Removal Research of Modified Zeolite Phosphorus in Wastewater

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Abstract-Recently years many large lakes are eutrophic or in serious state of eutrophication. And most eutrophic water from phosphorus control action is the amount of input, so how to effectively reduce the phosphorus content of sewage has become noticeable within the field of environmental protection issues. In the present study natural zeolite as material and finding that the original zeolite adsorption effect only is 8%-18% . Due to the removal effect, choose modified zeolite, through to the acid and alkali salt for respectively , then insure that using 20% MgCl2 best of static test examines the pH , temperature, adsorption time , the effects of the removal rate could reach 70%-85% . The last time, dosing quantity for the orthogonal experiment research, determine the optimum condition of the adsorption is at 25 ℃, 160min, 5g respectively, and the removal efficiency can reach 82%.

Keywords-Zeolite ; Adsorbent influence ; Phosphorus removal adsorbent; Modification; Secondary sewage discharge standards;

I.　Introduction

With the rapid development of industry and agriculture, high concentrations of phosphorus- containing wastewater and domestic sewage is not treated directly discharged into water bodies, resulting in excessive levels of nitrogen and phosphorus in the water, causing eutrophication. Zeolite is zeolite minerals in general, are widely distributed in the Earth's crust. Zeolite is a shelf-like aluminum silicate, a high water content of the alkali and alkaline earth metals are a prerequisite for the formation of zeolite.

Adsorption properties of zeolite: Zeolite has a large internal surface area, up to $500 \sim 1000 m^2/g$, so the zeolite has a large diffusion capacity, but also has good adsorption properties. In exchange properties of the zeolite: the spatial structure of the zeolite base unit 4 is an oxygen atom and a silicon atom or a silicon atom piled into alumina tetrahedral.

Choose some place of natural zeolite with phosphorus additives together with the activation treatment of wastewater, the modified zeolite can effectively remove the sewage phosphide, but based on poly phosphide phosphorus wastewater treatment effect is not ideal. Phosphorus optimum conditions are: zeolite particle size 0.5-1.6mm,water pH=4-12, a phosphorus concentration of 30mg/L, filtration speed 3m/h. Based on the experience of phosphorus modified zeolite materials and foreign scholars, this paper intends to use alkali treatment, alt treatment, high temperature roasting method of combining natural zeolite modified.

II. MATERIAL AND METHODS

A. Materials

1) A natural zeolite

Zeolite is a family of frame-like structure of hydrous aluminum silicate minerals. It mainly contains Na and Ca, and a small number of Sr, Ba, K, Mg and other metal ions. Since silicon different oxygen tetrahedron connection, he formation of many voids and pores in the zeolite structure, his unique structure and chemical properties of the zeolite crystal has excellent physical and chemical properties, uch as ion exchange, adsorption, thermal stability resistance, cid resistance.

2) Test water

Phosphorus content is at 2-4mg/L, nitrogen and COD content is at 15-20mg/L and 100 mg/L.

B. Methods

Measurement items and equipment

Experimental determination the project are mainly phosphorus concentration, pH. Phosphorus concentrations of molybdenum, antimony anti-spectrophotometric instrument with 722 spectrophotometer, pH was measured using a pH meter.

1) A basic principle

Under acidic conditions, the positive reaction with Ammonium phosphate, potassium tartrate antimony oxide, generating phosphomolybdic heteropoly acid. Stannous reducing agent is restored , turn blue complex, commonly referred to as phosphorus molybdenum blue. The color of the 700nm wavelength has a strong absorption.

2) Determination of step

a) The calibration curve

Take six 50ml stoppered colorimetric tube were added phosphate standard solution 0, 0.50, 1.00, 3.00, 5.00, 7.00 and 10.0ml, diluted with water to the mark.

Color : add 5 ml molybdate solution, mix, stannous chloride solution was added to 0.25ml colorimetric tube ,and mix.

Measurement: room temperature (20℃) after 20min placed at a wavelength of 700nm, optical drive 10mm cuvette with distilled water as a reference, measure the absorbance. From the measured absorbance of the sample by subtracting the absorbance of the reference water, the corrected absorbance plotted phosphorus content (μg) of the corrected absorbance of the calibration curve.

b) Determination of water samples

Take the right amount of water samples (make phosphorus does not exceed 30μg, usually raw water 1ml, water 5ml) in colorimetric tube, diluted with water to the mark. The following steps according to the standard curve for color measurement. Subtracting the absorbance of the blank test, and a phosphorus content isolated from the calibration curve.

