Removing ammonium from water and wastewater using cost-effective adsorbents: A review

Jianyin Huang[1,2,3,*], Nadeeka Rathnayake Kankanamge[3], Christopher Chow[1,2], David T. Welsh[3], Tianling Li[3], Peter R. Teasdale[1,2]

1. *Natural and Built Environments Research Centre, School of Natural and Built Environments, University of South Australia, SA 5095, Australia*
2. *Future Industries Institute, University of South Australia, SA 5095, Australia*
3. *Environmental Futures Research Institute, School of Environment, Griffith University, Gold Coast campus, QLD 4215, Australia*

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ABSTRACT

Ammonium is an important nutrient in primary production; however, high ammonium loads can cause eutrophication of natural waterways, contributing to undesirable changes in water quality and ecosystem structure. While ammonium pollution comes from diffuse agricultural sources, making control difficult, industrial or municipal point sources such as wastewater treatment plants also contribute significantly to overall ammonium pollution. These latter sources can be targeted more readily to control ammonium release into water systems. To assist policy makers and researchers in understanding the diversity of treatment options and the best option for their circumstance, this paper produces a comprehensive review of existing treatment options for ammonium removal with a particular focus on those technologies which offer the highest rates of removal and cost-effectiveness. Ion exchange and adsorption material methods are simple to apply, cost-effective, environmentally friendly technologies which are quite efficient at removing ammonium from treated water. The review presents a list of adsorbents from the literature, their adsorption capacities and other parameters needed for ammonium removal. Further, the preparation of adsorbents with high ammonium removal capacities and new adsorbents is discussed in the context of their relative cost, removal efficiencies, and limitations. Efficient, cost-effective, and environmental friendly adsorbents for the removal of ammonium on a large scale for commercial or water treatment plants are provided. In addition, future perspectives on removing ammonium using adsorbents are presented.

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* *Corresponding author*. E-mail: Leslie.Huang@unisa.edu.au (Jianyin Huang).

Introduction

Ammonium concentrations in unspoiled waterways are usually low (Marañón et al., 2006); however, these days, agricultural, domestic and industrial effluent and runoff contribute substantially to ammonium pollution of surface water and groundwater resources. This pollution finds its way into these vital resources *via* various point sources such as: municipal and industrial wastewater, leachate and runoff from waste disposal sites, construction sites, animal feedlots and so on (Camargo and Alonso, 2006; Carlson et al., 2013; Chen et al., 2002; La Cour Jansen et al., 2004), as well as non-point sources such as agricultural runoff, atmospheric deposition and land developments nearby waterways (Camargo and Alonso, 2006; Nolan and Hitt, 2006; Zhu et al., 2013). High nutrient loads can stimulate nuisance algal growth in polluted waters, which can contribute to hypoxia or anoxia zones, and highly undesirable changes in ecosystem structure and function (Bhatnagar and Sillanpaa, 2011; Camargo and Alonso, 2006; Smith et al., 1999). In addition, ammonium needs to be removed from the grey water for reuse purposes due to its potential risk to human health (Britto and Kronzucker, 2002). This is especially true in the case of laundry, bathroom, and swimming pool wastewaters (Widiastuti et al., 2011).

Ammonium (NH_4^+) and unionised ammonia (NH_3) are readily interchangeable depending upon the pH and temperature of natural and urban waters (Nollet, 2013). Unionised ammonia is much more toxic than ammonium (Batley and Simpson, 2009; CCME, 2007; USEPA, 2006) because it is a neutral molecule that freely diffuses across the epithelial membranes of aquatic organisms. It can damage gill epithelia causing asphyxiation, stimulate glycolysis, and suppress the Krebs cycle leading to progressive acidosis which reduces the oxygen-carrying capacity of blood, disrupts blood vessels, and affects liver and kidney functions (Augspurger et al., 2003). However, in natural waters, ammonium is present in much greater concentrations than ammonia due to the predominance of circum-neutral pH. A number of guidelines to protect against the impacts of eutrophication have been developed to deal with global concerns regarding the ecological effects of ammonium (ANZECC, 2000; CCME, 2007; EU, 2006; USEPA, 1999).

Accordingly, many methods, such as biological, physical, chemical, or a combination of these methods, have been developed for the removal of ammonium from wastewaters and other point sources. They mainly include ion exchange and adsorption, biological technology, air stripping, breakpoint chlorination, chemical precipitation, reverse osmosis, microwave radiation, and supercritical water oxidation (Bermejo et al., 2008; Bernet et al., 2000; Bodalo et al., 2005; Booker et al., 1996; Guštin and Marinšek-Logar, 2011; Huang et al., 2015a; Lin et al., 2009; Siegrist, 1996; Turan, 2016). The advantages and disadvantages of these technologies are summarised in Table 1. There are several limitations of the current technologies, including high cost, low removal rate, high sensitivity to pH and temperature, and introducing new pollutants (Bermejo et al., 2008; Bernet et al., 2000; Bodalo et al., 2005; Booker et al., 1996; Guštin and Marinšek-Logar, 2011; Huang et al., 2015a; Lin et al., 2009; Siegrist, 1996; Turan, 2016). Compared to other techniques, ion exchange and adsorption technique have many favourable characteristics. It demonstrates a high affinity towards ammonium, high removal efficiency, low-cost, simplicity of application and operation as well as environmental friendliness (Turan, 2016; Uğurlu and Karaoğlu, 2011; Widiastuti et al., 2011). These advantages make it competitive to apply on a large scale for commercial and water treatment plants to remove ammonium. Therefore, the following study focuses on this method. In this review, over 70 adsorbents are presented, and their performance in removing ammonium is compared based on several criteria, which examine the efficiency, cost-effectiveness, ease of use, and environmental friendliness of adsorbents in the removal of ammonium.

1. Removal of ammonium from water and wastewater using the adsorption and ion exchange method

This review provides criteria based on source, process, and waste to identify the most suitable adsorbents for removing

Table 1 – Technologies to remove ammonium from water and wastewater.

Removal technologies	Removal efficiency	Advantages	Disadvantages	Ref.
Ion exchange and adsorption	80%–95%	Easy operation Effectively remove ammonium Low cost Relatively low TDS (Total dissolved solids) effluent	Certain pH ranges Different adsorbents have different removal efficiencies Require waste brine disposal	(Gupta et al., 2015; Marañón et al., 2006; Mazloomi and Jalali, 2016; Millar et al., 2016; Turan, 2016; Uğurlu and Karaoğlu, 2011; Widiastuti et al., 2011)
Biological method	70%–95%	Most commonly used method Effectively remove ammonium	High cost Require certain temperature and climate conditions High energy use High risk during subsequent processes High ammonium concentration after treatment	(Bernet et al., 2000; Feng et al., 2012; Siegrist, 1996; Thornton et al., 2007; Turan, 2016)
Air stripping	50%–90%	Widely used process for wastewater pre-treatment Simple equipment Not sensitive to toxic substances	Require certain pH, temperature, and flow rate Require large stripping towers Time consuming process High energy consuming Scaling and fouling on packings	(Guštin and Marinšek-Logar, 2011; Halling-Sørensen and Jorgensen, 1993; Huang et al., 2015a; Liao et al., 1995)
Breakpoint chlorination	80%–95%	Low spatial requirement Effectively remove ammonium Not sensitive to toxic substances and temperature Adaptable to existing facilities	Sensitive to pH Disinfection by-products High chlorine consumption under high organic matter Require highly skilled operators	(Brooks, 1999; Charrois and Hrudey, 2007; Halling-Sørensen and Jorgensen, 1993; Pressley et al., 1972; Xue et al., 2017)
Chemical precipitation	20%–30%	A valuable slow-release fertiliser Medium cost Reduce the amount of sludge and maintenance costs	Require certain pH and temperature Affect by chemical position and other ions Introduce new pollutants	(Huang et al., 2015a; Uludag-Demirer et al., 2005; Yunnen et al., 2016; Zhang et al., 2011c)
Reverse osmosis	60%–90%	Low energy requirement Low field and space Easy and continuous operation, modular construction and design simplicity	High cost Membrane elements can be fouled by colloidal matter Iron and manganese can provoke decreased scaling potential Clean the membrane regularly	(Bodalo et al., 2005; Cancino-Madariaga et al., 2011; Häyrynen et al., 2009; Noworyta et al., 2003)
Microwave radiation	~80%	Medium cost Suitable for high ammonium concentrations	Affect by pH and radiation time, initial ammonia concentration and aeration Evaporation of NH_3 Difficult for full scale application	(Lin et al., 2009; Quan et al., 2004; Rabah and Darwish, 2013)
Supercritical water oxidation	>95%	Rapid destruction of organic wastes Produce water, carbon dioxide and molecular nitrogen	High cost High temperature and pressure Affect by temperature and excess oxygen Salt precipitation	(Bermejo et al., 2008; Du et al., 2013; Kritzer and Dinjus, 2001; Marrone et al., 2004)

ammonium from water and wastewater on a large scale (Fig. 1). To achieve that, the adsorbents need to be abundant, cost-effective, easy to process and environmentally friendly to dispose of. The article presents existing and potential adsorbents based on published data. Important findings and recent literature on this topic are provided along with an elaborate discussion of the relevant published studies on adsorbents such as adsorption capacities, contact times, sizes, pH, and temperature ranges. These data are presented and summarised in Tables 2–9. Due to a large number of adsorbents, the adsorbents with high removal capacities which are highlighted in the italic script in each section are selected and further compared based on several criteria. This will allow us to find out a cost-effective and environmental friendly adsorbent on a large scale for commercial or wastewater treatment plants.

1.1. Natural zeolites and clays

Natural zeolites are available in abundance, approximately 3 to 4 million tonnes of natural zeolites are produced annually the world over with the major producers being China (2 million ton), South Korea (210,000 ton), Japan (150,000 ton), Jordan (140,000 ton) and Turkey (100,000 ton). Although pricing of natural zeolites varies with zeolite content and processing, prices are low, ranging from $30 to $70 per ton for granular products and $50 to $120 per ton for finer ground material (Clark et al., 1993). Natural zeolites and clays are the most common adsorbents. They consist of three-dimensional frameworks of aluminosilicate tetrahedral where aluminium and silicon structured atoms are bound by covalent bonds over common oxygen atoms to form interconnected cages and channels
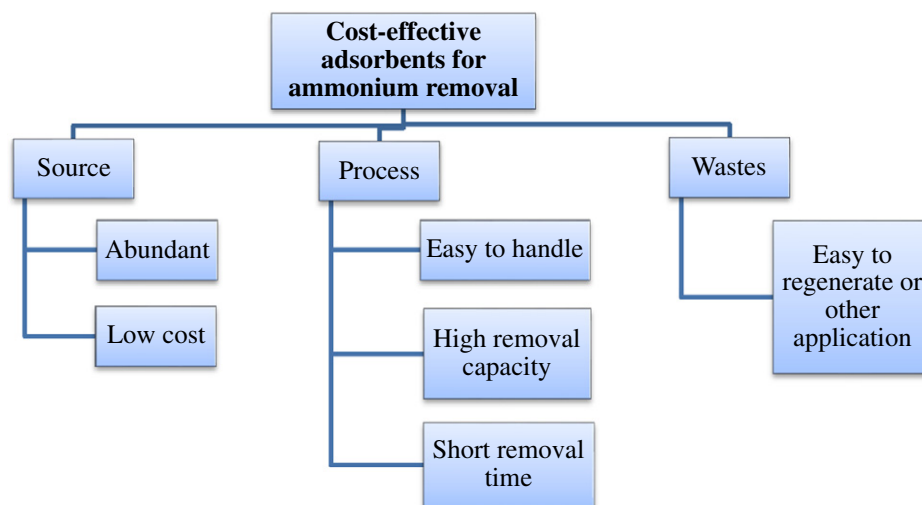
Fig. 1 – Criteria for selecting a suitable adsorbent to remove ammonium from water and wastewater.

