

Experimental study on the effect of combined modified aluminum and magnesium and phosphorus removal of zeolite

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Zeolite is an excellent water treatment agent, packing for the artificial wetland. Will have broad application prospects in the field of water treatment, the data showed that zeolite adsorption of ammonia nitrogen amount is larger, but phosphorus adsorption in water quantity is small, this undoubtedly denitrification and phosphorus removal for wastewater caused great limit. Therefore, the modification research of zeolite are valuable. Salt modification method is determined, by using MgCl₂ and AlCl₃ solution soaking, high temperature calcination method by certain proportion of zeolite was modified to improve its adsorption of phosphorus removal performance. Through the contrast test alone, finally determine the zeolite: MgCl₂: the mass ratio of 3:1:1 AlCl₃ as the optimal conditions. Conform to the Langmuir and Freundlich isothermal equation as a result, under the condition of the experiment, the modified zeolite adsorption of phosphorus were 1.1924 mg/g, 9.54 times that of 0.125 mg/g before modification. The experimental results show that the method of modified zeolite adsorption quantity of phosphorus increased significantly, the effect is good, is applied to the artificial wetland and other water treatment method is more in the promotion value.

Key words: Zeolite, Salt modification, Adsorption, Phosphorus removal, Elution regeneration.

INTRODUCTION

Zeolites are widely distributed in the earth's crust, porous aluminosilicate an aqueous alkali metal or alkaline earth metal. Zeolite with 400m²/g surface area, so much better chemical and biological stability. It is a kind of polar adsorbent, has good adsorption properties and exchange properties [1, 2], can be adsorbed with polar molecules of bacteria. So the natural zeolite is a kind of biological carrier ideal. Characteristics of zeolite is cheap, non-toxic side effects, regeneration method is simple, the sewage treatment effect is good, no two pollution, therefore suitable as substrates in constructed wetland.

Some experts and scholars have modified zeolite to do some research. [3] studied the preparation of modified zeolite and its adsorption of ammonia nitrogen. The adsorption properties of natural zeolite to ammonia nitrogen is better, but the adsorption capability of phosphorus. The zeolite modified to improve a lot on the adsorption properties of ammonia nitrogen, but the study on modified zeolite adsorption of phosphorus is less, and the modification method of zeolite modified with acid, alkali modification and organic modification of the economic costs of these

methods are high [4], so to carry out the test of salt modified natural zeolite for adsorption of phosphorus.

THE MECHANISM

Natural zeolite is a kind of aluminosilicate minerals, a frame structure, crystal has a large number of internal connect to each other, connected to the outside world, the channel hole; the internal structure of zeolite by silicon oxygen tetrahedron and stepwise formation unit loop, dual ring, multi ring cage [4, 5] constitute the main three-dimensional space frame shaped crystal polyhedron. Therefore, the zeolite has a large surface area, and the special molecular structure formation of electrostatic larger. The adsorption properties of zeolites and silica alumina ratio of zeolite [6, 7], the cation exchange is one of the important characteristics of. Zeolite contained K⁺, Na⁺, Ca²⁺ and the crystal structure of the combination is not tight, therefore, in the solution of other cations and reversible exchange. In zeolite Mg²⁺, and Ca²⁺, Fe²⁺, Al³⁺ can occur chemical reaction to generate precipitation and phosphate ions in wastewater. In the phase interface, material concentration automatic accumulation or enrichment and adsorption. Although adsorption can occur in different phase interfaces, but in water treatment, basic is the use of porous solid material, so that one or more substances in waste water was adsorbed on the solid surface and achieve the

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purpose of removal.

We usually by isothermal adsorption equation to determine the theoretical maximum adsorption capacity and adsorption type adsorbent, adsorbent adsorbed on the basis of comparison. The adsorption isotherm equation commonly used are two, respectively is Langmuir and Frenundlich isothermal adsorption equation.

The Langmuir isothermal adsorption equations: the equations by assuming that conditions for the adsorption material is only for single molecule layer derived from solid medium, can determine the theoretical maximum adsorption capacity and adsorption strength through the equation.

$$c/m = C/Xm + 1/Km$$

The Frenundlich isothermal adsorption equations: the equation is the empirical formula, K, n are empirical constants, said the relationship between the equilibrium solute concentrations of solid surface adsorption and liquid.

$$\ln m = 1/n * \ln c + \ln K$$

Among them, C is the original solution concentration, mg/L; C equilibrium concentration, the adsorption of mg/L; m mg/g; Xm maximum adsorption capacity, adsorption capacity, mg/g; Km, N, K are the model constants.

MATERIALS AND METHODS

Material

Natural zeolite (30 eyes), MgCl₂, AlCl₃, K₂S₂O₈, K₂SbC₄H₄O₇, KH₂PO₄, ammonium molybdate, ascorbic acid, sulfuric acid and other reagents were analytically pure.

Table 1. Experiment with zeolite main performance index.

