Nitrogen and phosphorous adsorption from post-hydrothermal liquefaction wastewater using three types of zeolites

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Abstract: Hydrothermal liquefaction (HTL) has been studied as a promising technology for converting wet biomass into bio-crude oil and the nutrient-rich post-hydrothermal liquefaction wastewater (PHWW) could be reused for algae and bacteria production. However, the PHWW from HTL contains various types of contaminants that need to be removed before reuse. Too high nutrients (nitrogen and phosphorous) contents, such as ammonium, are inhibitive to algal growth and bacteria species in anaerobic process. It is desirable to reduce nutrients concentration in PHWW to an acceptable level using zeolite adsorption. This study investigated nitrogen and phosphorous adsorption efficiencies from PHWW using three types of zeolites: activated clinoptilolite, natural clinoptilolite and Na-modified zeolite. Effects of ions and pH in the adsorption process were also investigated. Results showed that three zeolite variables affecting ammonium adsorption process could be ranked as follows: zeolite dosage > type > particle size, via an orthogonal experiment design. Activated clinoptilolite, with a particle size of 0.18-0.30 mm and a dosage of 0.4 g/mL demonstrated the highest ammonium adsorption efficiency of 54.92%. Zeolite could also adsorb organic nitrogen and had a high adsorption efficiency of phosphorous (97.85%). This study showed that zeolite is effective to adsorb nutrients in PHWW. The adsorption treated PHWW can then be used for culturing algae or anaerobic treatment, and the adsorbed nutrients can be reused later.

Keywords: adsorption, ammonium, nutrients; phosphorous, zeolite, post-hydrothermal liquefaction wastewater (PHWW)
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1 Introduction

Post-hydrothermal liquefaction wastewater (PHWW) contains abundance of nutrients[1-5]. Minowa and Sawayama[6] reported that all nitrogen in the microalgae was converted to ammonia (9 000 mg/L) during the hydrothermal liquefaction process, and the ammonia was dissolved in the recovered solution. The nutrient-rich PHWW is a valuably concentrated nutrient source. However, it is not suitable for direct use in algae cultivation and anaerobic digestion, because the high concentration of ammonia is toxic to algae[7] and methane bacteria[8]. Therefore, ammonium must be reduced in the PHWW in order to be used for subsequent anaerobic digestion or algae cultivation.

A direct method to reduce the ammonium in the aqueous stream is dilution. Jena et al.[3] and Zhou et al.[5] adopted the dilution method to reduce the ammonium concentration and the toxicity of PHWW for algae cultivation. However, direct dilution uses a large

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amount of water and may cause secondary pollution. In addition to dilution, other methods include air stripping, ion exchange, and biological nitrification-denitrification, are also possible methods to reduce nutrients concentration[9]. Among those, ion exchange has some distinct advantages, including little influence at low temperature, simple operation, no need for addition of chemicals to water, and no sludge generation. The iron exchange method is especially cost-effective as there is an abundance of natural materials that can be used as ion exchangers[10,12].

Zeolites are microporous aluminosilicate minerals with a three-dimensional framework of AlO_4 and SiO_4 tetrahedral[13]. The tetrahedrons are bound together by covalent bonds over common oxygen atoms forming interconnected cages and channels[12,15]. When an aluminum atom is substituted for the silicon atom in the silicon-oxygen tetrahedral, a negative charge appears in the lattice, which is balanced by positively charged metal cations, generally alkali metal or alkaline earth metal ions[13,17]. As a result, the physical and chemical structure of zeolite determines its ion exchange capacity and adsorption properties. Zeolite is produced world-wide, and is widely used in water treatment. Zeolites synthesized from coal fly ash were proved to play an important role in the removal of methylene blue from aqueous solution[18]. Effective ammonium adsorption of synthetic NH_4^+-N solutions at a low concentration (<5 000 mg N/L) could be achieved using zeolite[17,19]. Grey water[11] and municipal wastewater[20] can also be treated using zeolite. With a wide range of studies using zeolite, there has been no report on the application of zeolite to PHWW for wastewater treatment and nutrient recovery.

The objectives of this study were to determine nutrients (mainly ammonium and phosphorous) adsorption in the nutrient-rich PHWW using three types of zeolites at a constant temperature of 35°C, which is beneficial for subsequent mesophilic fermentation of the supernatant. The adsorbed nutrients were intended for reuse in subsequent algae culture which is for the next round of bio-crude oil conversion via hydrothermal liquefaction. The effects of key zeolite variables, including zeolite type, particle size and dosage (gram of zeolite per milliliter of liquid), on nitrogen and phosphorous adsorption efficiency were evaluated via an orthogonal design. Effects of ions and pH in the PHWW on nutrients adsorption efficiency were also investigated.