(Turan, 2016; Widiastuti et al., 2011) (Fig. 2). These adsorbents can present with a high negative charge due to their level of aluminium atom substitution. Adsorption occurs in the pores where negative charges are balanced and exchanged with positively charged cations, such as Na^+, K^+, Ca^{2+} and Mg^{2+} in solution. Fig. 2 shows a typical scheme for the adsorption of ammonium onto zeolite. Presently at installations worldwide, natural zeolites and clays, such as zeolite (Mazloomi and Jalali, 2016; Millar et al., 2016; Saltali et al., 2007; Widiastuti et al., 2011), clinoptilolite (Wang et al., 2006; Weatherley and Miladinovic, 2004), mordenite (Weatherley and Miladinovic, 2004), sepiolite (Balci and Dincel, 2002), mesolite (Thornton et al., 2007) are used as ion exchangers in water and wastewater for ammonium removal owing to their high selectivity for ammonium, low-cost, relative simplicity of application and operation. Their products are released as non-toxic exchangeable cations into the environment (Wang et al., 2016; Widiastuti et al., 2011).

The following phenomena have been observed regarding natural zeolites' and clays' ability to remove ammonium from laboratory experiments: (a) the ammonium removal capacity of natural zeolites and clays increases while removal efficiency decreases with high initial ammonium concentrations; (b) removal efficiency increases with increased amounts of zeolite; (c) most ammonium adsorptions are exothermic with a few exceptions, and can be affected by increased temperature; (d) the optimum pH is between 6.0 and 8.0 due to H^+ competition at low pH and ammonium/ammonia equilibrium at high pH; (e) ammonium removal efficiency by natural zeolites is initially fast but gradually decreases with contact time. This is due to adsorbent sites being initially empty and the ammonium concentration gradient being high. As adsorption sites and the concentration gradient decrease, the rate of ammonium adsorption also decreases (Balci and Dincel, 2002; Booker et al., 1996; Karadag et al., 2008; Mazloomi and Jalali, 2016; Saltali et al., 2007; Wang et al., 2006; Widiastuti et al., 2011). In addition, Wang et al. (2006) and Erdoğan and Ülkü (2011) found clinoptilolite particle size as a crucial factor governing ammonium adsorption rates. This is to be expected since smaller particle size increases the available surface area to facilitate

ammonium absorption. Erdoğan and Ülkü (2011) showed the ammonium adsorption rate of clinoptilolite increased with agitation speed from 70 to 170 r/min. This phenomenon levelled off at higher agitation speeds, suggesting that adsorption was not equilibrated with ion transfer rates at external boundary layers, but was dominated by surface reactions. Furthermore, Wang et al. (2006), Weatherley and Miladinovic (2004), Mazloomi and Jalali (2016) and Marañón et al. (2006) indicated that the presence of cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, Zn^{2+} and Cd^{2+}) in solution could reduce the ammonium removal efficiency of natural zeolites. Anion concentrations (Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) also negatively influenced the ammonium removal efficiency of natural zeolites (Mazloomi and Jalali, 2016; Marañón et al., 2006). Moreover, the presence of low molecular weight organic acids (oxalic acid, malic acid, and citric acid) increased ammonium adsorption onto natural zeolites (Mazloomi and Jalali, 2016), because the presence of organic compounds possibly reduced surface tension in the aqueous phase to the point of enhancing access of counter-ions to fixed sites and the microporous and mesoporous structure of zeolite.

Additionally, Karadag et al. (2008) applied NaCl solutions with two concentrations (10 and 20 g/L) at 15 and 23 hr to regenerate exhausted natural zeolite, indicating that higher NaCl concentrations achieved more complete regeneration than lower concentrations over the same regeneration time. In addition, the results showed that regeneration improved the adsorption capacity of clinoptilolite by more than 50% and ammonium exchange capacity by 19%, possibly due to the replacement of K^+, Ca^{2+} and Mg^{2+} in the natural clinoptilolite structure by Na^+ during regeneration and the expanded size of micropores in regenerated clinoptilolite.

Some natural zeolites and clays have been used in real situations, although many are only tested under laboratory conditions. For instance, natural Gordes clinoptilolite was applied to remove ammonium from sanitary landfill leachate (Karadag et al., 2008). Natural zeolite was used to remove ammonium from anaerobic digested wastewater (Guo et al., 2013). Wang et al. (2016) investigated the dynamic adsorption

Table 2 – Adsorption capacities and other parameters for ammonium removal by natural zeolites and clays (the adsorbent with the highest removal capacity is highlighted in the italic script).

Adsorbent	Capacity (NH$_4$-N, mg/g)	Concentration range (NH$_4$-N, mg/L)	Optimised removal efficiency (%)	Contact time	Size (mm)	pH	Temperature (°C)	Ref.
Australian natural zeolite	6.30	5–120	97	8 hr	–	4–6	25–45	Widiastuti et al. (2011)
Natural Iranian zeolite	8.51–10.39	40	90	30 min	0.25–2	~7	25	Mazloomi and Jalali (2016)
Romanian volcanic tuff	19.00	20–300	83	3 hr	0.16–0.25	~7	–	Marañón et al. (2006)
New Zealand mordenite	9.48	0–200	–	3 days	0.5–0.71	7.5	–	Weatherley and Miladinovic (2004)
Chinese clinoptilolite	11.20	15–150	–	1.5–2.5 hr	0.45–0.90	~6	20	Wang et al. (2006)
Gordes clinoptilolite	9.47/16.32	10–300/100–1000	–/85	–/3 hr	0.60–2.8/–	~7/6–8	25, 40	Erdoğan and Ülkü (2011)/ Karadag et al. (2008)
Natural Herschelite-sodium chabazite	26.6	1.4–280	–	6 hr	–	4–8	21–23	Kuokkanen et al. (2016)
Natural Herschelite-calcium/sodium Chabazite	16.4	1.4–280	–	6 hr	–	4–8	21–23	Kuokkanen et al. (2016)
Mesolite	49	0–2000	55	4 hr	0.1–0.6	6–7	20	Thornton et al. (2007)
Zeolite Australia (ZA)	8.64	250–1000	–	–	0.5–1	–	30	Millar et al. (2016)
Castle Mountain Zeolites (CMZ)	13.32	250–1000	–	–	0.5–1	–	30	Millar et al. (2016)
Natural Western Azerbaijan zeolite	43.47	10–200	94.4	45 min	–	7.5	20–40	Khosravi et al. (2014)
Turkish (Yıldızeli) zeolite	30.12	20–400	–	–	–	~7	21–50	Saltali et al. (2007)
Turkish sepiolite (Tacir)	49	116–3111	60	1000 s	2.05	~7	25	Balci and Dincel (2002)
Chinese zeolite	12.60	20–49	–	5–600 min	1–10	6.8	26	Wang et al. (2016)

Table 3 – Adsorption capacities and other parameters for ammonium removal by synthetic zeolites and clays (the adsorbent with the highest removal capacity is highlighted in the italic script).

Adsorbent	Capacity (NH$_4$-N, mg/g)	Concentration range (NH$_4$-N, mg/L)	Optimised removal efficiency (%)	Contact time	Size (mm)	pH	Temperature (°C)	Ref.
NaCl-modified Yemeni zeolite	11.18	10–250	99	120 min	–	4–8	25–35	Alshameri et al. (2014)
NaCl modified zeolite	11.0–17.3	10–4000	–	12 hr	–	3.4–8.6	25–45	Lin et al. (2013)
NaCl modified clinoptilolite	11.44	50	–	–	–	–	–	Zhang et al. (2016)
NaOH modified mordenite	53.91	10	81	24 hr	0.85–1.70	6.5	30–40	Soetardji et al. (2015)
NaOH-autoclave-treated in distilled water	–	280, 560, 28,000	–	–	–	–	–	Ruiz et al. (1997)
Ultrasound-modified zeolite	2.1	50	84.6	45 min	3	7	20	Zieliński et al. (2016)
Microwave-treated zeolite	23.83	0–200	–	4 hr	–	~6	25	Lei et al. (2008)
Fused with NaOH and hydrothermal treated	19.29	50–250	–	–	–	–	–	Wang et al. (2007)
MgO modified zeolite	24.9	1281.3	100	210 min	–	8.3	25	Guo (2016)
Zeolite 13X	8.61	5–400	90	30 min	4–6	–	25	Zheng et al. (2008)
Geopolymer	21.07	10–1000	75	24 hr	0.063–8	4–8	22	Luukkonen et al. (2016)
Ceramic adsorbent	75.5	2500–10,000	19.4	480 min	2–3	–	25	Zhao et al. (2013)
Magnetic zeolite NaA	10.53	63.75	85	12–129 min	0.02	~7.9	16–70	H.B. Liu et al. (2013)
Birnessite-type manganese oxides	22.61	2–50	–	30 min	–	5–7	10–40	Cheng et al. (2017)

Table 4 – Adsorption capacities and other parameters for ammonium removal by polymeric ion exchangers (the adsorbent with the highest removal capacity is highlighted in the italic script).

Adsorbent	Capacity (NH_4-N, mg/g)	Concentration range (NH_4-N, mg/L)	Optimised removal efficiency (%)	Contact time	Size (mm)	pH	Temperature (°C)	Ref.
Dowex 50w–x8 and Purolite MN500	40	25–200	–	4 days	~0.185	–	–	Jorgemsen and Weatherley (2003)
Amberjet 1200 Na	27	0–40	96.4	4 hr	0.6–0.7	5–7	25	Chen et al. (2002)
KU-2-8	74.7	27–580	>94	–	0.6–1.2	–	–	Malovanyy et al. (2013)
Purolite C160H	–	–	70	10 min	0.3–1.2	4–9	–	Imchuen et al. (2016)
Purolite C150H	28.23	25–150	>65	90 min	–	6.5	–	Sica et al. (2014)

efficiency of ammonium by natural Chinese zeolite from a paddy rice field during rainfall runoff, showing that the adsorption rate was highest when adsorption barriers had a base angle of 45°. A high initial removal rate was observed at low flow rates while high adsorption was achieved at high flow rates over the entire runoff process.

1.1.1. Comparison of natural zeolites and clays
As natural zeolites are abundant, cheap and easy to handle, those with the highest ammonium adsorption capacity are preferred. Mesolite and Turkish sepiolite were presented in papers by Thornton et al. (2007) and Balci and Dincel (2002), respectively, and recognised for their adsorption capacity (Table 2). Each can absorb 49 mg of ammonium per g, which is the highest among studied zeolites. Next in order of absorption capacities are Western Azerbaijan zeolite, Turkish (Yıldızeli) zeolite and Herschelite-sodium chabazite at 43 mg/g, 30 mg/g, and 27 mg/g, respectively (Khosravi et al., 2014; Kuokkanen et al., 2016; Saltali et al., 2007). Other natural zeolites and clays examined in the literature have relatively low adsorption capacities of only about 10 mg/g or less. Another consideration is removal time efficiency. Between mesolite and Turkish sepiolite, the latter has a shorter removal time of just 1000 s. Based on absorption capacity and an efficient removal time, Turkish sepiolite presents as the best natural zeolite for removing ammonium from wastewater in this section. Although Balci and Dincel (2002) did not present the regeneration of Turkish sepiolite, it can be regenerated potentially using NaCl solutions based on Karadag et al. (2008).

1.2. Synthetic zeolites and clays

Although natural zeolites are available in abundance, their relatively small adsorption capacities for ammonium and lower efficacy are still key problems for their wider application in water-purification processes. Many synthetic zeolites have been developed using physical and chemical methods to improve adsorption capacities and removal efficiencies (Alshameri et al., 2014; Lin et al., 2013; Soetardji et al., 2015). Most of the presented synthetic zeolites below showed higher ammonium adsorption capacity (>15 mg/g) compared to natural zeolites, due to a higher proportion of sodium and other cation ions, higher specific area, bigger total pore volume, and lower average pore size after modification (Alshameri et al., 2014; Lin et al., 2013; Soetardji et al., 2015). This sub-section focuses on presenting and comparing different synthetic methods and their resultant modified zeolites.

