

# Preparation and application of modified zeolites as adsorbents in wastewater treatment

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## ABSTRACT

Natural zeolite has been recognized as a useful adsorbent for wastewater treatment for removing cations. Natural zeolite is a kind of porous material with large specific surface area but limited adsorption capacity. In recent years, emphasis has been given to prepare the surface modified zeolite using various procedures to enhance the potential of zeolite for pollutants. Modification treatment for zeolite can greatly change surface chemistry and pore structure. The article describes various modification methods of zeolite, and introduces the removal mechanisms of common pollutants such as ammonium, phosphorus and heavy metals. In addition, this review paper intends to present feasibility of applying modified zeolite to constructed wetlands which will be beneficial to achieve higher removal effect.

**Key words** | application, constructed wetland, modified zeolite, pollutants

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## INTRODUCTION

Water pollution is becoming more and more serious nowadays. Water pollution can threaten public health, industry and agriculture production, in addition to the economy (Pandi & Paudel 2006; Govender *et al.* 2011; Smith & Siciliano 2015). Conventional methods of removing pollutants from water include biological treatment, filtration, chemical coagulation, sedimentation, electrocoagulation, crystallization and adsorption (Tadkaew *et al.* 2011; Walker *et al.* 2011; Gollavelli *et al.* 2013; Pirsahab *et al.* 2015). Among these methods, adsorption is considered to be one of the most prospective approaches (Meng *et al.* 2013).

In recent years, zeolite has received much attention in the scientific field due to its accessible source, special property and low cost. So far, more than 60 types of naturally occurring zeolites have been discovered (Ghasemi *et al.*

2016). Natural zeolites are widely used in various fields; for wastewater treatment, natural zeolite can not only reduce turbidity and chromaticity but also degrade ammonium, heavy metal cations and other cationic pollutants (Syafalni *et al.* 2014). However, it is well known that natural zeolite has been found to be very efficient for removing cations than phosphorus and heavy metal oxyanions. Efforts are ongoing to substantially improve the potential of zeolite surface by using various modified methods. Modified zeolites for wastewater treatment is attracting new research interests mainly due to not only the significant occurrence and properties (Dionisiou *et al.* 2013a, 2013b), but also the optimized performance and low cost (Hammond *et al.* 2010).

Modified zeolite has been broadly reported for removing pollutants in water recently, however, no such review has been published. This review concludes the preparation

methods and mechanism of modified zeolite, provides an overall assessment on the choice of modification methods in different water quality conditions, summarizes the application of modified zeolite for wastewater treatment, and also introduces the application status in constructed wetland briefly. Overall, this article will lead to a deep understanding of modification of zeolite and comprehensive prospect on the application in the future.

## PREPARATION AND ADSORPTION MECHANISM OF MODIFIED ZEOLITE

Natural zeolites are porous hydrated minerals with anionic framework, the crystalline structure comprises of silicon (aluminum) and oxygen tetrahedron, and the pore is formed by a combination of different tetrahedra (Malamis & Katsou 2013). Zeolites have the ability to exchange cations in structures, losing or accepting water molecules (Srdan *et al.* 2014). The removal mechanisms of natural zeolite for pollutants are following below: (a) ordered and communicated holes or channels in the crystal interior (Hoang *et al.* 2012); (b) excess negative charges of zeolite framework could be balanced by monovalent or two valence cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) (Ghasemi *et al.* 2016).

The results have demonstrated that natural zeolite shows good performance for ammonium removal with 3.0 mg/g adsorption capacity at 150 min, as is shown in Figure 1 (Widiastuti *et al.* 2011). Besides, natural zeolite is a potential adsorbent for heavy metals cations removal. For copper, the equilibrium time was reached at 180 min, with 96.0% removal; for chromium, the equilibrium time was reached at 300 min, with 85.1% removal; and for iron, the removal rate can reach up to 95.4%, after 360 min (Zanin *et al.* 2017).

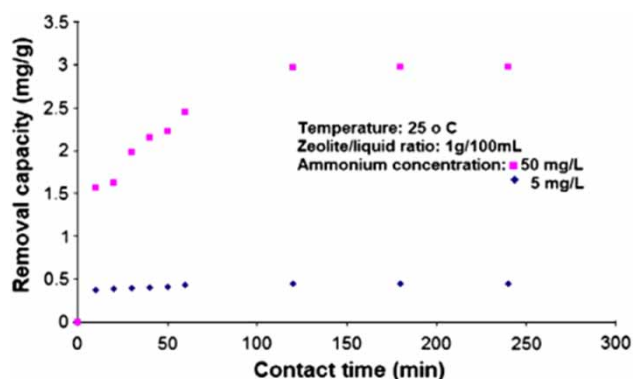


Figure 1 | Effect of contact time on ammonium removal capacity (Widiastuti *et al.* 2011).

Modified zeolite can improve the adsorption ability under certain conditions, since the pore of natural zeolite may trigger blocking problem due to impurities (Kragovi *et al.* 2012). In general, modification methods can be divided into physical modification, chemical modification and composite modification.

### Physical modification

Physical modification includes thermal modification and ultrasonic modification. Thermal modification is generally produced by muffle furnace heating or microwave heating, high temperature can reduce the surface resistance of zeolite and improve its exchange adsorption capacity. Ultrasonic modification utilizes ultrasound to eliminate impurities in the zeolite pores, thereby increasing the adsorption efficiency (Zielinski *et al.* 2015). The mechanism and advantages/disadvantages of different physical modification are in Table 1.

Typically, muffle furnace modification is to heat natural zeolite for 2–5 h in muffle furnace with temperature 200–600 °C. Heating temperature is an important factor affecting removal efficiency of modified zeolite, excessive temperature will destroy the original structure of zeolite (Sannino *et al.* 2012).