2 Materials and methods

2.1 Materials

The PHWW was obtained in a HTL process of a high-protein (63.63±0.70)% and low-lipid (3.60±0.10)% microalgae, *Spirulina*. The production and separation process of PHWW were using the methods of Li et al.[21] The reaction mixture from HTL was separated into raw oil and liquid phase by filtration, and the bio-crude oil was extracted from the raw oil using acetone. By the method of ethyl ether extraction, the light oil and aqueous stream were obtained. The remaining aqueous stream is considered as the PHWW for this research.

The concentrations of total nitrogen (TN), total phosphorus (TP), total organic carbon (TOC) and the chemical oxygen demand (COD) in PHWW were measured as (11 525±738), (1138±94), (78 960± 960) and (169 600±950) mg/L, respectively (Table 1). Nearly 60% of the TN was in the form of ammonium (NH_4^+-N), which was obviously much higher than that of TP. For that reason, the ammonium adsorption was the main objective in this study.

Table 1 The characteristics of the PHWW

TN/mg·L^{-1}	TP/mg·L^{-1}	NH_4^+-N/mg·L^{-1}	TOC/mg·L^{-1}	COD/mg·L^{-1}	pH
11 525±738	1138±94	6549±749	78 960±960	169 600±950	8.24±0.55

Three types of zeolites were used in this study: activated clinoptilolite, natural clinoptilolite and Na-modified zeolite (Table 2). The activated and natural clinoptilolites were obtained from Beijing Kangwen Changsheng Trade Co., Ltd, and the Na-modified zeolite was obtained from Shanghai Shentan Environmental Protection New Materials Co., Ltd. The Si/Al ratios of the activated and natural clinoptilolite were both 4.86, lower than that of the Na-modified zeolite. The high Si/Al ratio indicates that there are much more unsteady alkali metal and alkaline earth metal ions, which will lead to stronger ion-exchange capacities with ammonium. Ammonium adsorption is also affected by other factors and barriers, such as the specific surface area influenced by the density of zeolite. All materials were pretreated via crushing and sieving, and then divided into three levels of particle sizes: 0.18-0.30, 0.30-0.45 and 0.45-0.90 mm.

Table 2 The characteristics of zeolites

	Natural clinoptilolite	Activated clinoptilolite	Na-modified zeolite
Specific gravity	1.60	1.40	1.60
Si/Al mass ratio	4.86	4.86	5.00
Density/g·cm^{-3}	2.00-2.60	1.80-2.20	1.60-2.00

2.2 Methods

The lipid content of *Spirulina* was determined using Soxhlet extraction, and the crude protein content was measured using the Kjeldahl method[2].

The TN was measured through a potassium persulfate oxidation method using an Ultraviolet and Visible Spectrophotometer (UV-1800, Meipuda Instruments Co., Ltd., Shanghai, China). NO_3^- and NO_2^- were measured using a Continuous Flow Analyzer (Analytical-AA3, SEAL Co., Ltd., Germany). The TP was measured using molybdenum antimony anti-spectrophotometry. The ammonium concentration was determined using salicylic acid-hypochlorite spectrophotometry. The TOC was tested using a TOC Analysis Meter (TOC-VCPN, Shimadzu Company, Tokyo, Japan). The COD was measured using a potassium permanganate oxidation method. The ions in solution were tested using an Optical Emission Spectrometer (Optima-8300, PerkinElmer Instruments Co., Ltd., Shanghai, China). The pH was measured using a digital pH meter (FE20, Mettler Toledo Co., Inc., Shanghai, China).

GC-MS (Model QP2010, Shimadzu Company, Tokyo, Japan) was used to analyze the organic compound of the original PHWW and the supernatant from the optimal set of orthogonal experiments. Helium (99.999%) was used as the carrier gas at a constant flow rate of 1 mL/min at a pressure of 100 kPa, and GC was operated on a 30 m capillary column with an inner diameter of 0.25 mm and a film thickness of 0.25 μm. One milliliter of dichloromethane extract was injected with a split ratio of 10:1. The initial temperature of the column was first set to 40°C and held for 5 min. Next, the temperature increased from 10°C to 150°C at a heating rate of 20°C/min, and this temperature was then held for 2 min. Finally, the temperature was then increased to 270°C at a rate of 10°C/min and held for 3 min.

All water quality indexes above were tested using the APHA standard method[22].