A common synthetic procedure is the crystallization of silica-alumnia in the presence of salt and alkalis solutions. Product properties depend on reaction mixture composition, pH of the system, operating temperature, pre-reaction and reaction times, and templates used (Alshameri et al., 2014; Lin et al., 2013; Ruiz et al., 1997; Soetardji et al., 2015). Lin et al. (2013) prepared modified zeolite by immersing 5 g natural zeolite in 100 mL of 2 mol/L NaCl solution at 35°C and 100 r/min in a thermostatic shaker for 24 hr. NaCl modification enhanced ammonium adsorption capacity from 11.0 to 17.3 mg/g. The X-ray diffraction (XRD) patterns showed that the crystal frame structure of zeolite was intact after NaCl modification and higher Na^+ contents were observed. Additionally, the surface of modified zeolite became rougher and more irregular compared with the natural zeolite. Alshameri et al. (2014) modified natural zeolite at 1 mol/L NaCl solution at 80°C with a 1 hr stirring time. The content of Na^+ increased from 0.42% to 2.32% after modification and decreased to 0.87% after adsorbing ammonium (Fig. 3), and ion exchange capacity of modified zeolite was higher compared to natural zeolite of the same initial ammonium concentration. Another modified natural clinoptilolite was prepared in 15% NaCl solution at 40°C with a 48 hr stirring time, with increasing BET surface area, average pore diameter and cation exchange capacity (CEC) compared to natural clinoptilolite (Zhang et al., 2016).

Additionally, Ruiz et al. (1997) modified 15 g bentonite in 3.75 mol/L NaOH solution in distilled water and (in a separate experiment) in seawater using a reflux system, and an autoclave. The modifications observed were greater in the samples treated in the autoclave than by reflux, and also greater in distilled water media than seawater. Modified bentonite by alkaline treatment in distilled water had higher CEC (increased from 25 to 36.8 mg/g) while the modified bentonite by alkaline treatment in seawater was more selective for ammonium removal. Moreover, natural mordenite was modified in 6 mol/L NaOH at 75°C for 24 hr by Soetardji et al. (2015). XRD patterns showed no change or degradation of the mordenite after modification, suggesting that NaOH modification had little or no influence on the crystallinity of mordenite. The adsorption capacity increased from 7.94 to 53.91 mg/g after modification. Cheng et al. (2017) synthesized birnessite-type manganese oxides with interlayer K^+ and Na^+ ions by redox reactions between $KMnO_4$ and $MnCl_2$ under alkaline conditions and the Na-rich birnessite had the ammonium adsorption capacity of 22.61 mg/g.

Moreover, ultrasound (Zieliński et al., 2016), microwave irradiation (Lei et al., 2008), fusion (Wang et al., 2007) and

Table 5 – Adsorption capacities and other parameters for ammonium removal by carbon-based adsorbents (the adsorbent with the highest removal capacity is highlighted in the italic script).

Adsorbent	Capacity (NH$_4$-N, mg/g)	Concentration range (NH$_4$-N, mg/L)	Optimised removal efficiency (%)	Contact time	Size (mm)	pH	Temperature (°C)	Ref.
Combination of PAC and PZ	–	18	49.15	20 min	0.50–0.85	–	25	Liao et al. (2015)
Organic acid modified activated carbon	19.34	–	30	30 min	–	8–9	25	Halim and Latif (2013)
Activated bulgarian lignite	29	35–280	90	2 hr	0.7–1.25	–	–	Vassileva et al. (2009)
Na$^+$ impregnation activated carbon	1.19	0.45–12	68.2	24 hr	–	4.17–6.43	–	Shi et al. (2013)
Multi-wall carbon nanotube	9.31	10–140	97	35 min	–	–	15–50	Moradi and Zare (2013)
Coconut shell-activated carbon	2.26	50–2000	–	120 min	0.3–0.6	9	10	Boopathy et al. (2013)
Barbecue bamboo charcoal	1.75	60	~85	80 min	0.075–0.18	6–10	30	Zhou et al. (2015)
Peanut shells	313.9	10–500	–	5–10 hr	0.9–1.2	~7	25–50	Liu et al. (2016)
Corncobs	373.1	10–500	–	5–10 hr	0.9–1.2	~7	25–50	Liu et al. (2016)
Cotton stalks	518.9	10–500	–	5–10 hr	0.9–1.2	~7	25–50	Liu et al. (2016)
Pyrolyzed wood biochar	44.64	250–1400	90.8	96 hr	0.25–0.5	5–8	25–45	Kizito et al. (2015)
Rice husk biochar	39.8	250–1400	84.1	96 hr	0.25–0.5	5–8	25–45	Kizito et al. (2015)
Cacao shell biochar	0.852	0.1–50	–	2–4 days	–	~10	–	Hale et al. (2013)
Oak sawdust biochar	10.1	25.7	–	24 hr	–	–	25	Z. Wang et al. (2015)
Maple wood	5.44	0–100	–	–	–	–	Room temperature	B. Wang et al. (2015)
Giant reed straw	1.49	30–80	–	25 min	0.425–1	7–9	10–40	Hou et al. (2016)
Bentonite hydrochar	23.67	200	100	25 hr	0.15–0.18	6	30	Ismadji et al. (2016)

PAC: powdered activated carbon; PZ: powdered zeolite.

Table 6 – Adsorption capacities and other parameters for ammonium removal by hydrogels (the adsorbent with the highest removal capacity is highlighted in the italic script).

Adsorbent	Capacity (NH$_4$-N, mg/g)	Concentration range (NH$_4$-N, mg/L)	Optimised removal efficiency (%)	Contact time	Size (mm)	pH	Temperature (°C)	Ref.
Hydrogel	42.74	13–130	–	30 min	0.19–0.38	3–8	30–50	Zheng et al. (2011)
Hydrogel composite chitosan and rectorite	123.8	10–1000	–	30 min	0.075	4–9	23–51	Zheng and Wang (2009)
Hydrogel composite chitosan and vermiculite	78.23	25–1000	–	30 min	0.19–0.38	4–8	30	Zheng et al. (2012)
Hydrogel nanocomposite	7.43	10–400		250 min			25–45	Shahrooie et al. (2015)
Palygorskite nanocomposite	237.6	100	60	15 min	0.16–0.425	4–8	20–30	Wang et al. (2014)
Superabsorbent resin	147.3	25–200	–	–	0.165	5–8	20	J. Liu et al. (2013)

calcination (Guo, 2016) and other methods (Zhao et al., 2013; Zheng et al., 2008) have also been employed to increase the adsorption capacity of natural zeolites. Zieliński et al. (2016) modified 50 g natural zeolite in 1 L distilled water with 35 kHz ultrasound and a power density of about 5 W cm^2, 20°C for different time periods (15, 30, 45, 60, 90 min); however, no significant difference was found in the particle sizes of natural zeolite and modified zeolite using statistical analysis and modified zeolite exhibited very low adsorption capacity, only 2.1 mg/g. The modified Chinese zeolite was prepared by Lei et al. (2008) in 2.5 mol/L NaCl solution under microwave irradiation at 119 W, 2450 MHz for 10 min. The adsorption capacity of microwave-treated zeolite was increased up to 23.83 mg/g. The XRD patterns showed that the microwave-treated zeolite (3.04%) and thermal-treated zeolite (2.85%) had higher sodium contents than the original zeolite (2.19%). Wang et al. (2007) fused the Chinese natural clinoptilolite with NaOH powder at 550°C for 2 hr prior to hydrothermal reaction (autoclave at 100°C for 8 hr) and salt treatment (1 mol/L NaCl) to form zeolite Na-Y, for which the ammonium uptake values increased from 10.49 to 19.29 mg/g. Another modified zeolite was prepared by calcining the mixture of

natural zeolite and MgO with a weight ratio of 6:1 at 400°C for 4 hr in a muffle (Guo, 2016). The ammonium adsorption capacity of modified zeolite increased from 12.6 to 24.9 mg/g. The study showed that particle diffusion was the rate-limiting step for ammonium adsorption and ammonium adsorption mainly occurred on the surface of zeolite with monolayer molecular adsorption. Zeolite 13X was developed by mixing potassium feldspar power and Na$_2$CO$_3$ (molar ratio of 1.3:1), and baking at 845°C for 150 min (Zheng et al., 2008). The product was added M$_2$O/SiO$_2$ (molar ratio of 1.5:1) and H$_2$O/M$_2$O (molar ratio of 40:1), then homogenized in a water bath at 95–100°C for 8 hr. Zhao et al. (2013) developed a novel ceramic adsorbent with an ammonium adsorption capacity of 75.5 mg/g using mixed and sieved Kanuma mud, Akadama mud, zeolite powder, soluble starch, and Na$_2$SO$_4$ at the optimum mass ratios of 2:2:3:2:1, and sintered at 600°C for 1.5 hr. The BET surface area increased from 33.59 to 36.80 m^2/g, and the total pore volume enlarged from 0.08 to 0.10 mL/g. The SEM results of the ceramic adsorbent before and after ammonium adsorption indicated that ammonium adsorption not only occurred on the surface of the particles inevitably but also existed inside the surface area of the pores. In addition,

Table 7 – Adsorption capacities and other parameters for ammonium removal by industrial wastes (the adsorbent with the highest removal capacity is highlighted in the italic script).

Adsorbent	Capacity (NH$_4$-N, mg/g)	Concentration range (NH$_4$-N, mg/L)	Optimised removal efficiency (%)	Contact time	Size (mm)	pH	Temperature (°C)	Ref.
Fly ash	0.297	–	–	120 min	0.035–0.15	7–9	20–40	Uğurlu and Karaoğlu (2011)
Fly ash using hydrothermal method	7.02	52.2	84	0.5 hr	<0.8	7.7	25	Juan et al. (2009)
Fly ash with based and acid treatment	–	25	60	–		5.5–10.5	–	Zhang et al. (2007)
Fly ash using fusion method	24.3	43–348	70	0–360 min	<0.15	~8	25	T. Zhang et al. (2011)
Ferrosilicon alloy	78.74	–	–	180 min	–	6–9	–	Darvishi Cheshmeh Soltani et al. (2015)
Slag	3.1	10–300	–	2.5 hr	~0.149	7–11	25	Zhang et al. (2013)
Honeycomb-cinder	5.0	10–300	–	2.5 hr	~0.149	7–11	25	Zhang et al. (2013)
Coal gangue	6.0	10–300	–	2.5 hr	~0.149	7–11	25	Zhang et al. (2013)
Red mud	17.5	5–500	>50	–	~0.149	4–7	–	Zhao et al. (2016)
Paper sludge ash using hydrothermal treatment	–	–	–	–	–	–	–	Wajima and Munakata (2011)

Table 8 – Adsorption capacities and other parameters for ammonium removal by agricultural wastes and plant materials (the adsorbent with the highest removal capacity is highlighted in the italic script).

Adsorbent	Capacity (NH₄-N, mg/g)	Concentration range (NH₄-N, mg/L)	Optimised removal efficiency (%)	Contact time	Size (mm)	pH	Temperature (°C)	Ref.
Synthesised zeolite from rice husk ash	42.37	50	70	1.5 hr	–	4–6	Room temperature	Yusof et al. (2010a)
P. oceanica fibers	1.80	10–50	–	30 min	–	6–10	20–60	Wahab et al. (2010)
Boston ivy leaves	6.71	25, 50	100	18 hr	–	–	30	Liu et al. (2010a)
Phoenix tree leaves	4.62	25, 50		18 hr	–	–	30	Liu et al. (2010a)
Acid activated avocado seeds	5.4	50–450	–	–	–	5	25	Zhu et al. (2016)

different amounts of Fe_3O_4 was added into zeolite to easily separate adsorbed zeolite from ammonium solutions (Liu et al., 2013a). Magnetic zeolite NaA with different Fe_3O_4 loadings was prepared by hydrothermal synthesis based on metakaolin and Fe_3O_4. The SEM results showed that the added Fe_3O_4 did not affect the morphology of zeolite NaA. However, the ammonium removal efficiency decreased from 83% to 75% with the increase of Fe_3O_4 loading because the magnetic zeolite was covered by some nano-particles which could block some pores and cavities.

For regeneration purposes, a mixture of NaCl and NaOH in solution was selected as the regenerant (Zhang et al., 2016). The results showed ammonium desorption efficiency increasing with increased NaCl (by percentage mass) from 0 to 10%. After 10%, there was no significant change. Further, the desorption rate of ammonium increased significantly with increasing NaOH concentration from 0 to 0.6% under the same NaCl concentration.

Many studies have indicated that various parameters such as contact time, initial ammonium concentration, adsorbent dosage, temperature, competing cations and anions, and dissolved organic matter could influence ammonium adsorption by synthesised zeolites and clays (Cheng et al., 2017; Lei et al., 2008; Lin et al., 2013; Wang et al., 2007; Zhang et al., 2016; Zhao et al., 2013). These results were similar to those given in Section 1.1. Under real conditions, only a few synthetic zeolites have ever been used. For examples, Luukkonen et al. (2016) synthesised geopolymer from metakaolin and applied it to remove ammonium from landfill leachate. Zhang et al. (2016) applied the mixture of Na-modified zeolite and an anion exchange resin in the advanced treatment municipal effluent with a high ammonia-nitrogen content. The results showed that the average ammonium removal efficiency was greater than 95%.