In microwave heating mechanism, natural zeolite is placed into the microwave oven and then heated at various microwave power. Increasing power of microwave and heating time are beneficial to increase the adsorption capacity of modified zeolite, because excessive power and prolonged heating may destruct lattice structure of zeolite. Fahmy *et al.* 2016 used zeolite treated with microwave to remove divalent cadmium ion from wastewater, the results revealed that the optimum conditions of the adsorption process are zeolite dose = 0.25 g in 25 mL of Cd with contact time 140 min.

Ultrasonic modified zeolite is prepared by sound waves of different frequencies and powers. Research showed that 40 min heating of zeolite at 560 W could get the highest removal rate of ammonium of about 86.9%, and there was adsorption equilibrium after 120 min (Wang *et al.* 2014).

### Chemical modification

Chemical modification includes acid-base modification, salt modification, cationic surfactant modification and rare earth modification. The mechanism and advantages/disadvantages of different chemical modification are in Table 2.

**Table 1** | Characteristics of physical modification

Methods	Mechanism	Pollutants	Advantages	Disadvantages	Reference
Muffle furnace-heating	Water evaporation and smoothing the channel and hole	Ammonia	Simple and convenient	Power-wasting; inefficient	Ali et al. (2014)
Microwave oven-heating	Elimination of impurities from channel; increase hole diameter; uniform pore size	Ammonia	Heating time saving; good penetration; high efficiency	Uneven heating because of moisture in the zeolite	Gracia et al. (2013), Bagheri et al. (2015)
Ultrasonic	Elimination of impurities from channel; increase surface area	Ammonia	Good penetration; removal of impurities from channel	Inefficient; always combined with other methods	Zielinski et al. (2015)

**Table 2** | Characteristics of chemical modification

Methods	Mechanism	Pollutants	Advantages	Disadvantages	Reference
Acid	H <sup>+</sup> replaces Ca <sup>2+</sup> and Mg <sup>2+</sup> in zeolite which have large diameter to increase specific surface area and microporosity	Ammonia, antimony (III), uranium (VI)	Simple and convenient, improving cations adsorption capacity	Low cation exchange capacity due to H <sup>+</sup> competition and dissolution of Si-tetrahedra and free linkages	Zhang et al. (2014b), Matijasevic et al. (2016), Christidis et al. (2003)
Alkali	a. Dissolve silicon reduce Si/Al from zeolite; make uniform pore size b. Electrostatic interaction and form covalent bonds	Organics Ammonia, manganese (II), lead (II), copper (II), cadmium (II)	Simple and convenient, improving the removal rate of cations	Destruction of crystal structure by poor concentration control, reduction in absorption rate	Sancho et al. (2017), Guaya et al. (2015), Ali et al. (2014), Ates & Akgül (2016), Wen et al. (2016)
Salt	a. Exchanging with Ca <sup>2+</sup> and Mg <sup>2+</sup> in the zeolite, increasing the pore size b. Ligand-exchange and electrostatic interaction	Ammonia, iron (II), calcium (II), magnesium (II), manganese (II), copper (II), zinc (II), nickel (II), uranium (VI) Phosphorus, fluoride, chromium (VI), arsenic (III), arsenic (V), lead (II)	High pollutants removal efficiency	Expensive salt solutions	Huang et al. (2014), Jevti et al. (2014), Jiang et al. (2013), Ali et al. (2016), Ates (2014), Akigbe et al. (2016), Bakatula et al. (2011), Lofu et al. (2016), Awuah et al. (2016)
Cationic surfactant	a. Anions adsorption and associated compounds formation b. Cations exchange c. Organics adsorption by hydrophobic alkyl chain	Tungstate, antimonate phosphorus Ammonia, copper (II), nickel, iron Aniline, EDTA	Increase anion removal rate	More expensive than salt modification. Complicated modification process	Syafalni & Nair (2013), Pawaiya & Tomar (2014), Wingenfelder et al. (2016), Hussein et al. (2014), Khazaei et al. (2015)
Rare earth	a. Cations exchange b. Oxides and hydroxides formation on the surface of zeolite, electrostatic interaction, ligand-exchange reaction	Ammonia Phosphorus	Utilization of mineral resources and pollutants removal simultaneously	Expensive and secondary pollution	Zhang et al. (2012), Yang et al. (2014)

## Acid modified zeolite

Acid modified zeolite is made through acid impregnation. The most commonly used acids are hydrochloric acid, sulphuric acid, nitric acid, oxalic acid, citric acid and acetic acid (An *et al.* 2013; Dong *et al.* 2015). Acids can dissolve impurities in pores to dredge the channels,  $H^+$  can partly displace  $K^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  from layers to increase porosity, so as to improve the adsorption capacity.

Increasing the concentration of acid during modification is beneficial to improve the removal rate of pollutants, but excessive acid may result in destruction of zeolite surface and internal pore structure. Zhang *et al.* (2014b) reported a study of acid treatment of natural zeolite using  $HNO_3$  solution at varying concentrations (0.2–1 M) to remove  $Sb^{3+}$ , when the  $HNO_3$  concentration increased from 0.2 M to 0.8 M, the removal rate of  $Sb^{3+}$  increased from 63.1% to 82.7%, and when the concentration of  $HNO_3$  was up to 1 mol/L, the removal rate reduced to 62.8%.

## Alkali modified zeolite

The alkali modification is to soak zeolite in NaOH solution. Alkali has potential to dissolve zeolite silicon, decreasing the ratio of silicon to aluminium (Si/Al), and forming mesoporous with relatively fine pore size.