2.3 Batch study

Nutrient adsorption experiments were operated in a thermostat oscillator (SHA-B, Changzhou Guohua Electric Appliance Co., Ltd., Jiangsu Province, China). For each test, thirty milliliters PHWW and selected dosage of zeolite were added to the glass bottle, and the zeolite-liquid mixture was shaken at 180 r/min for 9 h at a temperature of 35°C.

To investigate the feasibility of ammonium adsorption from PHWW using the three zeolites, a set of preliminary tests were firstly conducted under the condition of intermediate particle size and dosage, namely with a dosage of 0.3 g/mL and a particle size of 0.30-0.45 mm for the three types of zeolites. Thirty milliliters PHWW without any zeolites was as the blank test and the equilibrium studies were performed for the time intervals ranging from 15 min to 2 h.

An orthogonal experimental design (3-variable and 3-levels, Table 3) was used. The three factors were zeolite type, particle size, and zeolite dosage. Each factor had three levels of treatment: zeolite type included activated clinoptilolite, natural clinoptilolite and Na-modified zeolite; particle size included three size ranges (0.18-0.30, 0.30-0.45 and 0.45-0.90 mm); and zeolite dosage had three levels (0.2, 0.3 and 0.4 g/mL). Samples were taken at the first hour and then every two hours to measure pH, TN, NO_3^-, NO_2^-, TP, NH_4^+-N, and typical positive ions (K^+, Na^+, Ca^{2+} and Mg^{2+}) in order to systematically study the adsorption efficiency of zeolite in the nutrient-rich PHWW.

According to the results of the orthogonal experiments, the influence of particle size and dosage of activated clinoptilolite on the ammonium adsorption efficiency was investigated in further detail. Two sets of experiments were conducted: effect of the smaller particle sizes (<0.18 mm) of the activated clinoptilolite with a dosage of 0.4 g/mL; and confirmation of the positive correlation property between the ammonium adsorption efficiency and the dosages (0.3-0.5 g/mL) of the activated clinoptilolite.

Table 3 Ammonium adsorption analysis of orthogonal experiment results at the equilibrium time

No.	A Zeolite types	B Zeolite particle sizes	C Zeolite dosages	Adsorption efficiency/%
1	1 (Activated clinoptilolite)	1 (0.45-0.90 mm)	1 (0.3 g·mL^{-1})	34.24
2	1	2 (0.30-0.45 mm)	2 (0.4 g·mL^{-1})	54.91
3	1	3 (0.18-0.30 mm)	3 (0.2 g·mL^{-1})	27.06
4	2 (Na-modified zeolite)	1	2	40.17
5	2	2	3	17.71
6	2	3	1	31.85
7	3 (Natural clinoptilolite)	1	3	6.78
8	3	2	1	24.16
9	3	3	2	36.04
$\bar{K}_{1j}^{*}$	38.21	26.97	27.72	
$\bar{K}_{2j}^{*}$	30.37	30.76	44.85	
$\bar{K}_{3j}^{*}$	20.38	31.23	16.39	
$R_j^{\dagger}$	17.83	4.26	28.46	
Factors: primary → secondary	Zeolite dosages > types > particle sizes			
Optimal solution	Activated clinoptilolite, 0.18-0.30 mm, 0.4 g·mL^{-1}			

Note: * The average value of the test results when factors in *j* column taking horizontal *i*;

† The range of factor in column *j*.

All the experiments were performed in triplicate. One milliliter sample was obtained from the glass bottle at the targeted time of each experiment. Samples were filtered via a 0.45 μm water membrane and then stored at 4°C to test related indicators. The adsorption efficiency q_t (%) at time *t* was calculated according to Equation (1),

$$q_t = \frac{c_0 - c_t}{c_0} \times 100 \qquad (1)$$

where, c_0 is the initial ammonium concentration, mg/L; c_t is the ammonium concentration at time *t*, mg/L.

3 Results and discussion

3.1 The results of feasibility study

Figure 1 shows the ammonium adsorption efficiency of the three zeolites at 35°C at different contact times. There was virtually no NH_4^+-N volatilization during the experiments (CK: no zeolite). The high ammonium concentration in PHWW was reduced by 18.01%-29.99% from its initial concentration. It was clear that most of the final ammonium uptake was obtained within the first hour, indicating the ammonium adsorption process was very fast. This was due to the high initial concentration of ammonium and the larger adsorption capacity at the beginning. After one hour, the ammonium adsorption efficiency reduced rapidly and approached nearly zero after 3-5 h for all three zeolites. These results were consistent with the fact that the ion-exchange surface was becoming increasingly saturated with ammonium[23,24]. Both activated clinoptilolite and Na-modified zeolite, with a particle size of 0.30-0.45 mm and a dosage of 0.3 g/mL, obtained similar adsorption efficiencies of 29.96% and 31.12%, respectively. These results were higher than that of the natural clinoptilolite (18.99%) under the same conditions. The results indicated that the ammonium adsorption ability of the natural clinoptilolite was much weaker than the other two zeolites.