1.2.1. Comparison of synthetic zeolites and clays

The sources of synthetic zeolites and clays are natural zeolites and clays, which are abundant and low cost. Those with the highest ammonium adsorption capacity, short removal time and easy to handle are preferred. Compared to many other synthetic zeolites in Table 3, the novel ceramic adsorbent

using Kanuma clay and Akadama clay had the highest adsorption capacity for ammonium, which was 75.5 mg/g at an initial ammonium concentration of 10,000 mg/L, a dosage of 20 g/L, and contact time of 480 min. NaOH modified mordenite (53.91 mg/g) came second, followed by MgO modified zeolite (24.9 mg/g), microwave-treated zeolite (23.83 mg/g) and geopolymer (21.07 mg/g). The ammonium adsorption capacity of other synthetic zeolites is over 10 mg/g, except zeolite 13X and ultrasound-modified zeolite.

In this section, the ceramic adsorbent can be more competitive than other synthetic zeolites and clays, due to its high removal capacity and reasonable cost. Although it needs to be modified at relatively high temperature (600°C), it only takes 1.5 hr which cannot be costly for industrial manufacturing, compared to other modified zeolites that need to be heated at 75°C for 24 hr. The cost for ceramic adsorbent is at least $800 per ton, which includes Kanuma mud and Akadama mud (both are quite cheap), zeolite powder ($300–400 per ton), soluble starch ($400 per ton), and Na_2SO_4 ($100 per ton). Although other adsorbents are also promising, they have some limitations. For instance, NaOH modified mordenite needs to be modified in 6 mol/L NaOH, which is not only costly but also a safety issue when using such high concentration of NaOH solution. In addition, microwave radiation can reduce the reaction to a few minutes, but it is hard to produce microwave-treated zeolite in large amounts at one time.

1.3. Polymeric ion exchangers

Polymeric ion exchangers are in the form of resin beads. These beads are widely used in decontamination processes (Sica et al., 2014). The most common polymers used for ion exchange resins are polystyrene cross-linked with divinylbenzene. Polymeric ion exchangers have high absorption capacity, high kinetics, and good chemical and mechanical stability, giving them favourable stability at different temperatures (Malovanyy et al., 2013, 2014).

The performance of several polymeric ion exchangers with sulfonic acid functional groups but different forms (Na⁺ or H⁺) have been compared to natural and synthetic zeolites. Jorgemsen and Weatherley (2003) compared the performance of Dowex 50w–x8 resin, Purolite MN500 resin, and clinoptilolite

Table 9 – Adsorption capacities and other parameters for ammonium removal by nanoparticles.

Adsorbent	Capacity (NH₄-N, mg/g)	Concentration range (NH₄-N, mg/L)	Optimised removal efficiency (%)	Contact time	Size (mm)	pH	Temperature	Ref.
Fe_3O_4 nanoparticles	133.21	80–140	–	40 min	–	10	298 K	Zare et al. (2016)
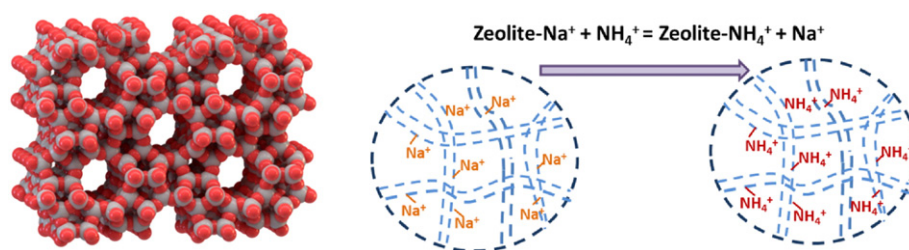
Fig. 2 – The microporous molecular structure of ZSM-5 (Zeolite Socony Mobil–5) zeolite (Splettstoesser, 2016) and model scheme for the adsorption of NH$_4^+$ onto zeolite (Huang et al., 2015b).

to remove ammonium in the presence of organic contaminants. The results showed that Dowex 50w–x8 (~40 mg/g) had the highest adsorption capacity for ammonium, followed by Pruolite MN500 (~25 mg/g) and clinoptilolite (~20 mg/g). Purolite MN500 had a higher selectivity for ammonium than clinoptilolite. The ammonium uptake of clinoptilolite and Purolite MN500 increased under the presence of citric acid possibly due to the micro and macroporous structure of clinoptilolite and Purolite MN500, and a reduction in surface tension facilitated by citric acid. However, no increase was observed for Dowex 50w–x, probably because Dowex 50w–x did not contain macropores. Additionally, Malovanyy et al. (2014) compared the performance of KU-2-8 and Purolite C104 resin, natural and synthetic zeolites in the removal of ammonium from mainstream municipal wastewater. Results indicated that KU-2-8 resin (74.7 mg/g) had the highest ammonium adsorption capacity among the studied materials. Natural and synthetic zeolites had similar capacities, but they were about 40% lower than KU-2-8. Purolite C104 did not show a high exchange capacity for ammonium. The study observed that natural zeolite was more selective for ammonium, while synthetic zeolite, KU-2-8, and Purolite C104 resin were more selective for water hardness ions than for ammonium.

Studies in this section also presented the effects of adsorbent dosage, pH, competing cations and anions, and dissolved organic matters on ammonium adsorption by polymeric ion exchangers (Chen et al., 2002; Imchuen et al., 2016; Sica et al., 2014). For instance, the ammonium removal efficiency increased with increasing amounts of resin (Purolite C150H and Amberjet 1200 Na) (Sica et al., 2014; Chen et al., 2002). Sica et al. (2014) presented there was a maximal amount of resin in solution after which adding additional resin did not increase ammonium removal. Chen et al. (2002) showed that Na$^+$ and K$^+$ could significantly reduce ammonium removal efficiency of Amberjet 1200 Na. They also demonstrated that Mg^{2+} and Ca^{2+} could have negative influences. The effects of pH and competing ions on Purolite C160H resin for ammonium removal were reported by Imchuen et al. (2016). As mentioned above, Jorgemsen and Weatherley (2003) presented the positive effect of citric acid on Purolite MN500 but no effect on Dowex 50w–x due to their different structures. Furthermore, the diffusion of ammonia and ammonium ions in gel Purolite SGC 100 × 10 MBH and macroporous Purolite C 160 MBH from solutions were investigated (Kaušpėdienė and Snukiškis, 2006). Results showed that effective intraparticle diffusivity largely depended on

solution pH because of the shrinkage in alkaline and swelling in acidic media. Since ion exchange contributed to a decrease in pH, swelling occurred accompanied by an increase in effective intraparticle diffusivity from 0.1 to 0.34 × 10^{-10} m^2/sec for gel Purolite SGC 100 × 10 MBH; only a small variation of 0.18–0.11 × 10^{-10} m^2/sec occurred for macroporous Purolite C 160 MBH due to its resistance to shrinkage and swelling.

Other resins have been used under real conditions. For instance, Amberjet 1200 Na resin was applied in the removal of ammonium from the synthetic industrial effluent (Chen et al., 2002). The results indicated that breakthrough in ammonium removal occurred at 57, 63 and 88 BV when influent flow rates were 0.6, 0.4 and 0.2 l/hr, respectively. The treated BV by Amberjet 1200 Na is comparable to that of natural zeolite (Green et al., 1996). Purolite C160H resin was used to remove ammonium from the effluent of a nZVI-induced nitrate reduction process as ammonium was the major undesired product (Imchuen et al., 2016).

1.3.1. Comparison of polymeric ion exchangers

Among all the tested polymeric ion exchangers, KU-2-8 resin showed the highest removal capacity for ammonium at 74.7 mg/g, followed by Purolite C150H (28.2 mg/g) and Amberjet 1200 Na (27 mg/g) (Table 4). However, polymeric ion exchangers are more expensive than natural and synthetic zeolites and clays, ranging from several hundred dollars to thousands of dollars per ton. The cost of KU-2-8 resin is about $800–$1200 per ton. Despite the high cost of KU-2-8 resin, the regeneration and application of KU-2-8 resin in a real situation are provided. In general, it is more competitive than other polymeric ion exchangers in this section. Malovanyy et al. (2013 and 2014) presented the use of NaCl (10, 20 and 30 g/L) and HCl (6.24 g/L) solutions to regenerate ion exchangers and natural and synthetic zeolites. Ammonium concentration in spent regenerants decreased more than 50% with decreased NaCl concentrations. Results show that the regeneration of KU-2-8 using 30 g/L NaCl is faster than the regeneration of synthetic and especially natural zeolites. Regeneration with HCl did not prove to be more beneficiary than regeneration with NaCl as the low pH of spent regenerants had implications in consequent treatments. Furthermore, KU-2-8 resin was applied in a packed bed column to remove ammonium from mainstream municipal wastewater of pH about 7 (Malovanyy et al., 2013 and 2014). The breakthrough (defined as the phenomenon when the effluent concentration of the solution from the column is about 3%–5% of the influent concentration)
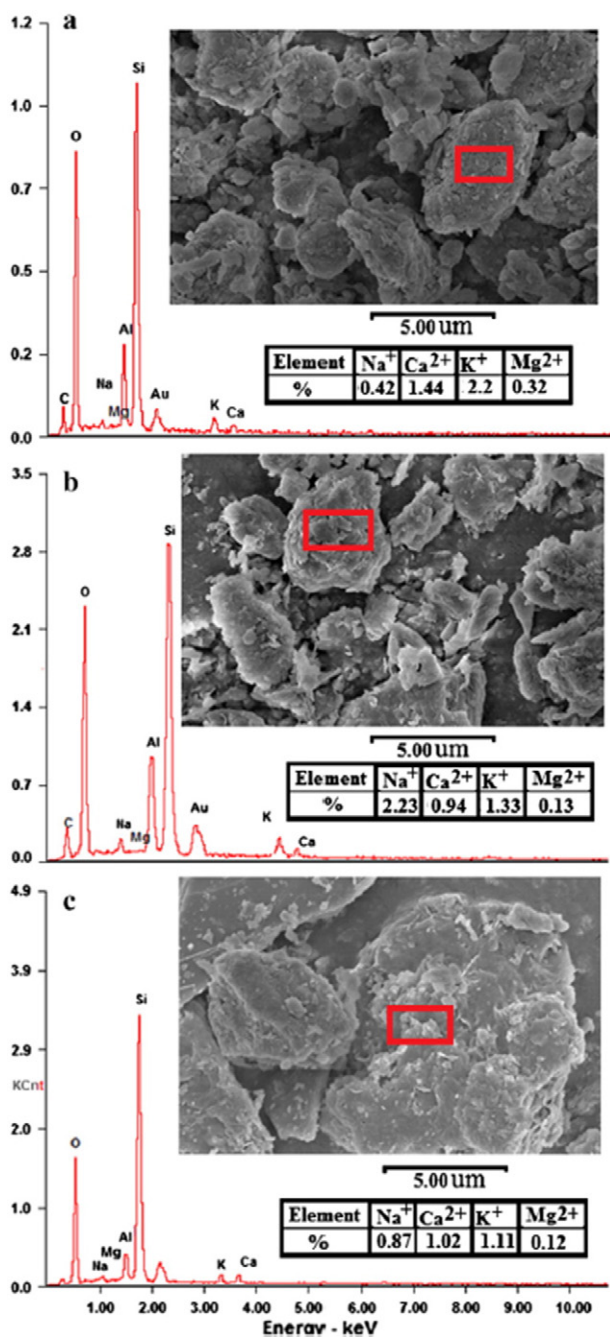
Fig. 3 – Scanning electron microscope (SEM) and energy-dispersive spectrometry (EDS) analyses of zeolite grain of natural zeolite (NZ) (a), Na-modified zeolite (SNZ) (b), and used zeolite (Used-Z) after ion exchange (c) (Alshameri et al., 2014).

was reached after pumping 143–202 bed volumes (BV = volume of treated solution/volume of resin) of wastewater; breakthrough capacities of KU-2-8 resin were from 10.4–15.8 mg/g.

