adsorbate interaction has reached equilibrium, it is also found that these values are considerably lower than those obtained in the case of methanol.

These results show more or less marked differences, depending on the granulometry of the adsorbent (grain, powder) between the adsorption capacities of methanol and ethanol. The comparative study shows the superiority of the zeolite powder at C_0 = 281 mg/L.

Effect of the mass of zeolite 4A (powder and grains) on the removal rates of methanol and ethanol Methanol

Table 5 Effect of the mass the 4A powder and grain on removing methanol in batch system (C_0 = 281mg/L).

Mass of 4A (g)	The 4A powder		The 4A grain	
	C (mg/L)	R (%)	C (mg/L)	R (%)
0.5	251.41	10.53	271.21	3.48
1	220.89	21.39	239.05	14.93
1.5	191.22	31.95	229 .50	18.33
2	187.17	33.39	211.58	24.70
2.5	184.55	34.32	199.19	29.07
3	184.57	34.32	199.40	29.04

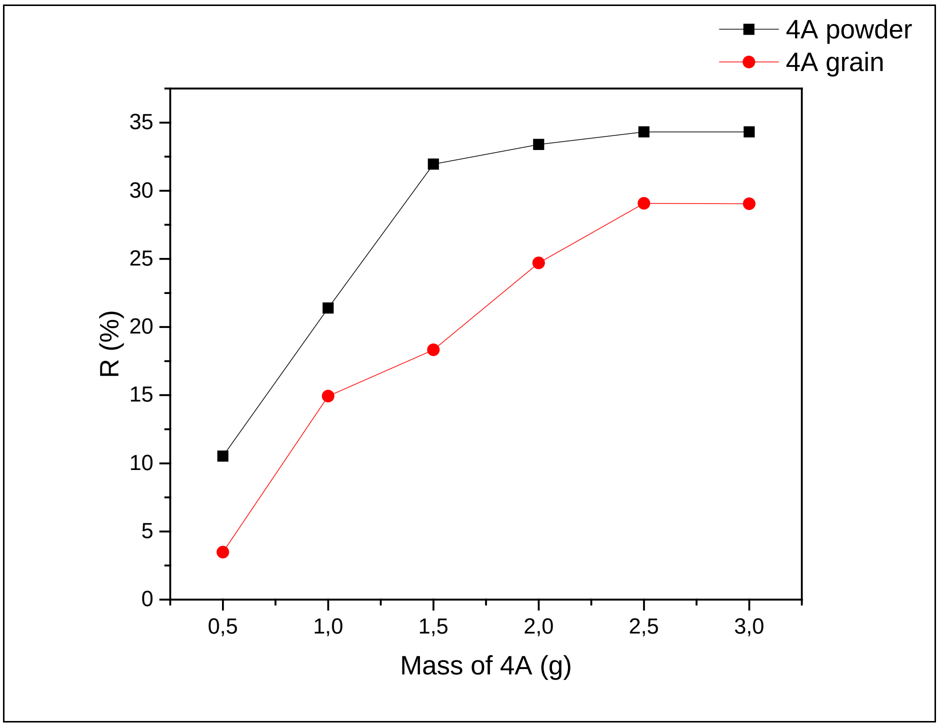

Fig. 7: Mass Effect 4A powder and grain on methanol elimination rate.

Ethanol

Table 6 Effect of the mass the 4A powder and grain on removing ethanol

masse de 4A (g)	La 4A poudre		La 4A grain	
	C (mg/L)	R (%)	C (mg/L)	R (%)
0.5	260	7.47	270.71	3.66
1	244.29	13.06	257.14	8.49
1.5	208.57	25.77	243.57	13.32
2	205	27.05	229.28	18.40
2.5	204.60	27.19	224.28	20.18
3	204.42	27.25	223.57	20.44