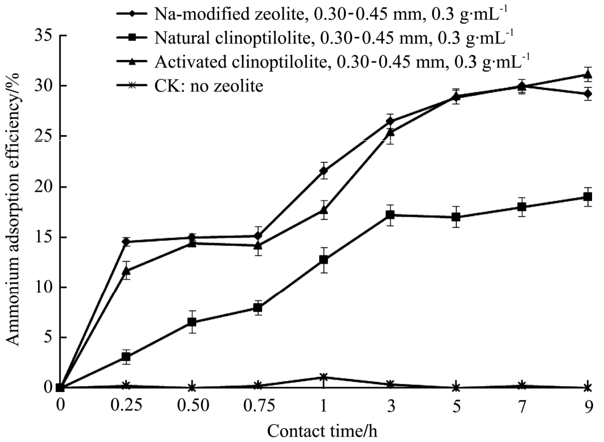

Figure 1 Effect of three types of zeolite on ammonium adsorption efficiency at different contact time

3.2 Effects of zeolite variables on the application of zeolite in nutrient-rich PHWW

3.2.1 The nitrogen adsorption efficiency

Figure 2 shows the results of the orthogonal experiments on ammonium adsorption. The adsorption efficiency generally followed a first-order pattern with some fluctuations, possibly due to the high initial ammonium concentration (6549±749) mg/L. Other impurities in the PHWW (Table 4) likely had some effect on the adsorption capability of the zeolites.

The adsorption efficiency of the Na-modified zeolite was found to be the highest in the initial one hour, followed by the activated and natural clinoptilolite, owing to the higher concentration of Na^+ in its spatial structure and the larger specific surface as a result of its smaller density (Table 2). The equilibrium time of the Na-modified zeolite occurred within 3 h, while the activated and natural clinoptilolite took 5-7 h. This was due to the different spatial structures of the different zeolites[20].

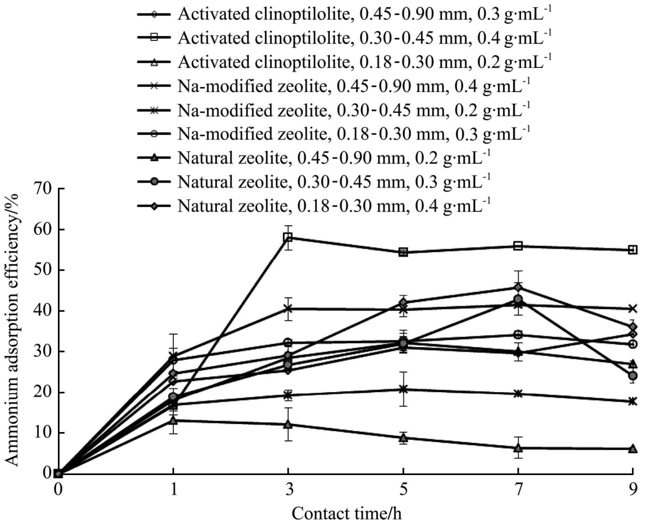

Figure 2 Effect of particle sizes, dosages and zeolite types on ammonium adsorption efficiency

The total ammonium adsorption efficiency in the equilibrium time of the activated clinoptilolite was the highest, followed by the Na-modified zeolite and natural clinoptilolite. This is the result of several factors including the smaller density, the larger specific surface area, and the lower Si/Al mass ratio of the activated clinoptilolite (Table 2), all leading to a stronger ion exchange capacity with ammonium among the three zeolites.

According to the results of variance analysis, the type, particle size and dosage of zeolite were proven to have a significant effect on the ammonium adsorption efficiency within the three hours (p<0.05). As the reaction progressed, effect of zeolite type and dosage were obviously more significant (p<0.01), while that of particle size was less (p>0.05). Particle size became a non-significant factor after reaching the equilibrium of each zeolite. The results of variance analysis at the equilibrium times (Table 3) indicated that the dosage of zeolite was the dominant factor and the type of zeolite ranked second. The activated clinoptilolite, with a particle size of 0.18-0.30 mm and a dosage of 0.4 g/mL, reached the highest ammonium adsorption efficiency in the orthogonal experiment. Table 3 also shows that the adsorption capacity of the particle size 0.18-0.30 mm was higher than that of the particle size 0.30-0.90 mm due to the larger specific surface area[25], and the ammonium adsorption efficiency significantly increased with increasing zeolite dosage because of more vacant adsorbent sites[11].