1.4. Carbon-based adsorbents

Activated carbon (AC) is characterized by having many small, low volume pores that increase the surface area available for absorption. Just one gram of activated carbon can have a surface area of 3000 m^2. It is known as an alternative

adsorbent for the removal of different organic and inorganic pollutants from aqueous media (Bhatnagar et al., 2013; Gupta et al., 2013a; Li et al., 2002; Lian et al., 2012). AC has high adsorption capacity, a high degree of surface reactivity, and good mechanical strength and resistance to heat and radiation (Bhatnagar et al., 2013; Gupta et al., 2013a; Li et al., 2002). Besides AC, biochar which is a precursor of activated carbon, is a high-carbon, fine-grained residue that is produced through modern pyrolysis processes and suitable for ammonium adsorption. In addition, carbon nanotubes (CNTs) have also been proposed as potential adsorbents and received attention from many researchers. CNTs have been shown to be superior adsorbents especially in the removal of many types of organic and inorganic contaminants, such as dyes (Gupta et al., 2013b), heavy metals (Mubarak et al., 2016), organic contaminants (Kang et al., 2017). This section focuses on presenting and comparing the performance of various carbon-based adsorbents in removing ammonium.

1.4.1. Activated carbon

Previous studies have reported general AC as having poor adsorption of substances with polar molecular structure (Halim et al., 2010; Park and Kim, 2005). This issue is dealt with by modifying AC with a combination of zeolite and chemical methods to increase its adsorption capability under various applications (Halim and Latif, 2013; Liao et al., 2015; Vassileva et al., 2009). The combined powdered activated carbon (PAC) and powdered zeolite (PZ) of different amounts was developed to enhance ammonium removal in micro-polluted raw water (Liao et al., 2015). A combination of 40 mg/L PAC and 2 g/L PZ exhibited slightly higher removal efficiency (6.53% higher) compared to any other combination. The results indicated that a synergistic effect existed between PAC and PZ, which promoted removal efficiency of ammonium. In addition, organic acid modified activated carbon (AC-RCOONa) *via* chemical modification methods (Yin et al., 2007) was also applied to the removal of ammonium (Halim and Latif, 2013). Compared to pristine AC (4.5 mg/g), AC-RCOONa (19.34 mg/g) removed ammonium more efficiently in aqueous solution, and the removal efficiency ranged from 20% to 94.3% over the first 40 min and reached a constant removal rate of 56.7% after 100 min. Furthermore, Vassileva et al. (2009) modified two coal-based activated carbons (ACN: commercial product and ACCh: the Bulgarian lignite) by oxidization under three conditions: concentrated HNO$_3$ for 14 days (ACN_N and ACCh_N), 30% H$_2$O$_2$ (ACN_P and ACCh_P) for 3 hr and moist air for 18 hr (ACN_MA and ACCh_MA), respectively. Among initial and activated carbons, oxidized carbons with HNO$_3$ had the highest adsorption capacities (ACN_N: 29 mg/g and ACCh_N: 28 mg/g), followed by ACCh_P (26.3 mg/g) and ACCh_MA (21.3 mg/g). The modified activated carbons were of the same mixed micro-mesoporous type but had different surface area values and porous texture parameters. The results showed that HNO$_3$ treatment had the greatest impact on carbon surface area and porosity; however, effects on the two initial carbons were opposite to each other. HNO$_3$ treatment of ACCh resulted in approximately a 1.1-fold increase in the specific surface area (A$_{BET}$) and total micropore volume (W$_0$) but a 2-fold decrease in mesopore volume (V$_{ME}$). By contrast, HNO$_3$ treatment of ACN

led to a 1.1-fold decrease in A_{BET} and 1.2-fold increase in V_{ME}. The effects of oxidation with H_2O_2 and moist air on the texture parameters of ACCh and ACN are similar. Moreover, Shi et al. (2013) modified two kinds of activated carbon by Na^+ impregnation after pre-treatment involving oxidation by HNO_3 (AC/N-Na) or acidification by HCl (AC/HCl-Na) to remove ammonium. 2 g clean AC was oxidized by 100 mL 5 mol/L HNO_3 and in the other experiment 2 g AC was acidified by HCl, then 2 g of each oxidized AC was stirred in 0.5 mol/L NaCl solution for 6 hr. Compared to the initial AC, AC/N-Na showed a slight decrease in BET surface area and porosity due to the destruction of the pore walls resulting from the harsh action of HNO_3. For AC/HCl-Na, it also showed a slight decline in surface area but a

small increase in porosity because of an increase in surface functional groups resulting from HCl. The SEM results indicated that the external surfaces of AC/N-Na and AC/HCl-Na were flatter and more homogeneous than AC without modification (Fig. 4). Ammonium adsorption capability was in accordance with: AC/N-Na (1.19 mg/g) > AC/HCl-Na (0.66 mg/g) > AC (0.46 mg/g). This hierarchy was due to a higher number of surface functional groups and better intra-particle diffusion after treatment. However, ammonium adsorption capacity was still very low.

1.4.2. Biochar

Many types of biochar, modified from pyrolyzed wood and rice husks (Kizito et al., 2015), giant reed straw (Hou et al., 2016), maple wood (Z. Wang et al., 2015) and others, have been used to remove ammonium from aqueous systems. Biochar surfaces are often negatively charged (Yao et al., 2013), and can adsorb ammonium through electrostatic interactions (Kizito et al., 2015). Several kinds of biochar having higher ammonium adsorption capacities are presented. Liu et al. (2016) examined three alkali-modified biochars produced from peanut shells (mPS), corncobs (mCC) and cotton stalks (mCS) for ammonium removal. The three agricultural residuals were pre-treated with 1 mol/L NaOH solution at a solid–liquid ratio of 1.0 g to 2.5 mL for 2 hr, then the mixed materials were converted into modified biochars through slow pyrolysis at 300°C based on Gao et al. (2015). The Fourier Transform Infrared Spectroscopy (FT-IR) analysis indicated that new functional groups of C–O stretching vibration and C–H bending vibration appeared in mCS with maximum adsorption capacity increasing rapidly from 202.5 to 518.9 mg/g. Little change in surface functional groups was shown for mPS. Maximum adsorption capacity increased, however, but slowly from 243.3 to 313.9 mg/g. This was mainly due to an increase in the surface area and total pore volume after modification. For mCC, increased surface functional groups (C–H stretching vibration) also enhanced maximum adsorption capacity from 217.4 to 373.1 mg/g. In addition to the above experiments, a study has also been conducted on other biochars such as mixed wood cuttings and rice husks. These were subject to slow pyrolysis at 600°C before being used to remove ammonium (Kizito et al., 2015). SEM data showed that wood biochar had a high-crystalline structure with multiple voids and micropores while the rice husk biochar had a more amorphous but less porous structure (Fig. 5). FT-IR analysis indicated various functional groups for these two biochars that can enhance adsorption of ammonium. Maximum ammonium adsorption was about 44.64 and 39.8 mg/g for wood and rice husk biochar, respectively. Furthermore, a bentonite hydrochar composite was developed using bentonite and cassava peel by Ismadji et al. (2016). Both bentonite and cassava needed to be pre-treated before preparing a bentonite-biochar composite. The mixture of bentonite and cassava was carbonised at 500°C at a heating rate of 10°C/min. Nitrogen was pumped into the tube furnace at a flow rate of 3 L/min for the first 45 min, and then the gas was switched to carbon dioxide with the same flow rate for another 15 min. The structure of the resultant bentonite hydrochar composite was a combination of micropores and mesopores with 402 m^2/g BET surface area and 0.34 cm^3/g
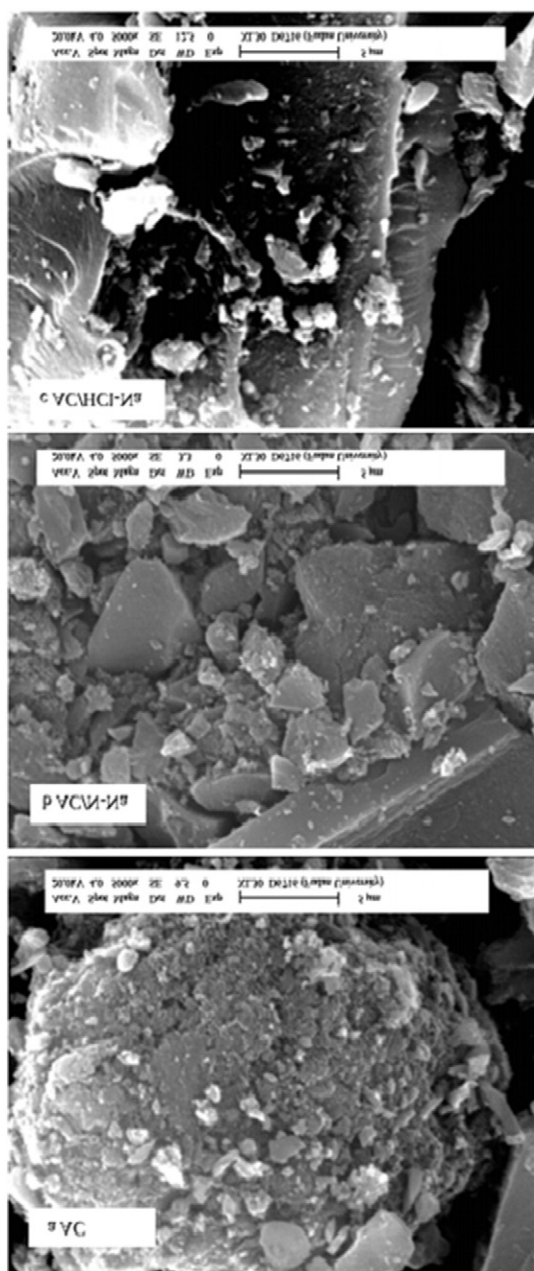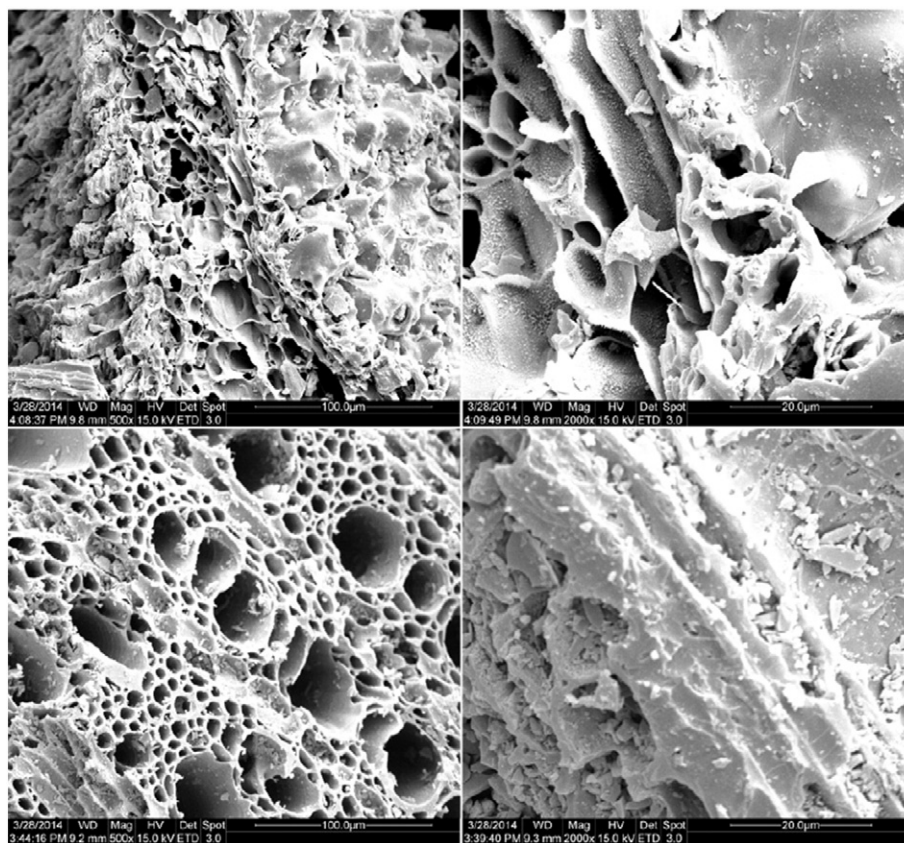

Fig. 4 – Scanning electron microscope (SEM) images of activated carbon (AC) (a), AC/N-Na (b) and AC/HCl-Na (c) (Shi et al., 2013).