III. RESULT

A. Natural zeolite adsorption

Weigh 5g original zeolite into 250ml Erlenmeyer flask, were added to 50ml phosphorus in water samples, 25℃ water bath oscillator oscillating 0.5,l,1.5,2,2,5 hours, sampling 5ml in colorimetric tube, fixed volume to 50ml. Molybdate solution was added 5mL mix, add a solution of stannous chloride 0.25ml stick sufficiently uniform, color 20minutes. Distilled water to make a reference, 700nm wavelength spectrophotometer absorbance was measured.

According to the experiment, we can conclude that the effect of the removal of contaminants in water samples with phosphorus relatively poor natural zeolite and phosphorus removal rate is only around 11%, so our natural zeolites can be used to remove phosphorus pollutants in water samples. The reason is that the original zeolite pores is no valid immobilized phosphate, making the zeolite pores in the phosphate free access, while a negative for some time after adsorption is due to the structure of the zeolite phosphorus out of the water samples free of phosphorus content increased. It can be seen, for the modification of the original zeolite shall have its inner surface and pores carrier absorption of phosphorus.

B. Select modifier

After soaking acid salt brine soak best analysis were obtained. After verification, soaked with 20% $MgCl_2$ best, take 5g original zeolite, the supernatant was poured into 250mL draw 25mL volumetric flask, dilute to volume, measured twice each parallel solution, the absorbance was measured.

Modified zeolite obtained optimum conditions for the test :

Zeolite into concentration 1mol/L NaOH solution in soaking 35℃ temperature oscillation, removed after soaking, cleaning and zeolite, washed with deionized water and dried. The treated zeolite is placed above the concentration of 20% $MgCl_2$ solution soak, 35℃ temperature oscillation, after soaking 2d removed, washed and dried. The zeolite after NaOH treatment and $MgCl_2$ placed in a muffle furnace, and calcined at 500 ℃ for 2h, after removing the natural dry.

C. Univariate tests of modified zeolite

1) Effect of soaking time on the adsorption of phosphorus

Take 6 volumes of 250ml Erlenmeyer flask, 50mL each bottle has been loaded with good phosphorus in water samples. Were added to each bottle modified zeolite. Placed in a water bath shaker at room temperature (25℃) oscillations, took out a flask at regular intervals, sampling 5ml in colorimetric tube, the volume to 50ml. Adding 5mL molybdate solution mix, 3 plus 0.25mL stannous solution thoroughly mixed, color 20 minutes. Distilled water to make a reference, 700nm wavelength spectrophotometer absorbance was measured. According to the standard curve to calculate the amount of

phosphorus, calculated removal and adsorption capacity for removal and adsorption capacity vs time, reaction time relationship with the phosphorus concentration in water is shown in Fig .1.
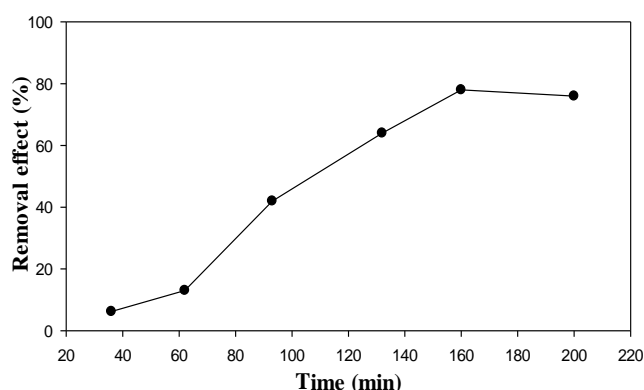

Figure 1. The time and removal rate curve

Obtained from the above experiment, the phosphorus-containing wastewater treatment, time to 160min degradation results were better than the maximum degradation rate of 72.33%.

2) The influence of temperature on the removal of the modified zeolite

Weigh 5g sample into 250ml conical flask, add 50ml water sample phosphorus, water bath oscillator, respectively, the temperature-controlled oscillator at 10,15,20,25,30 ℃ 3 hours, the test methods above, for the removal and adsorption the amount of change over time chart shown in Fig .2
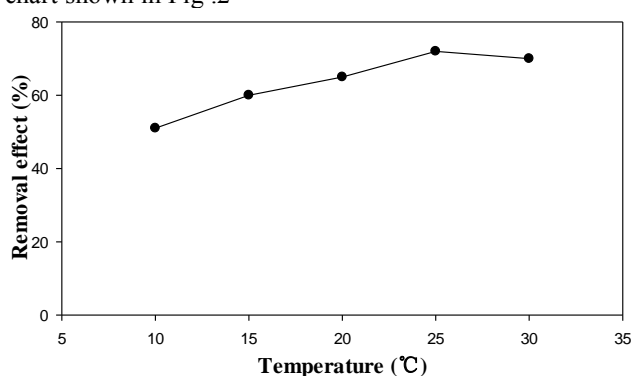