Figure 3 shows the total reduction of TN and inorganic nitrogen (NH_4^+-N, NO_3^- and NO_2^-) of the supernatant at their respective equilibrium times. There was hardly any NO_3^- and NO_2^- in solution, and the reduction of TN mainly appeared in the reduction of ammonium, indicating that the capacity of ammonium adsorption on zeolite was stronger than NO_3^- and NO_2^-. This maybe happened due to the higher capacity of ion-exchange than adsorption capacity of inorganic nitrogen. The reduction of TN was always much more than the total reduction of NH_4^+-N, NO_3^-, and NO_2^-, showing that zeolite had the ability to adsorb not only inorganic nitrogen, but also organic nitrogen.

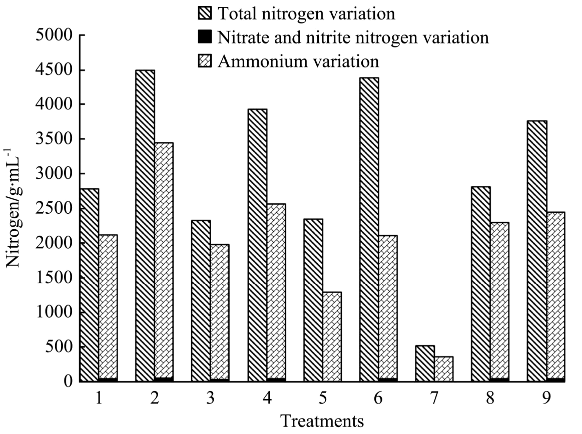

Figure 3 Total reduction of TN and inorganic nitrogen at equilibrium time

The major organic compounds of the original PHWW and the supernatant of the optimal set of orthogonal experiments are shown in Table 4. The organic components of the original PHWW are complex, including compounds such as pyrazine, pyridine, pyrrole, oxazole, styrene, phenylethanol and their derivatives, as well as some other nitrogen compounds that have been identified in previous studies[7,26]. Among these compounds, many are inhibitors of microalgae cultivation[3,27]. Whether these substances will negatively affect nutrient adsorption by zeolite should be further investigated.

By the analysis of the results, the zeolite treated PHWW had a smaller amount of nitrogen heterocyclic rings, such as aziridine. Pyrazine concentration was also decreased, while piperazinedione increased. N-containing organic compounds reduced during the nutrient adsorption process of zeolite, indicating that zeolite had a capacity of adsorbing organic nitrogen. However, the absorption capacity and the identification of the organic compounds absorbed needs to be further investigated.

Table 4 Major organic compounds of the original PHWW and the supernatant of the optimal set of orthogonal experiment