Fig. 5 – SEM images of rice husk biochar at magnification ×500 (top left) and ×2000 (top right), and wood biochar at magnification ×500 (bottom left) and ×2000 (bottom right) (Kizito et al., 2015).

pore volume. Several functional groups were found on the surface of the biochar *via* FT-IR analysis. The maximum ammonium adsorption capacity of this composite was 23.67 mg/g, which was higher than bentonite alone (12.37 mg/g) or biochar alone (9.49 mg/g).

1.4.3. Carbon nanotubes

Multi-walled carbon nanotubes were used to remove ammonium giving an adsorption capacity of 9.31 mg/g (Moradi, 2016; Moradi and Zare, 2013). Results showed that ammonium removal efficiency did not increase after 35 min and adsorption capacity decreased with increased temperature, suggesting the process is exothermic.

Past studies have also presented the effects of initial ammonium concentrations, adsorbent dosage, particle size, pH, competing cations and anions, and temperature on ammonium adsorption by the carbon-based adsorbents (Hou et al., 2016; Moradi, 2016; Vassileva et al., 2009; Zhou et al., 2015). The results of these studies were similar to those observed for the previous ion exchangers. Additionally, a few carbon-based adsorbents have been used under field conditions. For examples, pyrolyzed wood and rice husks biochar were used to remove ammonium from piggery manure anaerobic digestate slurry with a removal efficiency of 60% and 53%, respectively (Kizito et al., 2015). Ismadji et al. (2016) showed that bentonite hydrochar composite could effectively remove ammonium from a fish tank system which contained

500 L of water and 30 Japanese Koi within 60 min. All AC and CNTs studies have only been conducted under laboratory conditions.

For the regeneration, Halim and Latif (2013) presented the use of 1 mol/L NaCl to regenerate the composite adsorbent, and the performance of regenerated AC-RCOONa was comparable to fresh AC-COONa but better than pristine AC over the first 40 min. No studies, however, have been presented for the regeneration of biochars and CNTs.

1.4.4. Comparison of carbon-based adsorbents

Among all the studied materials, modified biochar made from cotton stalks had the highest adsorption capacity for ammonium at 518.9 mg/g (Table 5). Another two biochars (corncobs and peanut shells) studied in Liu et al. (2016) also had very high adsorption capacities at 373.1 and 313.9 mg/g, respectively. Pyrolyzed wood biochar (44.6 mg/g), rice husk biochar (39.8 mg/g) and HNO_3 activated commercial product (29 mg/g) were next. The extremely high adsorption capacity of cotton stalk biochar makes it very competitive compared to other carbon-based adsorbents. The preparation of modified cotton stalk biochar is not very difficult which requires 1 mol/L NaOH, compared to modifying AC under strong acid. Additionally, cotton stalks are abundant, and the use of cotton stalks can reduce agricultural waste. Compared to the costs of AC (several hundred dollars to thousand dollars per ton) and carbon nanotubes (several hundred dollars per gram), the

price of cotton stalks is cheap, about $100 per ton. The cost for preparing cotton stalk biochar is at least $450 per ton, which includes the cost of NaOH.

1.5. Hydrogels

Hydrogels are three-dimensional crosslinked polymeric networks that enable the adsorption of many cationic pollutants such as heavy metals (Irani et al., 2015), dyes (Panic et al., 2013), and ammonium (Zheng et al., 2011; Zheng and Wang, 2009). Recently, this material has attracted more attention due to its high-capacity and promising applications in sensors, separation membranes, and adsorbents (Zhang et al., 2014; Zhao et al., 2015). The porous three-dimensional structured network with high water content can reduce mass transfer resistance, thus allowing solutes to easily diffuse through the hydrogel structure (Zheng et al., 2011; Zheng and Wang, 2009). Fig. 6 dives a schematic model of the adsorption of ammonium onto hydrogel.

1.5.1. Hydrogels with inorganic clays
Considering the limitations of pure polymeric hydrogels, such as poor gel strength and stability, inorganic clay minerals have been incorporated into hydrogel matrixes to improve their performance in removing ammonium (Zheng et al., 2011). A hydrogel was developed based on different amounts of acrylic acid (AA), polyvinyl alcohol (PVA), and tourmaline (Tm) (Zheng et al., 2011). Optimized preparation conditions pertained to the degree of neutralization (ND) of AA of 70%, PVA:AA of 0.0833 and Tm:AA of 0.50. The mixtures of chemicals were polymerized at 65°C for 3 hr in an oil bath. The resulting granular product was cooled to room temperature and neutralized with 6.0 mol/L NaOH solution to pH 7.0. After that, it was dehydrated with methanol and dried at 60°C. The study indicated that hydrogel had an entangled three-dimensional network with the advantages of a fast adsorption rate (30 min) and high adsorption capacity for ammonium (42.74 mg/g at 30°C) in a pH range from 3.0 to 8.0. Additionally, Zheng and Wang (2009) developed a hydrogel composite chitosan (CTS) grafted poly (acrylic acid)/rectorite (CTS-g-PAA/REC (10 wt%)) to remove ammonium. The introduction of REC into the polymer matrix not only improved the thermal stability of the corresponding polymer but also reduced product cost. However, results indicated that increased amounts of REC in the polymer mix reduced the hydrogel's adsorption capacity due to REC's poor adsorption ability for ammonium. Testing showed the optimum amount of REC in the hydrogel was approximately 10%. Adsorption equilibrium could be achieved within 3 to 5 min. A hydrogel composite with REC had a higher adsorption capacity (123.8 mg/g) for

ammonium than pure polymeric hydrogel, and it could work in a wide range of initial pH levels from 4.0 to 9.0. No significant changes in adsorption capacity were found over the temperature range studied. Additionally, the same authors developed another granular composite hydrogel-chitosan grafted poly(acrylic acid)/unexpanded vermiculite (CTS-g-PAA/UVMT) with an adsorption capacity of 78.23 mg/g (Zheng et al., 2012).

1.5.2. Wheat straw cellulose based semi-interpenetrating polymer network (IPNs) hydrogel
J. Liu et al. (2013) developed a wheat straw cellulose-g-poly(potassium acrylate)/polyvinyl alcohol (WSC-g-PKA/PVA) semi-IPN superabsorbent resin (SAR) from graft copolymerization. A superabsorbent resin was a loosely cross-linked hydrophilic polymer with a network structure, which could adsorb and retain large amounts of aqueous fluids. Semi-IPN was a polymer network where one or more linear or branched polymers were characterized by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched macromolecules (Sperling, 1984). The semi-IPN system exhibited high adsorption capacity with WSC-g-PKA/PVA semi-IPN SAR reaching 147.3 mg/g.

1.5.3. Hydrogel nanocomposites
Other than conventional hydrogels, hydrogel nanocomposites have been developed to remove ammonium. A palygorskite nanocomposite was developed using biodegradable carboxymethyl chitosan (CMCS) and N-maley chitosan (N-MCS) as graft copolymerization material and crosslinker, respectively (Wang et al., 2014). Palygorskite (PGS) was incorporated into polymer matrices as nanofiller to form the composite hydrogel. The SEM results demonstrated that CMCS-g-PAA/PGS composite hydrogel had relatively uniform and smaller pore size due to the introduction of PGS into the polymeric networks, and CMCS-g-PAA/PGS composite hydrogel showed open channels and entangled three-dimensional networks with thin pore walls. The results demonstrated that CMCS-g-PAA with 30 wt% PGS had a high adsorption capacity at 237.6 mg/g due to its high surface area and porosity. Also, Shahrooie et al. (2015) investigated a new starch-based hydrogel nanocomposite made from starch and polyvinyl alcohol (PVA) blended as the polymeric matrix and fumarate-alumoxane (Fum-A) and maleic anhydride (MA) as cross-linking agents for ammonium removal from aqueous solutions. However, the capacity of this hydrogel nanocomposite was low, only 7.43 mg/g.

Studies of various hydrogels showed that (a) ammonium adsorption efficiency increased with increased initial ammonium concentrations and adsorbent weight; (b) hydrogels worked in a wider pH range from about 3.0–8.0 compared to previously
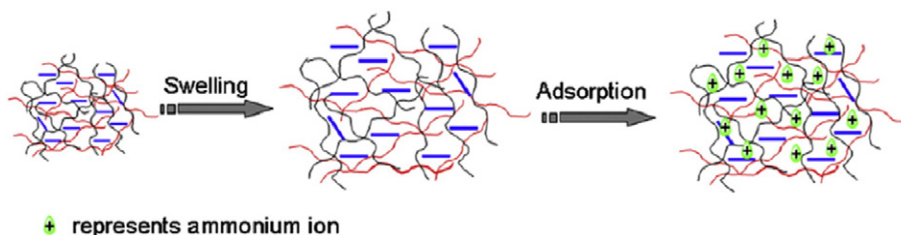

+ represents ammonium ion

Fig. 6 – Model scheme for the adsorption of NH$_4$-N onto hydrogel (Zheng et al., 2012).

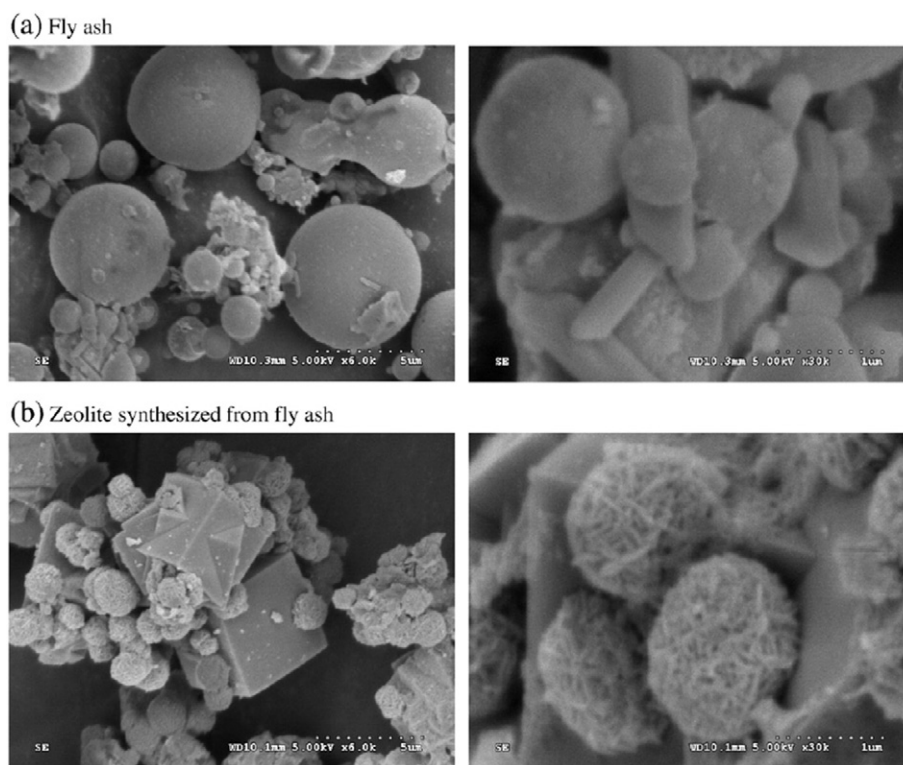**Fig. 7 – SEM images of fly ash and its synthesized zeolite (Zhang et al., 2011a).**

discussed adsorbents (this is because at pH lower than 3.0, –COO⁻ groups are converted into –COOH groups, leading to electrostatic attraction between ammonium and hydrogels. When pH is higher than 8.0, NH_4^+ changes into NH_3 gas); (c) the adsorption of ammonium was a very fast process, the removal time of most hydrogels was less than 30 mins; (d) adsorption capacity was affected by other cations (cation concentrations >0.05 mmol/L result in the decreased adsorption capacity of CTS-g-PAA/REC and effects of multivalent cations are more serve). The temperature indicated different impacts on hydrogels. Zheng and Wang (2009) reported that temperature had little effect on the adsorption capacity of ammonium onto chitosan-g-poly (acrylic acid)/rectorite hydrogel composites while a decrease in ammonium adsorption capacity with increased temperature was reported previously for natural zeolites (Alshameri et al., 2014; Saltali et al., 2007). Shahrooie et al. (2015) also reported that ammonium adsorption efficiency of nanocomposites increased with an increase in temperature.