Increasing concentration of alkali has great impact on pollutants removal. However, excessive amount of alkali can damage the zeolite surface and microporous structure (Shahmirzadi *et al.* 2016). Soetardji *et al.* (2015) tested the removal rate of  $NH_4-N$  using zeolites modified by 1–6 M NaOH, the result revealed that with the increase of NaOH concentration, the adsorption rate of ammonium increased from 50.0% to 80.0%. The maximum ammonium adsorption capacity of ammonia to zeolite modified with 6 M NaOH is 53.9 mg/g, and the system reach equilibrium state after 8 h, compared with 12 h of natural zeolite for ammonium adsorption.

## Salt modified zeolite

The salt modified zeolite is a mixture of natural zeolite and salt solution. The most commonly used solutions are sodium chloride, magnesium chloride, aluminium chloride and ammonium chloride (Guaya *et al.* 2016; Sugawara *et al.* 2016). Salt solution can remove water/inorganic impurities from the zeolite channel, and exchange zeolite cations with cations in the salt solution (Cheng *et al.* 2012). Cheng & Ding (2014) reported that the ammonia exchange capacity of zeolite modified by NaCl is 1.4–1.5 times of that of natural zeolite.

Removing ammonium and heavy metals ordinarily use  $Na^+$  and  $NH_4^+$  which each have a small radius, instead, removing inorganic oxyanions can select larger radius cations such as  $Ca^{2+}$  and  $Al^{3+}$ . Waghmare *et al.* (2015) carried out a study for fluoride sorption, found that zeolite modified by salt solution of aluminum chloride and calcium chloride 2:1 showed the maximum adsorption capacity of 18.6 mg/g; the optimization contact time for adsorbents is about 200 min. Currently, the studies on removal of pollutants by salt modified zeolite are extensive, and the partial adsorption capacity of zeolites are in Table 3.

## Cationic surfactant modified zeolite

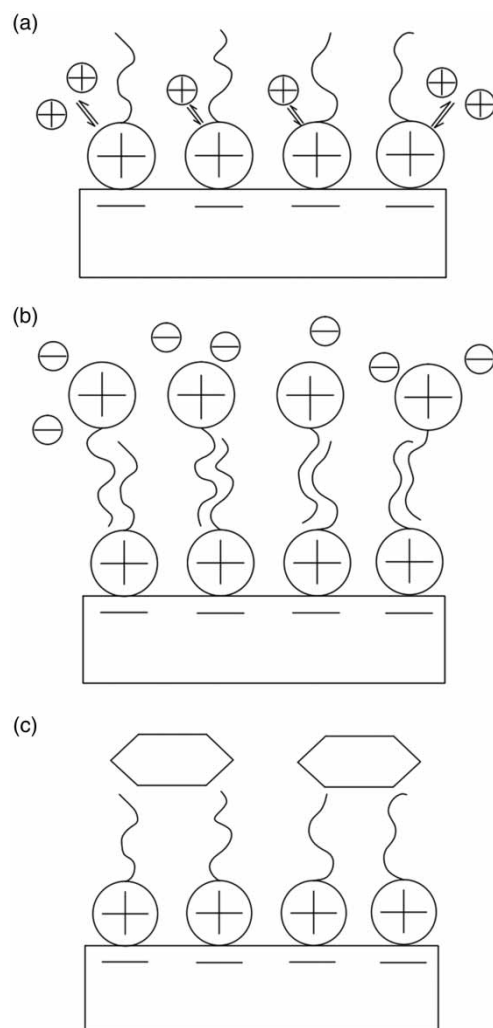
The surfactant modified zeolite (SMZ) is obtained by mixing natural zeolite into a cationic surfactant solution. The cationic SMZ can solve the problem low removal rate for anions (Jiménez-Castañeda *et al.* 2017). When the surfactant concentration is equal to or less than its critical micelle concentration (CMC), the negative charge of the zeolite surface can adsorb surfactants cations by electrostatic force, so that the contaminated cations in wastewater can exchange with the exchangeable cations of the zeolite. If the surfactant concentration in the solution exceeds the CMC, the alkyl chains of surfactant are attracted to each other by hydrophobic interaction, so that the bilayer molecules with the positively charged head group are produced on the zeolite surface to adsorb anionic contaminants. In addition, the modified

**Table 3** | Adsorption capacity of salt modified zeolite for different pollutants

Salt	Pollutants	Adsorbent capacity (mg/g)	Temperature (°C)	pH	Adsorption isotherm	References
NaCl	manganese	10.0	25	–	Langmuir	Ates (2014)
$NH_4Cl$	manganese	24.3	25	–	Freundlich	Ates (2014)
$Al_2(SO_4)_3$	manganese	25.1	25	–	Freundlich	Ates (2014)
$NH_4Cl$	uranium	2.1	25	3.0	Langmuir	Bakatula <i>et al.</i> (2011)
NaCl	$NH_4-N$	11.3	–	8.0	Langmuir	Cheng <i>et al.</i> (2017)

zeolite can also remove organic matter in wastewater because of the hydrophobic alkyl chain. The specific mechanism is shown in Figure 2. The most commonly used cationic surfactants are: N, N-dimethyl dehydroabietylamine oxide (DAAO), hexadecyltrimethylammonium (HDTMA), cetyl trimethylammonium bromide (CTMAB), cetylpyridinium bromide (CPB), sodium dodecyl sulfate (SDS).

Pollutants removal rate is related to loading rate (depend on concentration of surfactant solution) of the surfactant. Awad *et al.* (Elsheikh *et al.* 2017) presented a study of using HDTMA modified zeolite to remove humic acid (HA), HDTMA loading levels range from 0–200.0% external cation exchange capacity (ECEC) of zeolite, the results indicated that SMZ with HDTMA loading of 75.0% of ECEC



**Figure 2** | Mechanism of cations (a), anions (b) and organics (c) removal by cationic surfactants on zeolite surface.

had the highest removal efficiency of HA. Szala *et al.* (2015) used zeolite modified with HDTMA which loading rate is 100.0% and 120% to adsorb Cr(VI), respectively. The adsorption capacity of Cr(VI) to zeolite (108.0 mmol/kg) was observed with 120.0% ECEC, while after modification at 100.0% ECEC the maximum sorption was smaller (96.0 mmol/kg). Pollutants removal by cationic SMZ were widely researched, and the partial adsorption capacities are shown in Table 4.