Figure 2. The temperature and removal rate curve

3) The impact of the dosage of modified zeolite and phosphorus removal

Take different amounts of modified zeolite material handling 1,2,3,4,5 g of phosphorus in water samples 50mL, measured adsorption 3h. Test methods, test methods above, removal and adsorption capacity for change with time chart, the test results are shown in Fig .3:
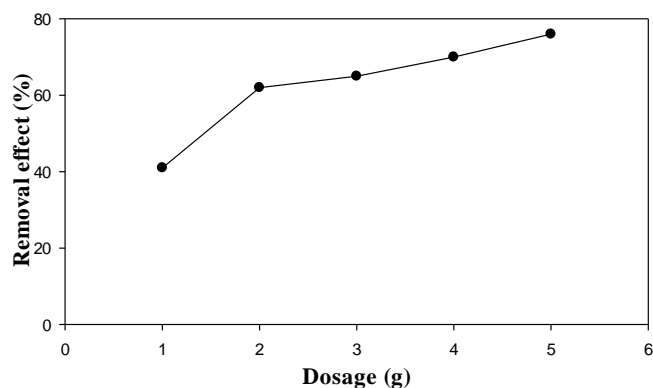

Figure 3. Dosage and removal rate curve

It is shown in the chart that with the increase in dosage is getting better adsorption, absorption is best when adding 5g, 5g so experiments were taken as the standard.

4) Orthogonal modified zeolite and phosphorus removal

a) Orthogonal take three factors in selecting

Univariate analysis using orthogonal experiment and method of combining research and phosphorus modified zeolite to various factors. Orthogonal mainly consider the following factors:

l. Effects of soaking time, the impact of different zeolite adsorption time of phosphorus removal efficiency. The trial investigated 120min, 150min, 180min, affecting three times zeolite removal of phosphorus.

2. Temperature. This test uses 20 ℃, 25 ℃, 30 ℃ for the three levels of orthogonal experiment.

3. How much influence the dosage and zeolite catalytic water samples, the greater the dosage under normal circumstances, the higher the efficiency of the zeolite and phosphorus, but the dosage is too big, too expensive, not conducive phosphorus. This test uses 1g, 3g, 5g of three levels of orthogonal experiment. Orthogonal factor levels are shown in Table 1

TABLE I. THE ORTHOGONAL EXPERIMENT FACTOR LEVEL

Factor	Level 1	Level 2	Level 3
Time(min)	120	160	180
Temperature(℃)	20	25	30
Dosage(g)	1	3	5

b) Orthogonal test results and anal

TABLE II. THE ORTHOGONAL EXPERIMENT RESULT TABLE

Items	Time	Temperature	Dosage	Removal/%
1	1	1	1	61.6
2	1	2	2	62.2
3	1	3	3	65.3
4	2	1	2	71.5
5	2	2	3	77.6
6	2	3	1	68.2
7	3	1	3	74.3
8	3	2	1	67.4
9	3	3	2	66.6
K1	1.688	2.655	1.871	
K2	2.264	2.098	2.109	
K3	2.203	2.012	2.155	
Poor R	0.376	0.077	0.224	
Excellent level	A_1	B_2	C_3	

Analysis can be seen by the poor:

l. Size of each factor as follows: Time>dosage>temperature. The test results showed that the zeolite while phosphorus removal efficiency is relatively high, the need to further explore the mechanism of phosphorus removal.

2. The minimum temperature adsorption of zeolite.

3. From the test results, the time was 150min, temperature 25 ℃, the dosage is best to remove the effect of 5g.

IV. CONCLUSION

1.Use the following steps when natural zeolite modified phosphorus best: natural clinoptilolite washed with deionized water, NaOH solution and drying   1 mol /L of 35 ℃ soaking 1h, 20% $MgCl_2$: 35 ℃ under dynamic solution soak 2d, in a muffle furnace at 500 ℃ calcined at 2h, the 105 ℃ drying.

2. After the modified zeolite, the skeleton structure has not changed, but the silica to alumina ratio is changed, the porosity increases, and the load surface of the zeolite, magnesium hydroxide, so that the active adsorption sites increase, thereby increasing the adsorption of zeolite P performance. Natural zeolites have almost no phosphorus removal capabilities, and the ability of the modified zeolite adsorption greatly enhanced.

3. The adsorption capacity of modified zeolite is contact time, temperature, pH value of the solution, the dosage and other factors.

4. When the modified zeolite univariate tests found that the biggest factor affecting the time, and is not dosage, temperature and pH, and therefore the selected time, dosage, temperature do three factors and three levels orthogonal trials.

5. The orthogonal test showed: 160min, 25 ℃ and   5g the best results can be achieved by 82%.

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