Features	Density	Bulk density	Proportion	Void fraction	Specific surface area
Unit	g/cm ³	g/cm ³	g/cm ³	%	m ² /g
Specific parameters	1.8	0.95	1.6	40-50	500

Modification methods

Salt of zeolite modified test method: take 100 g dry 30 purpose test zeolite packing, quality ratio is shown in Table 2.

The five groups according to the mass ratio between the amount added zeolite filler, MgCl₂ and AlCl₃, MgCl₂ and AlCl₃ mixing with water to dissolve, static 24h, filtration, washed two times with distilled water, filtering to obtain zeolite, at a temperature of 105°C oven drying to constant

weight of filler, 1H culture at Ma Eph furnace are put into the 250°C, cooled out after preparing the modified zeolite standby.

Table 2. Zeolite and magnesium salt and aluminum salt mass ratio table.

	Zeolite: MgCl ₂				
The serial number	1	2	3	4	5
Design quality ratio	1:1	2:1	3:1	4:1	5:1
Actual quality ratio	1.08:1	2.04:1	3.15:1	3.98:1	5.16:1
	Zeolite: AlCl ₃				
Design quality ratio	1:1	2:1	3:1	4:1	5:1
Actual quality ratio	1.15:1	1.92:1	3.06:1	4.13:1	4.97:1

Phosphorus adsorption test method

Preparation of phosphate solution method: Phosphorus Solution of certain concentration gradient. A certain amount of dry KH₂PO₄ the preparation of 5,10,20,30, 40... 180, 190mg/L except for the first group outside with 10mg/L as the gradient of the solution of the 20 groups. 2G each dry 30 to 5 groups each of 3 copies of packing. In the centrifuge tube, with 50ml solution at 25°C, constant temperature oscillator, 200r/min oscillation in 24h, static 2h, phosphorus content of each supernatant.

Method: Determination of molybdenum antimony anti spectrophotometry; calculation formula: $M = (C-c) V / (1000W)$

Among them, adsorption, M adsorption of mg/g; C, C concentration, as before and after adsorption of phosphorus in L solution mg/; V the solution volume, taken as the adsorption test of mL; W as adsorbent dosage, G.

RESULTS AND ANALYSIS

Magnesium and aluminum salt proportion on the effect of modification of zeolite

Zeolite MgCl₂ and AlCl₃ soaked after 280°C calcination at high temperature 1H, the water inside the zeolite can be removed, and some volatile components were removed by calcination of zeolite, hydroxy will go, at the same time will generate some metal oxide, the metal oxide coordinatively unsaturated, in aqueous solution and water molecules ligand the reaction, which can cover the hydroxyl on the surface of zeolite, so more conducive to PO₄³⁻ ions to form coordination complexes, in order to increase the P adsorption capacity, you will have the following effect.

In the other conditions are the same, the magnesium salt and aluminum salt of different proportion of alone of zeolite was modified test, the quality of magnesium and aluminum salt on zeolite than were 1:1 supreme, but compared to the first three groups were matched, the modification effect and drug use is not a linear relationship between the 5, fourth, change the group the effect of decreased a lot. It is from the economic considerations, third group of 3:1 ratio of modified optimal. Therefore, selection of zeolite: the mass ratio of $MgCl_2:AlCl_3$ to 3:1:1 for further comprehensive test.

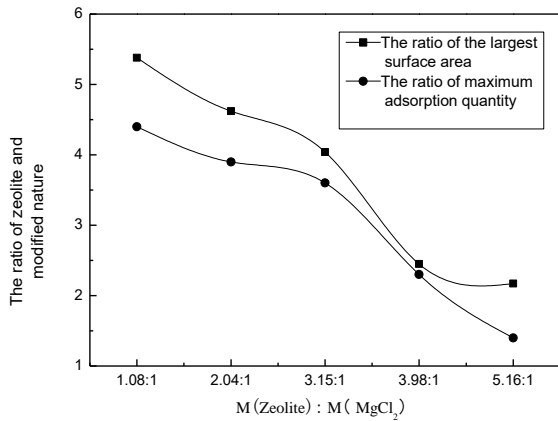


Fig. 1. Magnesium salt modified test.

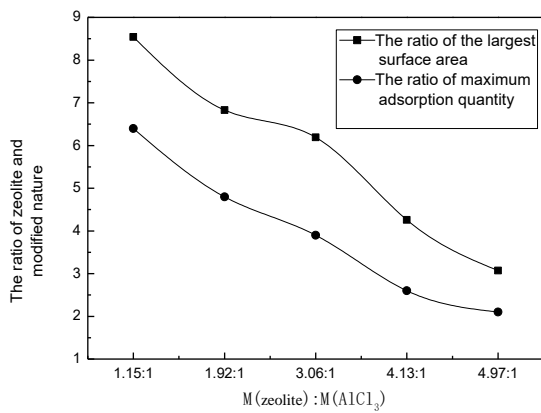


Fig. 2. Aluminium salt modified test.