### Rare earth modified zeolite

Rare earth modification is mixing natural zeolite into solution of rare earth with stirring, drying and crushing. The most commonly used rare earth materials include zirconium, lanthanum, cerium hydroxide and oxides. Rare earth modified zeolite has a good adsorption effect on ammonium and phosphate, the adsorption mechanism of ammonium is mainly comprised of the cation exchange with zeolite, and the adsorption mechanism of phosphate in wastewater is the exchange of ligands and electrostatic attraction (Lin *et al.* 2012).

### Composite modification

In addition to the single modification, there are also composite modifications, which combine several modifying methods. Composite modification can be divided into three categories: ultrasonic composite modification, heating composite modification, alkali/acid/salt composite modification. Pollutants removal by various modifications are shown in Table 5.

Ultrasound and salt solution composite modified zeolite cannot only replace the cation of the larger radius, but also dissolve impurities from the surface and pores, so as to shorten the reaction time and increase the adsorption capacity of zeolite. Wang *et al.* (2015) found that the modified zeolite has the best adsorption effect on ammonium, NaCl concentration is 0.8 mol/L with 560 W of ultrasonic power and the modification time is 40 min, that can give the highest removal rate up to 91.1%, and the equilibrium time is just 10 min, compared with 60 min of natural zeolite.

There are two ways of heating composite modification. First is to heat the zeolite at high temperature to increase the porosity then, to modify the zeolite by other methods; the second is in the reverse order. Zeolites obtained by the second modified methods usually achieve better adsorption effect. Yang *et al.* (2017) pretreated zeolites with 1.0 mol/L NaOH solution, and then treated them by 2 mol/L NaCl



**Table 4** | Adsorption capacity of cationic surfactant modified zeolite for different pollutants

Surfactant	Pollutants	Adsorbent capacity (mg/g)	Temperature (°C)	pH	Adsorption isotherm	References
DAAO	Anionic dye congo red	69.9–58.8	20–40	6.0	Langmuir	Liu <i>et al.</i> (2014)
HDTMA	As	1.6	23	7.0	Freundlich	Chutia <i>et al.</i> (2009)
	EDTA	159.8	25	7.5	Freundlich	Khazaei <i>et al.</i> (2015)
	Cr	5.2	25	6.0	Langmuir	Ramos <i>et al.</i> (2008)
	Phosphorus	0.2	25 ± 1	6.9	Langmuir	Dionisiou <i>et al.</i> (2013a)
CTMAB	Sodium dodecyl benzene sulfonate	18.5	25	6.0	Langmuir	Taffarel & Rubio (2010)
	Pb	3.3	35	–	Langmuir	Ren <i>et al.</i> (2016)
CPB	Tannic acid	111.0	30	5.5	Langmuir	Lin <i>et al.</i> (2011)
SDS	NOM	111.2	25	5.0	Langmuir	Mahvi <i>et al.</i> (2016)

solution for 2 h, and then heated at 400 °C for 0.5 h, the removal rate of ammonium increased from 54.4% to 98.3%, and according to adsorption kinetics curves, the reaction reached the equilibrium in 140 min.

Alkali/acid/salt composite modification has been studied in recent years. The zeolite is usually modified by salt or surfactant after the acid/alkali/salt pretreatment, composite modification can shorten the adsorption time. Dionisiou *et al.* (2013b) treated the natural zeolite with 1 M HCl at 60 °C for 24 h, and then added 0.05 M HDTMA-Br, then mixing at 25 °C for 24 h, the adsorption rate of boron on 10 mg/L reached up to 85.0% at pH 3.

## POLLUTANTS REMOVAL FROM WASTEWATER

Modified zeolite with different methods has diverse removal effects on pollutants. Physical modification is

considered to be simple and convenient, but it has more energy consumption and less efficiency. Chemical modification for pollutants removal was significantly higher than physical modified zeolite; however, complex process should be considered. Therefore, it is necessary to select the appropriate modification method according to the actual processing requirements. For wastewater consisting of different pollutant constituents, the removal rates are shown in Table 6.

## Ammonium

Ammonium is the main form of nitrogen contamination in some special conditions and significantly contributes to the typical eutrophication of surface waters (Li *et al.* 2014). Higher concentration of ammonium will cause obvious toxicity to fish and other organisms. Ion exchange

**Table 5** | Adsorption capacity of composite modified zeolite for different pollutants

Adsorbent	Method	Pollutants	Adsorbent capacity (mg/g)	Temperature (°C)	pH	Adsorption isotherm	References
Ultrasonic composite	Ultrasonic (550 W) + NaCl	Ammonia	12.8	Room temperature	–	Langmuir	Wang <i>et al.</i> (2015)
Heating composite	HCl + muffle (300 °C)	Nitrate	2.7	–	5.0	Langmuir	Ali <i>et al.</i> (2014)
	Ultrasonic (303 K) + Sodium acetate	Ammonia	6.6	30	–	Langmuir	Lin <i>et al.</i> (2015)
	Muffle (550–600 °C) + 1 M NaAlO <sub>2</sub> + 0.01NHCl + Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + CaSO <sub>4</sub>	Fluoride	2.6	25	8.0	Freundlich	Waghmare <i>et al.</i> (2015)
	Muffle (500 °C) + CTAB	Bisphenol	16.5	25	–	Freundlich	Wang <i>et al.</i> (2016)
Alkali acid/salt composite	2 M NaCl + 1 M HCl	Cr	6.3	Room temperature	–	Freundlich	Song <i>et al.</i> (2015)
	1 M HCl + 0.05 M HDTA-Br	Boron	–	24–26	–	–	Dionisiou <i>et al.</i> (2013b)
	2 M NaCl + 3 g/L HDTMA-Br	Melanoidin	918.9	35	–	Langmuir	Onyango <i>et al.</i> (2011)
	AlCl <sub>3</sub> + LaCl <sub>3</sub>	Phosphorus	2.4	20	7.0	Freundlich	Meng <i>et al.</i> (2013)