Different eluents (0.1 mol/L HCl, NaCl, and NaOH) were applied to regenerate exhausted hydrogels (Zheng and Wang, 2009). The results suggested that 0.1 mol/L NaOH solution obtained the highest recovery (approximately 100%) for ammonium. Additionally, 0.1 mol/L NaOH was also found to effectively desorb ammonium from the adsorbent and the regenerated SAR still had high adsorption capacity for ammonium (Liu et al., 2013b).

1.5.4. Comparison of hydrogel adsorbents

Among all tested hydrogels, palygorskite nanocomposite had the highest ammonium adsorption capacity at 237.6 mg/g, followed by superabsorbent resin (147.3 mg/g), hydrogel composite chitosan and rectorite (123.8 mg/g), and hydrogel composite chitosan and vermiculite (78.23 mg/g) (Table 6). The high removal capacity and short removal time (15 min) make palygorskite nanocomposite stand out compared to other hydrogels. Additionally, Wang et al. (2014) applied ammonium adsorbed nanocomposite as a multifunctional slow-release fertilizer which exhibited good slow-release properties with ammonium being 60% released in the soil for 10 days. The addition of ammonium adsorbed nanocomposite to soil could improve the water-holding and water-retention capacity of the soil. Although the regeneration of nanocomposite was not presented (Wang et al., 2014), it can be regenerated potentially using NaOH solutions based on Zheng and Wang (2009). At the same time, the preparation of this hydrogel is quite complicated, difficult and costly, which includes acrylic acid (AA, non-AR grade, $1000 per ton), chitosan (CTS, non-AR grade, $1000 per ton), natural palygorskite ($400–900 per ton), ferrous ammonium sulfate (non-AR grade, $100–500 per ton) and hydrogen peroxide solution (non-AR grade, $500 per ton).

1.6. Industrial wastes

Fly ash is a waste material generated from burning coal at electric power plants with a generation rate of more than 500 million ton per year worldwide (Zhang et al., 2011a); however, a great deal of fly ash is disposed of in the landfill or stored in great mounds at power stations. Fly ash can be modified to reduce its aluminium and silicon content, making it a good adsorbent of metals from acid mine drainage (Zhang et al., 2011a). Raw and modified fly ash have been utilised to remove ammonium from aqueous media (Uğurlu and Karaoğlu, 2011)

and it is priced at $15 to $40 per ton. Other industrial wastes have been used as adsorbents, including ferrosilicon alloy (Darvishi Cheshmeh Soltani et al., 2015), slag (Zhang et al., 2013), red mud (Zhao et al., 2016) and paper sludge ash (Wajima and Munakata, 2011). This section presents various industrial wastes to remove ammonium from aqueous media.

Uğurlu and Karaoğlu (2011) used raw fly ash to remove ammonium from aqueous solutions. The adsorption capacity of raw fly ash was very low, only 0.297 mg/g. The physical and chemical modification is required to enhance its adsorption capacity and removal efficiency. Modifications include alkali, salt, and fusion treatments. Three zeolite materials (NaP1, K-F and K-Phillipsite/K-Chabazite) were prepared from coal fly ash and treated under different alkali hydrothermal conditions (NaP1 at 0.5 mol/L NaOH 150°C for 72 hr, K-F at 3 mol/L NaOH 150°C for 24 hr, K-Phillipsite/K-Chabazite at 1 mol/L KOH 200°C for 72 hr) (Juan et al., 2009). No significant differences were found for the performance of different modified fly ash, which removed approximately 80% of ammonium from treated wastewater. Wu et al. (2006) improved ammonium removal capacity by modifying fly ash in various salt solutions (1.0 mol/L of NaCl solution or 0.5 mol/L of $CaCl_2$, $MgCl_2$, $AlCl_3$, and $FeCl_3$). The results indicated that different fly-ash cation types shown had very different ammonium removal efficiencies at low initial ammonium concentrations ($\leq$60 mg/L NH_4-N). Al-ZFA (aluminium-zeolite fly ash) had the highest removal efficiency (80% – 98%) for ammonium, followed by Mg- (43%–58%), Ca- (40%–54%), Na- (<20%), and Fe- (<1%). Fly ash was pre-treated by Zhang et al. (2007) in 2 mol/L NaOH for 48 hr, then boiled with reflux in H_2SO_4 with various concentrations. The results indicated the modified fly ash with treatment by 0.01 mol/L H_2SO_4 significantly improved the ammonium removal efficiency at low initial concentrations. However, the increased H_2SO_4 concentration led to the deterioration of the modified fly ash structure and a decrease in CEC.

Shigemoto et al. (1993) suggested that fly ash modified using conventional hydrothermal methods contained a considerable amount of fly ash residue, which can limit its adsorption capacity. A fusion method was recommended by which an alkaline fusion stage was introduced before the conventional hydrothermal process turning fly ash into high purity zeolite. Zhang et al. (2011a) applied the fusion method to synthetic zeolite from fly ash based on Shigemoto et al. (1993). A mixture of fly ash and NaOH powder at a ratio of 1:1.3 was heated at 600°C for 90 min (Zhang et al., 2011a, 2011b). The fusion products were ground and distilled water added to form a mixture containing 17.25% of the fusion product (W/W). The mixture was stirred intensely at 80°C for 1 hr, then kept in an autoclave at 100°C for 9 hr. XRD results indicated that fly ash was converted into high-crystalline zeolite after fusion (Fig. 7). CEC increased significantly from 0.033 meq/g of raw fly ash to approximately 1 meq/g of synthesised zeolite after application of the alkali hydrothermal method, then to 2.79 meq/g of synthesised zeolite after fusion. The results showed that removing ammonium by synthetic zeolite was a very rapid process and final ammonium uptake was almost complete within the first 10 min.

Additionally, many other industrial wastes have been utilised to remove ammonium from aqueous media. Darvishi Cheshmeh Soltani et al. (2015) applied ferrosilicon compound,

which contained silica and was produced during ferroalloy manufacturing, to adsorb ammonium from the aqueous medium with adsorption capacity of 78.74 mg/g. The XRD results demonstrated a crystalline nature of the adsorbent and XRF (X-ray fluorescence) analysis found that the major components of this compound were SiO_2 and Fe_2O_3. SEM image indicated a rugged and porous structure for the absorbent and FT-IR analysis determined various functional groups on the surface of the absorbent, including $Si-O-Si$ (bending), $Si-O-Si$ (asymmetric stretching), $S-H$, $C=O$ and $O-H$ groups. In addition, The adsorption behaviours of ammonium from three solid coal wastes, slag (SL), honeycomb-cinder (HC) and coal gangue (CG) were investigated by Zhang et al. (2013). Slag and honeycomb-cinder were the solid wastes produced from cooking and heating in most towns in China, and coal gangue was a complex of sandy shale and clay, which was produced during coal mining and washing. The XRF analysis showed that CG (12.63 m^2/g) had significantly higher surface areas than SL (4.02 m^2/g) and HC (2.13 m^2/g). FT-IR analysis determined various functional groups on the surface of the absorbent, including $Si-O-Si$ and $Si-O^-$, $O-Si-O$ and $O-Si-O^-$, $Al-O-Si$ and $Al-OH$ groups and so on. However, none of the coal wastes showed high adsorption capacity for ammonium, only about 3 to 6 mg/g. Furthermore, zeolite synthesised from red mud was applied to remove ammonium (Zhao et al., 2016). Red mud, a by-product generated during the alumina production, can be a suitable source for the synthesis of zeolite due to its high silicon and aluminium contents. The hydrothermal method was applied for the synthesis of zeolite. Extra silicon ($Na_2SiO_3 \cdot 9H_2O$) and NaOH solution were added to make the total mole ratio Si/Al of 4.5 and ratio Na/Si of 1.3. The mixture was heated in a homogeneous reactor for 8 hr aging time and 16 hr crystallization time at 120°C. The results showed that the CEC and SSA increased from 81.9 to 111 mmol/100 g and 17.8 to 28.1 m^2/g, respectively, during the synthesis process. The maximum ammonium adsorption capacity was 17.5 mg/g. Moreover, Wajima and Munakata (2011) synthesised zeolite from modifying paper sludge ash in 3 mol/L NaOH in an autoclave, which showed increasing CEC and removal ability for removing ammonium, comparing to raw ash due to the formation of zeolite structure, and higher specific surface areas.

The factors, including pH, initial ammonium concentration, adsorbent dosage, the particle size, temperature and competitive cations and anions could affect the removal efficiency of ammonium (Uğurlu and Karaoğlu, 2011; Zhang et al., 2011a, 2011c; Zhao et al., 2016), which is similar to previous studies in Sections 1.1 to 1.4. For instance, ammonium adsorption was largely affected by the particle size due to the specific surface area that promoted external surface adsorption, and the adsorption capacities decreased with increasing temperature (Uğurlu and Karaoğlu, 2011). In addition, the presence of individual cations and anions reduced the removal efficiency, following the orders of cations $K^+ > Ca^{2+} > Na^+ > Mg^{2+}$ and anions $CO_3^{2-} > Cl^- > SO_4^{2-}$ (Zhang et al., 2011a, 2011c). For the application of industrial wastes in real conditions, Juan et al. (2009) presented the application of modified fly ash in wastewater from sewage treatment plant after conventional treatment, and 80% removal efficiency was obtained, even in the presence of Ca^{2+}.

Among all the tested industrial wastes, ferrosilicon alloy has the highest ammonium adsorption capacity, which is about 78.74 mg/g (Table 7). Fly ash using fusion method came the second and had the adsorption capacity of 24.3 mg/g, followed by red mud (17.5 mg/g) and the adsorption capacities of rest industrial wastes are from 0.297 to 6 mg/g. Ferrosilicon alloy has more advantages compared to other tested industrial wastes due to high adsorption capacity, easy to handle and no requirement for further process, but also reduce the waste, bringing numerous benefits to the environment. Fly ash prices range from $15 to $40 per ton which could be similar to the cost of ferrosilicon waste.

1.7. Agricultural wastes and plant materials

Agricultural residues and plant materials are another types of low-cost materials that have been studied extensively as adsorbents to remove a variety of pollutants from aqueous solution, such as heavy metal (Bulut and Tez, 2007), dyes (Yagub et al., 2014) and nutrients (Bhatnagar and Sillanpaa, 2011). Using agricultural wastes and plant materials to remove ammonium is economical and eco-friendly due to their unique chemical composition.

  P. oceanica fibers, which were collected from Borj Cédria beach, were used to remove ammonium (Wahab et al., 2010). SEM data suggested that the fibers had a cylindrical shape and their external surfaces were irregular and characterized by the presence of furrows, which was important for ammonium adsorption and precipitation. Additionally, Ca^{2+}, Mg^{2+}, Na^+ and K^+ were found in the fibers, suggesting the ion exchange process between alkaline earth metals and ammonium. FT-IR analysis indicated that fibers had abundant carboxyl and hydroxyl groups, which may function as proton donors; hence deprotonated groups could be involved in coordination with ammonium. The results showed that the equilibrium states were reached at approximately 30 min. The adsorption capacity of *P. oceanica* fibers increased from 1.97 to 2.68 mg/g with the increase in temperature from 293 to 333 K, and *P. oceanica* fibers worked well from pH 6.0 to 10.0. The reason why *P. oceanica* fibers could work at a high pH is that the biopolymers, mainly lignin and cellulose chains, became negatively charged under alkaline conditions, which enhanced binding of positively charged ammonium cations. Moreover, Liu et al. (2010a) investigated the performance of 80 agricultural residues to remove ammonium from aqueous solutions. However, only 11 samples showed more than 60% of removal efficiency, and Boston ivy leaves and phoenix tree leaves showed 100% removal efficiency at an initial NH_4-N concentration of 25 mg/L. The negative results of zeta potential for these two samples at natural pH suggested that the electrostatic attraction between the adsorbent surface and ammonium ions might relate to adsorption. The adsorption capacities of Boston ivy leaves and phoenix tree leaves were 6.71 mg/g and 4.62 mg/g, respectively (Liu et al., 2010b).