Change the adsorption effect of phosphorus and analysis

We can see from Figure 3, the amount of phosphorus adsorption on modified zeolite increased significantly with the increase of concentration, and the adsorption capacity increased faster. At the same time simulation of isothermal adsorption of modified zeolite, with the former method.

Before modification zeolite theory of phosphorus adsorption quantity biggest is 0.125 mg/g, modified zeolite theory of phosphorus adsorption quantity

biggest is 1.1924 mg/g, 9.54 times that of before modification. In the process of modified zeolite framework in the position of the Si is the Al^{3+} ions in the solution, increased the amount of Al in the zeolite framework, at the same time increase the PO_4^{3-} and Al^{3+} exchange. The Mg^{2+} cation can compensate the excess charge instead of silicon,

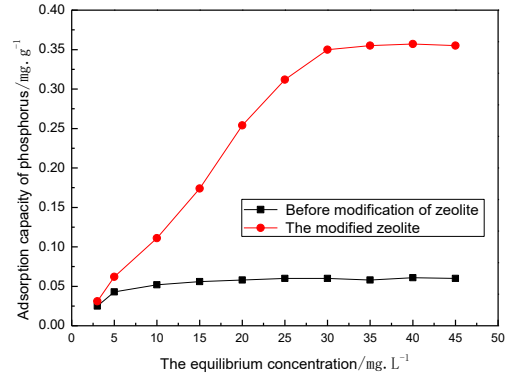


Fig. 3. Modified zeolites with different initial concentration of phosphorus adsorption quantity contrast figure.

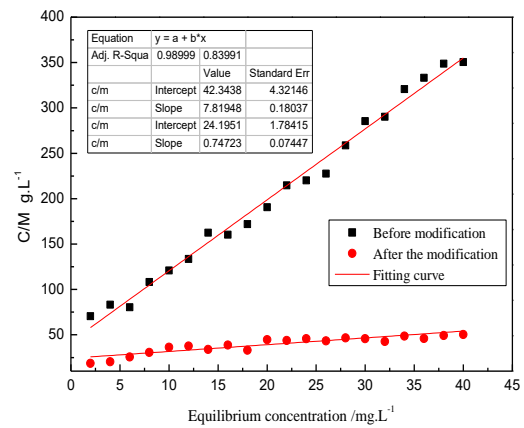


Fig. 4. Before and after the modification of zeolite to phosphorus Langmuir isotherm equation fitting curve.

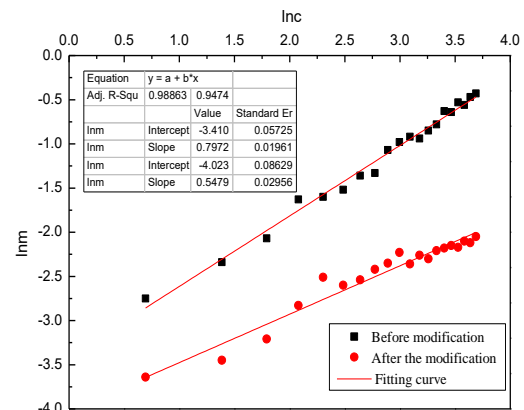


Fig. 5. Fitting curves of Freundlich isothermal equation of phosphorus in modified zeolite before and after modification.

and can work with zeolite channel K^+ , Na^+ , Ca^{2+} ions in ion exchange effect, so that the zeolite

channel more unobstructed; Too much of the Cl⁻ ions can also enter the zeolite ion exchange reaction channel, to improve its internal environment. Therefore, specific surface area and the modified zeolite internal structure all the corresponding improvement.

Table 3. Zeolite modified phosphorus isothermal adsorption equation and its parameters.

Before and after modification The fitting equation	Langmuir fitting equation		Frenundlich fitting equation	
	Formula	Decision coefficient	Formula	Decision coefficient
In front of the zeolite modified fitting equation	$y=7.8194x+42.343$	$R^2=0.9899$ $X_m=0.1250$	$y=0.5479x-4.023$	$R^2=0.9502$ $n=2.1164$
Zeolite modified fitting equation	$y=0.7472x+24.195$	$R^2=0.8399$ $X_m=1.1924$	$y=0.7972x-3.410$	$R^2=0.9892$ $n=1.3847$

CONCLUSIONS

Zeolite adsorption of phosphorus effect is relatively poor, by using MgCl₂ and AlCl₃ solution soaking, high temperature calcination methods of zeolite was modified to improve its adsorption of phosphorus removal performance. Zeolite modified filler to Langmuir isotherm equation fitting and Frenundlich isothermal equation fitting.

This low-cost adsorbent preparation, the method is simple, does not produce secondary pollution after use, after adsorption saturation of the adsorbent, using 1L 15 % NaOH + 5% NaCl eluent [8] the elution solution regeneration, control the eluent velocity, time after 1.5 h, adsorbent for phosphorus adsorption capacity can be up to 94% of the original sample regeneration can be recycled after processing, can be used as a plant of nitrogen and phosphorus compound fertilizer, has a certain economic and social benefits.

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