**Table 6** | Removal of pollutants from sewage by modified zeolite

Pollutants	Types of sewage (concentration)	Modifier	Removal rate	Sorption (mg/g)	Reference
NH <sub>4</sub> -N	Reclaimed water 6 mg/L	CH <sub>3</sub> COONa + microwave	93.3%	3.3	Lin et al. (2015)
	Reclaimed water 6 mg/L	NaCl	82.2%	2.5	Liu et al. (2016)
	Domestic sewage 30 mg/L	NaCl	89.7%	1.6	Xiao et al. (2015)
	Effluent from wastewater treatment plant 10 mg/L	Ultrasonic + NaCl	90.1%	3.6	Wang et al. (2015)
PO <sub>4</sub> <sup>3-</sup>	Industrial effluent 20 mg/L	Ce	67.3%	0.3	Cui et al. (2016)
	Industrial effluent 10 mg/L	AlCl <sub>3</sub> + LaCl <sub>3</sub>	96.6%	1.0	Meng et al. (2013)
	industrial effluent 12 mg/L	HDTMA-Br	83.3%	0.1	Dionisiou et al. (2013a)
	Domestic sewage 3 mg/L	ZrOCl <sub>2</sub>	50.0%	–	Yang et al. (2014)
Pb <sup>2+</sup>	Industrial effluent 100 mg/L	NaOH	100.0%	10.0	Wang et al. (2012)
Cu <sup>2+</sup>	Industrial effluent 100 mg/L	NaOH	95.0%	9.9	Wang et al. (2012)
Mn <sup>2+</sup>	Industrial effluent 100 mg/L	NaCl	>90.0%	21.2	Popov et al. (2012)
Ni <sup>2+</sup>	Industrial effluent 100–150 mg/L	NaCl/CH <sub>3</sub> COONa	86.0–90.0%	–	Panayotova (2011)
Cr (VI)	Industrial effluent 100 mg/L	HDTMA	77.50%	3.10	Ramos et al. (2008)
	5–80 mg/L	CTMAB	–	2.00	Ren et al. (2016)
	5–80 mg/L	CPB	–	1.43	Ren et al. (2016)

on zeolite seems a competitive solution for ammonium removal out of wastewater (Chmielewska 2014). Nowadays, modified zeolite was explored as an effective adsorbent because of the finite sorption capacity of natural zeolite.

Sancho et al. (2017) undertook a laboratory study of NaCl modified zeolite as a post-treatment step, an alternative to the biological removal process to remove ammonium from domestic wastewater. They investigated the equilibria and kinetic characteristics of ammonium exchange in the zeolite. The results revealed that the ammonium/sodium exchange process reached its maximum at the pH range between 4 and 6, at the form of NH<sub>4</sub><sup>+</sup>. The ion exchange order for ammonium, alkali and alkaline earth metals follows: K<sup>+</sup>>NH<sub>4</sub><sup>+</sup>>Ba<sup>2+</sup>>Na<sup>+</sup>>Ca<sup>2+</sup>, other ionic species could decrease ammonium sorption capacity due to competitive sorption. Soetardji et al. (2015) conducted an adsorption study using a real aquaculture system in order to test the effectiveness of the NaOH modified zeolite for ammonium removal. It was found that the adsorption in real system, the removal efficiency decrease from 81% to 66.9% because of the competition with other ions. The kinetic and equilibrium of ammonium ion uptake from aqueous biogas slurry using NaCl modified zeolite was reported by Cheng et al. (2017). The influences of pH, reaction time, zeolite dosages were investigated. The adsorption isotherm of NH<sub>4</sub><sup>+</sup>-N onto the adsorbent was well fitted to the Langmuir model and the maximum adsorption capacity was 11.25 mg/g.

The removal rate of ammonium are depended on zeolite modification methods. Xiao et al. (2015) found that acid, alkali, salt and thermal modified zeolite for ammonium removal was 75.8%, 87.2%, 89.7% and 81.3%, respectively. Among them, alkali modified zeolite and salt modified zeolite have the best removal effect. Liu et al. (2016) modified zeolite with five different valence state cationic salts, and compared ammonium adsorption capacity between different salt modified zeolites. The adsorption order was NaCl > AlCl<sub>3</sub> > CaCl<sub>2</sub> > MgCl<sub>2</sub> > KCl (adsorption capacity was 2.5 mg/g, 1.8 mg/g, 1.9 mg/g, 2.0 mg/g, 2.0 mg/g), which indicated that cation valence did not have positive correlation with cation-exchange capacity and ammonium removing ability.

The removal efficiency of ammonium was also different with the combination of microwave modification. Lin et al. (2013) prepared ecomaterials by adding different additives on natural zeolite with microwave, and investigated the effect on removal of ammonium. The tests showed that the adsorption followed an order of sodium acetate and microwave zeolite > NaCl-microwave zeolite > SDS and microwave zeolite > CTMAB and microwave zeolite > microwave zeolite > natural zeolite, the removal rate of ammonium of modified zeolites were increased to 92.5%, 93.3%, 90.9%, 84.9%, 76.3%, respectively, relative to 60.0% of natural zeolite. CTMAB and microwave zeolite has poor removal efficiency for ammonium, because the cationic surfactant belongs to macromolecule substance. Moreover, the zeolite collapses locally due to partial overheating while calefaction

process resulting in the specific surface area decreases conversely (Bai et al. 2012).