The original PHWW				The supernatant of the optimal set of orthogonal experiment			
RT*/min	Area/%	Compound name	Chemical formula	RT*/min	Area/%	Compound name	Chemical formula
3.075	4.66	3-Penten-2-one	C_5H_8O	10.135	1.33	Butanamide	$C_5H_{11}NO$
3.305	1.78	4-Penten-2-one	$C_6H_{10}O$	12.255	1.29	Hexanamide	$C_6H_{13}NO$
3.65	2.94	2-Methylpiperidine	$C_6H_{13}N$	12.435	2.25	Pentanamide	$C_6H_{13}NO$
4.535	2.98	3-Penten-2-one	$C_6H_{10}O$	13.63	3.3	2-Piperidinone	C_5H_9NO
4.875	3.27	Aziridine	$C_8H_{17}N$	18.17	10.02	Dimethyl phthalate	$C_{10}H_{10}O_4$
5.445	2.23	Pyrazine	$C_5H_6N_2$	21.18	9.06	Diethyl Phthalate	$C_{12}H_{14}O_4$
5.995	2.02	2-Pentanone	$C_6H_{12}O_2$	23.835	1.53	Diazabicyclo	$C_{10}H_{14}N_2O_3$
8.045	3.3	Aziridine	$C_8H_{17}N$	26.105	1.76	Actinomycin	$C_{63}H_{88}N_{12}O_{16}$
8.1	3.54	Pyrazine	$C_6H_8N_2$	26.76	9.35	Pyrazine derivatives	$C_1 1H_{18}N_2O_2$
8.265	5.49	Decane	$C_{13}H_{28}$	28.505	4.46	Pyrazine derivatives	$C_{11}H_{18}N_2O_2$
10.18	3.52	Butanamide	$C_5H_{11}NO$	28.69	4.49	Pyrazine	$C_{14}H_{22}N_2O_2$
10.26	2.04	Pyrazine	$C_7H_{10}N_2$	28.795	14.59	Pyrazine derivatives	$C_{11}H_{18}N_2O_2$
10.445	1.98	1-Butylpyrrolidine	$C_8H_{17}N$	28.87	5.62	L-Proline	$C_{27}H_{51}NO_3$
12.325	2.01	2-Cyclohexen-1-one	$C_8H_{12}O$	32.21	3.01	Phenylacetic acid	$C_{12}H_{14}O_2$
12.45	2.78	Hexanamide	$C_6H_{13}NO$	32.815	3.35	2,5-Piperazinedione	$C_{12}H_{14}N_2O_2$
13.68	5.17	2-Piperazinedione	C_5H_9NO	34.255	1.95	2,5-Piperazinedione	$C_{12}H_{14}N_2O_2$
15.335	1.95	2-Piperidine	$C_{17}H_{27}NO_2$	34.86	1.88	2,5-Piperazinedione	$C_{14}H_{18}N_2O_2$
21.18	5.84	Diethyl Phthalate	$C_{12}H_{14}O_4$	35.97	2.72	Piperazinedione	$C_{15}H_{20}N_2O_2$
26.79	9.67	Pyrazine derivatives	$C_{11}H_{18}N_2O_2$	36.125	4.74	Dihydroergotamine	$C_{33}H_{37}N_5O_5$
28.515	3.32	Actinomycin C2	$C_{63}H_{88}N_12O_{16}$	36.365	2.08	2,5-Piperazinedione	$C_{13}H_{16}N_2O_2$
28.695	4.87	Pyrazine derivatives	$C_{14}H_{22}N_2O_2$	37.425	1.73	Heptadecyl Trifluoroacetate	$C_{19}H_{35}F_3O_2$
28.805	13.66	Pyrazine derivatives	$C_{11}H_{18}N_2O_2$	40.62	1.61	2-Undecene	$C_{12}H_{24}$
28.885	4.98	L-Proline	$C_{27}H_{51}NO_3$	40.7	4.24	Octacosanol	$C_{28}H_{58}O$
36.14	4.09	Dihydroergotamine	$C_{33}H_{37}N_5O_5$	40.835	2.43	n-Tetracosanol-1	$C_{24}H_{50}O$
40.695	1.91	Octacosanol	$C_{28}H_{58}O$	43.96	1.21	1-Heptacosanol	$C_{27}H_{56}O$

Note: * Retention time.

3.2.2 The phosphorous adsorption efficiency

Figure 4 shows the changes of TP concentration in PHWW during the adsorption process. The results indicated that zeolite has an effective adsorption performance on TP, especially when there's hydrated magnesium existed in zeolite surface[28]. The TP in water mainly exists in the form of phosphate radical. Hydrated magnesium has good adsorption capacity on phosphate radical and enriches the phosphate radical in zeolite surface. The TP adsorption efficiency on zeolite is remarkably related to the operating conditions, such as the initial concentration of TP, initial pH value, temperature, and zeolite particle size, dosage and the amount of hydrated magnesium[30,31]. The highest ammonium adsorption using activated clinoptilolite was proved to be less effective in TP adsorption process with no equilibrium time. Moreover, it was obvious that a desorption phenomenon appeared in this process, which may be due to the spatial structure feature of the three zeolites. It is assumed that the activated clinoptilolite had a stronger capacity of ion exchange with ammonium filling its pores, which weakened the adsorption of TP. The natural zeolite with a particle size of 0.18-0.30 mm and a dosage of 0.4 g/mL showed the highest adsorption efficiency of 97.85% and reached an equilibrium time within 5 hours, while its ammonium adsorption capacity was the least. It is necessary to determine a balance between ammonium and phosphorus adsorption when using zeolite.