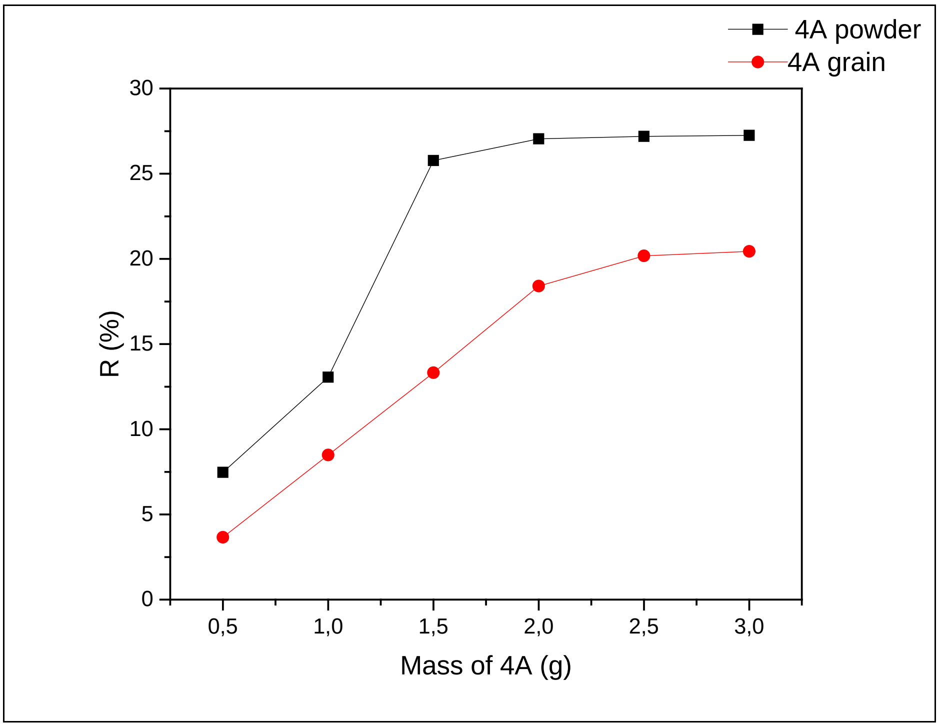

Fig. 8: Mass effect 4A powder and grain on ethanol elimination rate.

The results on the curves of Fig.7 show the evolution of the residual content of methanol versus the weight of zeolite 4A.

The shape of the curves shows a rapid growth of the ethanol elimination rate for a mass range of 0.5g and 2.5g zeolite and reaches a nearly constant value beyond a mass of 2.5g 4A which corresponds to an elimination rate of 34.32% for the 4A powder and 29% for grain 4A.

The curves in Fig.8 show that increasing the mass of the adsorbent causes an increase in the removal rate. For small amounts of zeolite of 0.5g and 1g we notice slightly increased removal rates of ethanol. A very important difference is observed between 1g and 3g to stabilize at around 27% 4A powder from a mass of 2g. This value is significantly higher than that obtained for the grain 4A where equilibrium is reached at 2.5g of zeolite with an adsorption rate of 20.18%.

4. Conclusion

The main objective of this study is the recovery and recovery of zeolite 4A already used for drying natural gas, with a view to adsorption removal of certain organic compounds likely to be present in industrial wastewater.

It enabled us to draw some important conclusions about the use of these zeolites and to indicate their possible developments.

We were able to show the possibility of treating liquid effluents (methanol, ethanol) by adsorption on the zeolite studied.

The zeolite 4A does not adsorb the organic compounds tested (methanol and ethanol) with the same capacity. In general, the adsorption capacities for the two pollutants by the recovered 4A is satisfactory in view of the material used. In addition, we found that methanol is more adsorbed than ethanol.

In the light of these results, it can be concluded that the spent zeolite 4A used in powder form has a greater adsorption capacity than that of the waste grain at 4A. The removal rates of these organic compounds increase with the contact time and the mass of the adsorbent until equilibrium is reached.

Finally, this study was intended as an important source of information on zeolite 4A, but the complexity of the subject leaves the way open for further work such as:

- The regeneration and reactivation of this recovered zeolite before its use to improve the adsorption capacity.
- Additional adsorption tests (on columns) on various industrial effluents are also necessary in order to envisage some applications, and to see the influence of the variation of other parameters, such as pH, temperature, ... on the rate of adsorption.

This study made it possible to show that a used industrial material, such as molecular sieve 4A, can be recovered through reuse in the treatment of polluted water in order to preserve a healthy and livable environment.

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