In conclusion, sodium chloride solution and its composite modified zeolite have the best effect on ammonium removal. Siljeg et al. (2010) transformed natural Serbian (SZ) and Croatian zeolite (CZ) to the Na-form (Na-CZ and Na-SZ) in order to increase the exchange capacity of zeolite, the amount of ammonium ions absorbed on zeolite is shown in Figure 3. Although the adsorption capacity of ammonium is different according to the type of natural zeolite, both the modified form can improve adsorption capacity to some extent.

## Phosphorus

Excess P and N is the main cause of eutrophication; in recent years, some scholars suggested that phosphorus is a significant limiting factor for water quality in river and lake waters for microorganism growth, according to the characteristics of nitrogen and phosphorus (Lee et al. 2012). Phosphorus removal in conventional small-scale wastewater treatment systems is a critical issue that has not yet been sufficiently solved (Vohla et al. 2011). In the past decades, various methods of phosphorus removal from water have been developed, adsorption is the widely used method.

Dionisiou et al. (2013a) evaluated the sorption of phosphorus on a HDTMA-Br modified zeolite. In their work, the effects of temperature, pH, and  $\text{NO}_3^-$  concentration on P adsorption on the SMZ were assessed. The P adsorption capacity of the SMZ increased with pH increase and although decreased with temperature increase, in the presence of a relative high  $\text{NO}_3^-$  concentration, remained appreciable in all cases. Guaya et al. (2016) modified zeolite

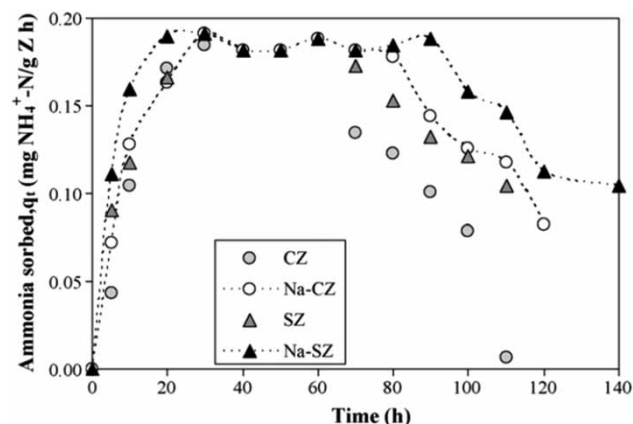


Figure 3 | The amount of ammonium ions sorbed on zeolite in time (Siljeg et al. 2010).

by incorporation of hydrated aluminum oxid (HAIO) for phosphate removal, the phosphate sorption increases from 0.6 mg-P/g for Z-N up to 7.0 mg-P/g. Desorption efficiency of phosphate from loaded zeolites using NaOH,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and mixtures of  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  were also summarized, which can reach up to 79.0% with 0.1 M  $\text{Na}_2\text{CO}_3$ .

Cationic SMZ and salt modified zeolite are common adsorbents for phosphorus removal in wastewater. Schick et al. (2012) concluded that phosphorus adsorption by organic cation SMZ was slightly higher than that of salt modified zeolite, preliminary experiments lead to the selection of the most efficient Ca modified LTA-type zeolite (Ca-LTA; Ca-FAU; Ca-HEU; HEU) and SMZ, adsorption kinetics of  $\text{H}_2\text{PO}_4^-$  is shown in Figure 4. Besides, rare earth modified zeolite also has a good removal effect on phosphorus. Cui et al. (2016) compared the adsorption capacity of lanthanum modified zeolite and Cerium modified zeolite for phosphate, the adsorption capacity of lanthanum modified zeolite was 0.3 mg/g, the adsorption capacity of cerium modified zeolite was 0.3 mg/g, both were 10 times higher than that of unmodified zeolite.

In summary, salt modified zeolite, cationic SMZ and salt-rare earth composite modified zeolite can achieve good results for phosphorus removal in wastewater. However, rare earth is scarce and expensive (Emsbo et al. 2015) which is not suitable to be used widely in engineering. It is economical and reasonable to choose low valent salt modified zeolite and cationic surfactant for zeolite modification.

## Heavy metals

Various industries produce and discharge wastes containing different heavy metals into environment, such as energy and

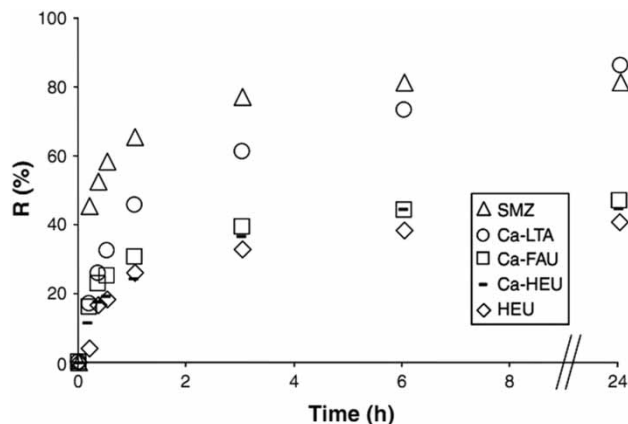


Figure 4 | Adsorption kinetics of  $\text{H}_2\text{PO}_4^-$  ions with a 0.8 mmol/L initial concentration (R% = removal rate) (Schick et al. 2012).