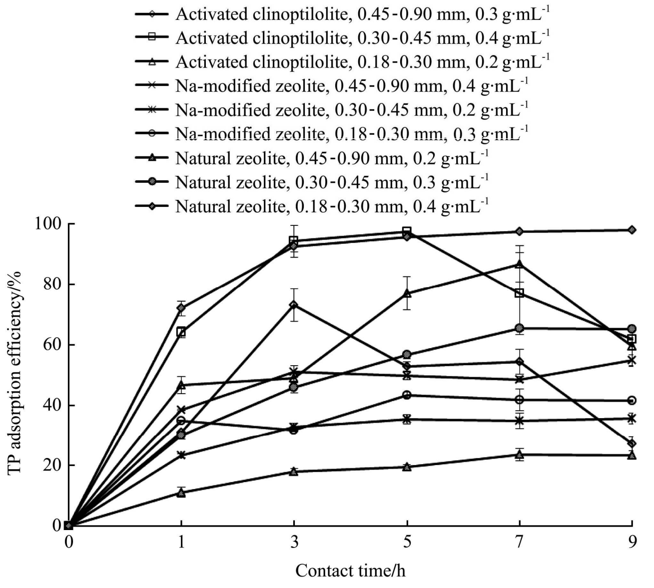

Figure 4 The adsorption efficiency of TP

3.2.3 The changes of pH and ion concentration

The PHWW (pH = 8.24 ± 0.55) was alkaline and the solid-liquid mixtures all maintained alkaline during the process (Figure 5). The pH values of the Na-modified zeolite were higher than that of the natural and activated clinoptiolite. This is caused by the different capacity of ammonium adsorption and the characteristics of the exchanging ions. Compared with the initial pH, the final pH value of the Na-modified zeolite and the natural clinoptiolite increased, while the activated clinoptiolite decreased. This is because as the pH increased, more NH_4^+ in the solution converted to ammonia in solution, which weakened the ammonium adsorption abilities of the zeolites[32]. As a result, the activated clinoptiolite obtained the best adsorption effect.

Du et al.[9] determined that the zeolite could be considered as a cost effective material for ammonium removal from wastewater, especially at pH 6, because the NH_4^+ had to compete with H^+ at a low pH value. When the pH value is higher, the NH_4^+ was transformed to aqueous ammonia. Therefore, for further study, adjusting the initial pH of PHWW was considered to be an effective method to enhance the ammonium adsorption efficiency.

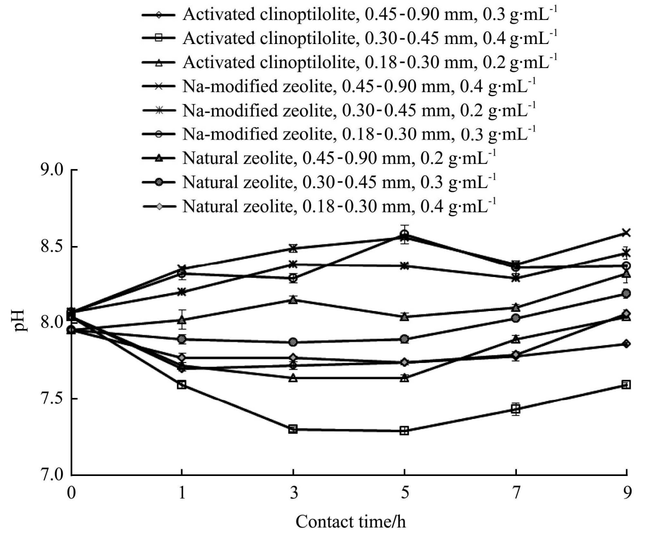

Figure 5 The pH changes of the solid-liquid mixtures with the contact time

Table 5 shows the changes of some positive ions. Lin et al.[19] researched the relationship between the variation of equivalent concentrations of K^+, Na^+, Ca^{2+}, and Mg^{2+} released into solution and the ammonium adsorption capacity of zeolites using ammonium chloride solution (100-4 000) mg/L. They found that the ion exchange capacity was almost equal to the sum of the exchanged cations. While in this study, there was no balance between NH_4^+-N and other ions in the solutions. The amount of NH_4^+-N and K^+ in the PHWW decreased after adsorption by zeolite, while that of Na^+, Ca^{2+} and Mg^{2+} increased. This is because the alkali metal and alkaline earth metal ions in zeolite exchanged with K^+ and NH_4^+ in solution during the process. It can be seen that the ion that increased in the solution was mainly Na^+, and there was only a little Ca^{2+} and Mg^{2+}, which indicated that Na^+ was the main ion in zeolite exchanged with NH_4^+ and K^+ in solution. There was a certain amount of K^+ in the wastewater, and a few were absorbed by zeolite, which was supposed to weaken the process of ammonium adsorption of zeolite. Meanwhile, the increasing concentration of Na^+ and the decreasing concentration of K^+ indicated that the adsorption ability of K^+ is prior to Na^+ for the three zeolites. Overall, Na-modified zeolite had a higher capacity of ion-exchange with K^+ than the activated and natural clinoptilolite. This is another reason that the ammonium adsorption capacity of Na-modified zeolite is less than that of the activated clinoptilolite. Even more, Na^+ in Na-modified zeolite may automatically dissolve in the ammonium adsorption process leading large Na^+ concentration.