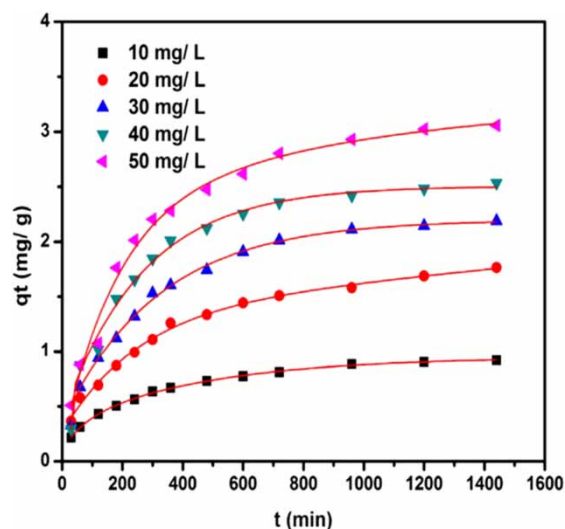


fuel production, metallurgy, iron and steel, metal surface treating, etc. (Wang & Chen 2009). Heavy metals cannot be degraded: they are deposited, assimilated, or incorporated in water, sediment, and aquatic ecosystems, which will threaten human health and ecosystems (Javanbakht *et al.* 2014), therefore, heavy metal pollution has become one of the most serious environmental problems today. Common heavy metals present in polluted waters include Cr, As, Pb, Zn, Cu, Ni, Cd, Mn, U, etc. In various water treatment techniques, methods for adsorbing with modified zeolites has been paid much attention.

Bakatula *et al.* (2011) presented a study of using ammonium modified zeolite to remove uranium from aqueous solution. The pH, carbonates and sulphates, contact time as well as coexisting ions were important factors to be considered on the uranium sorption process. The results showed that the presence of Ca, Sr and Mg ions led to the decrease of the adsorption of uranium (drop of 24.9%) due to competition for binding sites; on the contrary, the presence of  $\text{Fe}^{3+}$  in polluted acidic water enhanced the removal of uranium. Hamed *et al.* (2015) studied removal of heavy metals ( $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) in treated and raw water using  $\text{NH}_4^+$  modified zeolite, the best pH value for removal was found to be 4.5, with removal efficiency of  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  equal to 98.0%, 97.0%, and 94.9%, respectively.

Most heavy metal ions exist in wastewater in the form of cations, both alkali modification and salt modification can achieve good results for cationic heavy metal ions, and the smaller the cationic radius of the modifier, the greater the adsorption capacity. Natural zeolite had significant removal rate of  $\text{Ni}^{2+}$  in the first 30–60 min. Conducted experiments using natural zeolite modified with NaOH, NaCl, HCl and  $\text{CH}_3\text{COONa}$ , respectively, to remove  $\text{Ni}^{2+}$  from the wastewater. It was found that treatment with NaCl and  $\text{CH}_3\text{COONa}$  caused an increase in  $\text{Na}^+$  and a decrease in  $\text{Ca}^{2+}$  relative amounts in zeolite, thus, leads to an increase in  $\text{Ni}^{2+}$  uptake capacity with about 25–30% (Panayotova 2011). Popov *et al.* (2012) investigate the adsorption capacity of  $\text{Mn}^{2+}$  using NaCl, NaOH,  $\text{Na}_2\text{CO}_3$  and  $\text{NH}_4\text{Cl}$  modified zeolite at pH 6. The results revealed that NaCl and NaOH modified zeolite can achieve good adsorption effect, and adsorption capacity was up to  $0.8 \text{ meqMn}^{2+}\text{g}^{-1}$  and  $0.8 \text{ meqMn}^{2+}\text{g}^{-1}$ , respectively.

Some heavy metal ions also have the form of oxyanions in wastewater, such as arsenic, chromium and selenium. Awuah *et al.* (2016) found that adsorption of arsenic ( $\text{AsO}(\text{OH})_3$  and  $\text{As}(\text{OH})_3$ ) was favorable under anhydrous



**Figure 5** | Non-linear pseudo-second-order kinetic plot for adsorption of chromium(VI) ( $q_t$  = adsorption capacity at  $t$ ; adsorbent dosage = 1 g; temperature =  $29 \pm 2$  °C; pH = 5.6) (Hailu *et al.* 2017).

conditions for  $\text{Al}^{3+}$  modified zeolite, when the Si/Al ratio was 1.7. Natural zeolites or zeolites modified with acid, alkali or salt have little or no affinity to Cr(VI), whereas modification by cationic surfactants, such as HDTMA, would significantly enhance the adsorption capacity (Lu *et al.* 2014; Song *et al.* 2015). Hailu *et al.* (2017) used SMZ with HDTMA-Br loading of 200% ECEC to adsorb Cr(VI), result revealed that the rate controlling step on adsorption Cr(VI) onto SMZ was controlled by chemisorption, the non-linear pseudo-second-order kinetic plot is shown in Figure 5. Zeolites modified with CPB and CTMAB separately for Cr (VI) test (Ren *et al.* 2016), the adsorption rate were 1.4 mg/g and 2.0 mg/g, respectively, much higher than natural zeolite: 0.3 mg/g. The short chain of carbon of cationic surfactant can occupy more pore spaces of zeolite, which can provide a large amount of internal adsorption and anion exchange point and is beneficial to the adsorption of anions.

From the analysis above, it can be found that the removal of cationic heavy metal ions can select low valent alkali and salt modified zeolites, for anionic heavy metal ions, the cationic surfactant with shorter carbon chain can be selected to modify the zeolite.

## COST ESTIMATION

As mentioned above, zeolite is one of the most popular adsorbent for wastewater treatment. In South Korea, the

natural zeolite normally costs about  $1.6 \pm 0.5$  USD/kg (Nguyen & Lee 2015). In China, natural zeolite is pretty cheap, about 140 USD per  $m^3$  (particle size: 1 mm). However, the cost of modified zeolite for pollutants removal was seldom reported; most articles describe only batch experiments, because its cost strongly depends on many factors, such as availability of raw material, the processing required, modification methods and the treatment condition (Hokkanen *et al.* 2016). Besides, it is difficult to compare different adsorbents/modified methods due to inconsistencies in the data presentation.