Table 5 The change of typical positive ions at the equilibrium time (mol/L)

Test no.	K^+		Na^+		Ca^{2+}		Mg^{2+}	
	Original	After adsorption	Original	After adsorption	Original	After adsorption	Original	After adsorption
1	68.4±2.7	41.6±2.1	34.5±1.8	54.5±1.8	0	0.1±0.5	0	0.2±0.1
2		28.6±2.5		52.9±2.6		2.1±0.3		3.6±0.4
3		58.9±1.8		49.4±1.8		0		0
4		28.6±1.3		48.2±0.2		0.3±0.1		0.4±0.1
5		17.8±1.6		65.4±2.3		1.1±0.3		1.7±0.1
6		41.4±0.4		78.2±2.6		0		0
7		52.5±0.3		169.7±0.5		0		0
8		58.9±2.3		130.9±3.0		0		0
9		42.4±0.2		187.2±0.3		0		0

3.3 Effect of smaller particle size and higher dosage on ammonium adsorption

The basic trend was that the smaller the particle size of the zeolite, the higher the ammonium efficiency, because of the larger specific surface area of the smaller particle size. Figure 6 displays the ammonium adsorption efficiency from PHWW of the activated clinoptilolite of less than 0.18 mm (0.15-0.18 mm) in diameter with a dosage of 0.4 g/mL. It was only a little higher (about 2%) than that of particle size 0.18-0.30 mm. The results showed that when reaching a certain dosage, the ammonium adsorption efficiency of zeolite with a smaller particle could be no higher than that of a larger particle size. In other words, the importance of dosage on ammonium adsorption is much greater than that of the particle size, which is consistent with the results of the orthogonal experiment. In addition, considering the energy consumed and the materials loss during crushing process, particle size of 0.18-0.30 mm is more efficient.

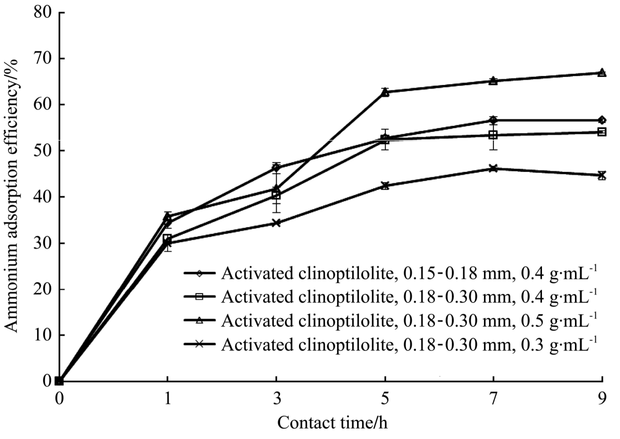

Figure 6 Effects of particle size and dosage of activated clinoptilolite on ammonium adsorption efficiency

Figure 6 also shows that the adsorption efficiency for ammonium of the activated clinoptilolite was positively correlated to the dosage. Higher dosage of zeolite provided a sufficient swap space and a larger contact area, resulting in a greater ammonium adsorption capacity. The ammonium adsorption efficiency of the activated clinoptilolite of 0.18-0.30 mm with a dosage of 0.4 g/mL was 54.92%, higher than that of the 0.3 g/mL. When the dosage was 0.5 g/mL, the adsorption efficiency rapidly increased to 66.87%. This simultaneously explained why the effect of zeolite dosage was more significant than that of particle size on ammonium adsorption.

4 Conclusions

Zeolite can adsorb nutrients (primarily nitrogen) in nutrient-rich PHWW at a relatively fast speed. The equilibrium time of the ammonium adsorption process occurred within 3 h for the Na-modified zeolite and 5-7 h for the activated and natural clinoptilolite. The ammonium adsorption process was confirmed to be affected by zeolite dosage, type and particle size. The dosage of zeolite was the dominant influence factor, and the type of zeolite was ranked second. Activated clinoptilolite, with a particle size of 0.18-0.30 mm and a dosage of 0.4 g/mL had a highest ammonium adsorption efficiency of 54.92%. The ammonium adsorption was negatively affected by the ion K^+ in the solution. Zeolite also can adsorb organic nitrogen and phosphorous. Natural clinoptilolite with a particle size of 0.18-0.30 mm and a dosage of 0.4 g/mL obtained the highest TP adsorption efficiency of 97.85%. The relationship between the nitrogen and phosphorous adsorption need to be further investigated.

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