## APPLICATION IN CONSTRUCTED WETLANDS

### Natural zeolite

The study of constructed wetlands (CWs) started earlier and the technology became mature by degrees. In recent years, the CWs with natural zeolite have been widely used in wastewater treatment plant effluent, low concentration domestic sewage and landfill leachate (Gikas & Tsihrintzis 2012; Mojiri *et al.* 2016), mainly adsorbing ammonium (Reddy *et al.* 2013). The removal rate of ammonium was more than 70.0% by constructed wetland with natural zeolites as substrates (Shuib *et al.* 2011; Araya *et al.* 2016). However, the removal rate of other pollutants (especially phosphorus) is very low, only 29.8% of the adsorption rate of phosphorus after running for 2 years (Stefanakis & Tsihrintzis 2012). Sarafraz *et al.* (2009) showed that the use of natural zeolite in a horizontal subsurface constructed wetland enhanced adsorption of Zn, and proposed zeolite as an alternative to sand and gravel. Allende *et al.* (2014) found that the zeolite wetlands, which were operated under a hydraulic loading of 30 mm/d, to treat acidic water with As = 2.3 mg/L, Fe = 97.3 mg/L and B = 30.8 mg/L, removed 99.9%, 96.1% and 12.0% of As, Fe and B.

### Modified zeolite

In the past 2 years, there have been many studies on the application of modified zeolites in CWs, but most of the studies are from Asia. Modified zeolite has high porosity and efficiency of pollutants, so using modified zeolite as substrate in CWs cannot only improve the removal rate of pollutants, but also alleviate clogging of wetlands.

Since salt modified zeolite has good adsorption effect on phosphorus and ammonium, it is common to use salt modified zeolite in CWs. Zhang *et al.* (2014a) coated layered double hydroxides (LDHs) which were formed by  $ZnCl_2$  and  $FeCl_2$  on the surface of zeolites, and conducted the experiments of purified phosphorus through a vertical-flow constructed wetland. The average removal rate of TP in wetland was over 90.0%, and the maximum theoretical adsorption amount was three times the natural zeolite. Wang (2013) applied NaCl modified zeolite as substrate in subsurface flow constructed wetland, the removal rate of ammonium, total nitrogen and total phosphorus reached 86.7%, 91.4% and 86.9%, respectively. The zeolites modified with 3 M NaCl and 2 M  $AlCl_3$  were also used as substrates in anaerobic baffled reactor and baffled flow constructed wetland (ABC + BFCW) (Wu *et al.* 2017). The results showed that the removal rate of nitrogen and phosphorus in the modified zeolite was good and stable, and phosphorus removal rate increased from 57.9% to 93.3% in winter. Thus, it can be seen that the constructed wetland with modified zeolite can greatly improve the removal rate of pollutants. The operations of constructed wetland using modified zeolite are shown in Table 7. For heavy metal removal, it may be preferable not only to rely on metal adsorption capacity by the plants, but also on high sorption capacity of the substrate (Philippe *et al.* 2013). As mentioned above, zeolite with NaOH and NaCl conditioning had the highest CEC and adsorption capacity, it is assumed that NaOH or NaCl modified zeolites are a possible solution to

Table 7 | Operation of modified zeolite constructed wetland

Type	Modified method	Operating time	Hydraulic load $L \cdot (m^2 \cdot d)^{-1}$	Influent (mg/L)	Mean removal rate	Reference
Vertical flow	ZnFe-LDHs	August–December	250	TP: 1.6–3.0	90.0%	Zhang <i>et al.</i> (2014a)
Subsurface flow	NaCl	–	93	NH <sub>3</sub> -N: 24.5–32.7 TN: 37.7–45.1 TP: 4.5–5.0	86.7% 91.4% 86.9%	Wang (2013)
Baffled flow	NaOH + $AlCl_3$	Summer Autumn Winter	152	TP: 4.3 TP: 7.7 TP: 8.6	92.0% 93.2% 92.0%	Wu <i>et al.</i> (2017)

remove heavy metals from wastewater. Inorganic substances, proteins, humic acid, polysaccharides and nucleic acid accounted for about 71.0% of the total mass of CW clog (Ye et al. 2014). Clogging of wetlands is related to the size and porosity of the substrate (Varga et al. 2013). The porosity of zeolite is greatly improved after modification, therefore, it is beneficial to alleviate the problem of substrate clogging (Yam et al. 2015).

## CONCLUSION AND FUTURE PERSPECTIVES

The article briefly introduced the modification of zeolite in terms of physical modification, chemical modification, and composite modification, which have been studied to increase the adsorption potential of zeolite for various pollutants from wastewater. The research on physical modification was only related to ammonium removal, chemical modification and composite modification were studied more widely for eliminating varied kinds of pollutants. The temperature, type and concentration of reagents will have a significant effect on the modification results. Although there are many methods for modification of zeolites, the most suitable modification should be chosen according to specific pollutants. In this paper, the application in the most popular engineering-constructed wetland has been intensively reviewed, however, in the recent years, most of the studies are from Asia. Modified zeolite as a substrate can greatly improve the removal rate of pollutants and alleviate the clogging conditions of CWs. From previous theory, the assumption that modified zeolite has a great impact on removing heavy metals by CWs still needs more proof.

In the past, most tests concentrate on removing single pollutants but, in practice, there is no qualitative or quantitative study to adsorption competition on the interface of zeolite inside the complex wastewater. It is suggested that, in the future, the study direction of modified zeolite can be based on analyzing the adsorption of modified zeolite simultaneously, so that it could deal with the complexity of the actual wastewater.

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