  However, the adsorption capacities of raw agricultural residues and plant materials are low, therefore physical and chemical modification is applied to enhance the adsorption capacity and removal efficiency. Yusof et al. (2010a) synthesised zeolite NaY from rice hush ash, a local agricultural waste, as an efficient alternative adsorbent for ammonium
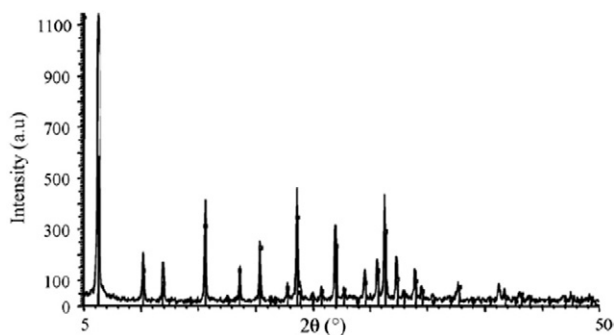

Fig. 8 – The X-ray diffraction (XRD) data of NaY from rice husk ash and was matched with sodium aluminum silicate hydrate zeolite Y (Yusof et al., 2010a).

removal and the performance of NaY was compared with natural mordenite in powdered (P-M) and granulated (G-M) forms. The dried rice husk was combusted at a temperature of 600°C for an hour in open air to produce amorphous silica in the ash, then was mixed with NaOH solution and heated at 100°C with autogenous pressure. The XRD data of NaY was matched with sodium aluminum silicate hydrate zeolite Y (Fig. 8). NaY had the highest CEC value with the lowest Si to Al (Si/Al) ratio according to EDX analysis. The adsorption capacity for NaY (42.37 mg/g) was found to be higher than that P-M (15.13 mg/g) and G-M (14.56 mg/g).

  Additionally, Zhu et al. (2016) developed a novel acidic adsorbent, which was prepared from avocado seeds via methanesulfonic acid activation (AAC-MA). The washed and dried avocado seeds were impregnated with 70 wt.% methanesulfonic acid for 17 hr with an impregnation ratio of 0.8. Then the methanesulfonic acid treated sample was dried at 95°C overnight and placed in a horizontal stainless steel reactor and carbonized at 700°C for 1.5 hr in a kiln and cooled down to room temperature in a flowing stream of nitrogen. SEM results showed that AAC-MA presented a high degree of cracks together with assorted size pores while the raw avocado seed exhibited an irregular non-porous surface, the pores of the adsorbent were covered uniformly after adsorbing ammonium (Fig. 9). Additionally, macrospores and large numbers of mesopores and micropores were found in AAC-MA. However, the ammonium adsorption capacity of AAC-MA was still low, only 5.4 mg/g.

  The factors, including initial ammonium concentration, contact time, adsorbent dosage, pH, and temperature could affect the removal efficiency of ammonium using agricultural residues and plant materials (Wahab et al., 2010; Yusof et al., 2010a; Zhu et al., 2016), and those effects were similar to the previous Sections 1.1 to 1.4. For instance, ammonium adsorption capacity of AAC-MA reached a peak at initial pH of 5, then decreased with increased pH. Fast ammonium uptake rate was observed at the initial removal stage. However, the regeneration of agricultural residues and plant materials was not presented.

  In this section, synthesised zeolite from rice husk ash has the highest adsorption capacity of 42.37 mg/g, and the rest of tested materials showed very low adsorption capacities,
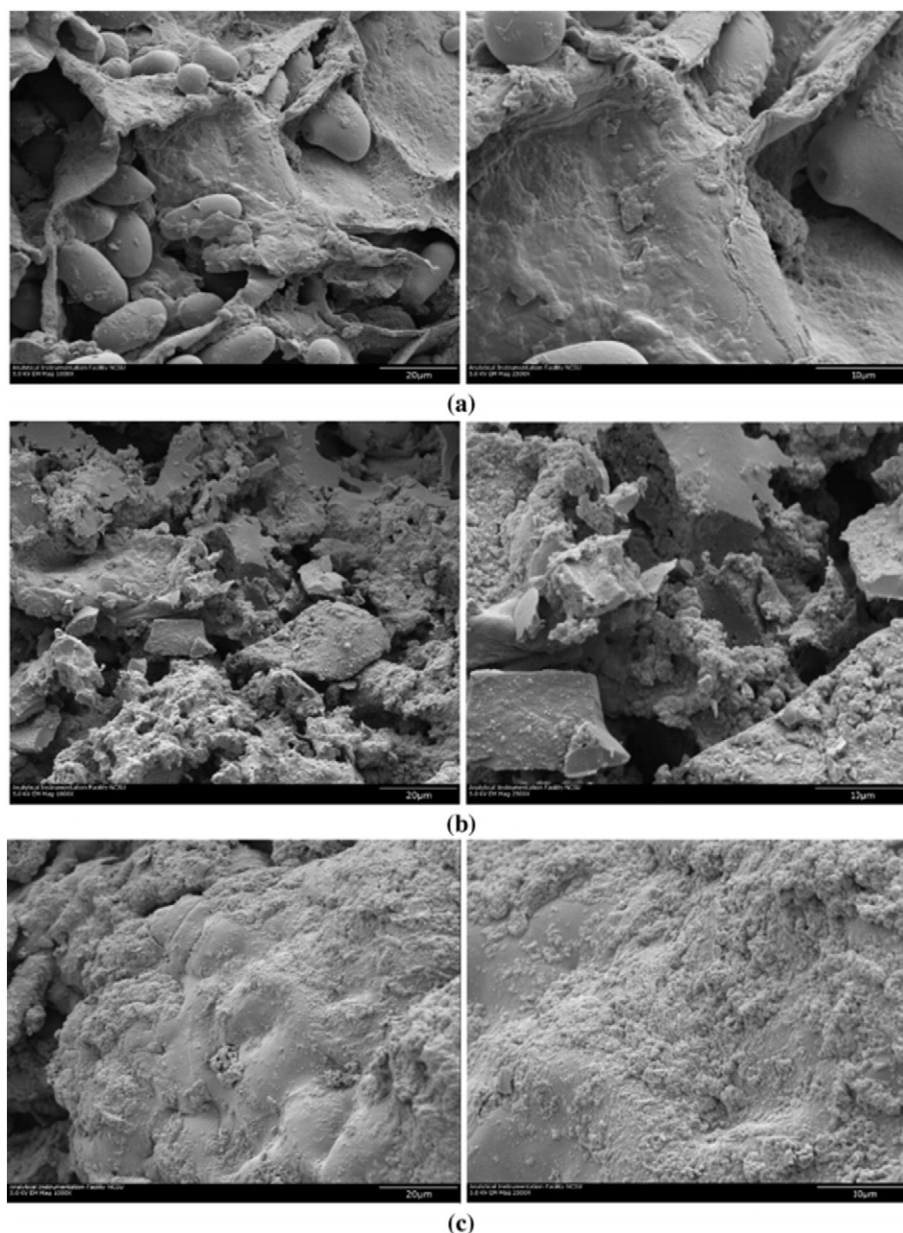
Fig. 9 – SEM images of (a) raw material of avocado kernel seeds, (b) methanesulfonic acid activation (AAC-MA) before adsorption and (c) AAC-MA after adsorption. Scale bars: 20 μm (left images) and 10 μm (right images) (Zhu et al., 2016).

ranging from 1.8 to 6.7 mg/g. Additionally, the price of rice husk is quite cheap, only about $100 per ton. Although the preparation requires the use of NaOH which costs about $350 per ton, the cost for the sources is still low. However, the preparation of synthesised zeolite from rice husk ash is time-consuming as it needs to be synthesised *via* seeding and aging techniques (Yusof et al., 2010b). Despite that, synthesised zeolite from rice husk ash will be best the option in this section due to its high adsorption capacity.

1.8. Nanoparticles

Recently, the development of nanoscience and nanotechnology has shown remarkable potential for the remediation of environmental problems (Rickerby and Morrison, 2007). Compared to traditional materials, nanostructure adsorbents exhibited much higher efficiency and faster rates in water treatment (Qu et al., 2013). A variety of efficient and eco-friendly nanomaterials have been developed and applied to remove ammonium and phosphate (Yang et al., 2013; Zare et al., 2016), heavy metals (Badruddoza et al., 2013) and organic compounds (Yang et al., 2012) from the water.

Zare et al. (2016) developed Fe_3O_4 nanoparticles as efficient adsorbents for the quick removal of ammonium ion from the solvent phase. The Fe_3O_4 nanoparticles were synthesized using a chemical co-precipitation method (Sadegh et al., 2014) and the structure of Fe_3O_4 nanoparticles was shown in Fig. 10. The removal rate of ammonium increased from 21.25% to

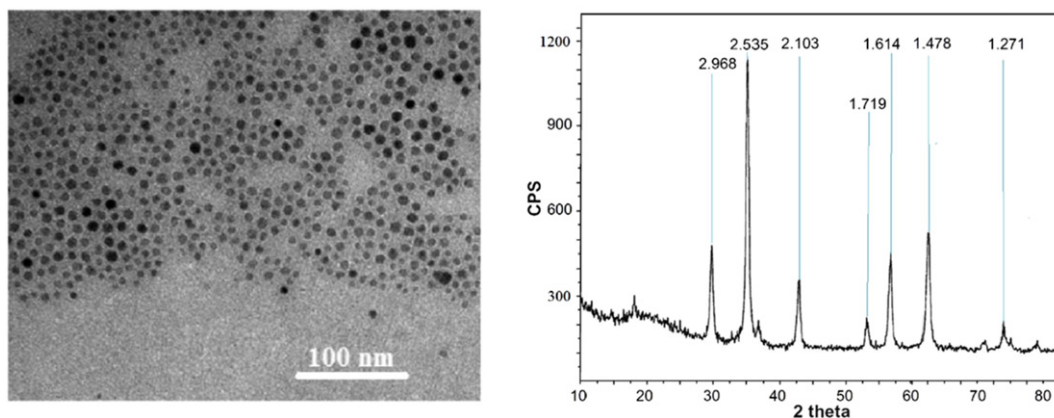**Fig. 10 – Representative TEM (Transmission electron microscopy) and XRD images of Fe$_3$O$_4$ nanoparticles (Zare et al., 2016).**

93.12% with the increase of pH from 1.0 to 10.0. The adsorption capacity of ammonium increased with increased initial ammonium concentrations but decreased with increased temperature. The optimised values are contact time 40 min, initial pH 10.0, temperature 298 K and initial ammonium concentration for adsorption 140 mg/L. The adsorption capacity of Fe$_3$O$_4$ nanoparticles was 133.21 mg/g (Table 9). In addition, the preparation of Fe$_3$O$_4$ nanoparticles is complicated where needs to use nitrogen gas and ammonia solution to adjust pH. The cost for preparing this material is not cheap, which includes FeCl$_2$·4H$_2$O and FeCl$_3$·6H$_2$O (both are the non-AR grade, $1000–2000 per ton).

2. Comparison of different adsorbents

The best adsorbents from among the adsorbents described in Sections 1.1 to 1.8 are further compared based on previously mentioned selection criteria to find a suitable adsorbent for large-scale removal of ammonium from water and wastewater (Fig. 11 and Table 10). The selected adsorbents are Turkish sepiolite, ceramic adsorbent, KU-2-8 resin, cotton stalks biochar, palygorskite nanocomposite, ferrosilicon alloy, synthetic

zeolite NaY from rice hush ash and Fe$_3$O$_4$ nanoparticles. To achieve large-scale removal of ammonium, adsorbents need to be abundant, cost-effective, easy to process and dispose of in an environmentally friendly manner. Among the adsorbents, Turkish sepiolite and rice husk ash are the most readily sourced and abundant, ferrosilicon alloy is the most cost-efficient adsorbent based on aluminium removal capacity per dollar spent, while Turkish sepiolite and palygorskite nanocomposite have the shortest removal times. These results show that Turkish sepiolite ranks higher than the other adsorbents due to its ready availability through abundant sources, ease of handling, fast removal time and relatively low cost. Although the removal capacity per g of sepiolite is low, the removal capacity per dollar is competitive when compared to many other adsorbents and its removal capacity can be improved by using physical and chemical treatments at relatively low cost. Although regeneration information has not been provided, past research shows it can be regenerated using NaCl solutions (Karadag et al., 2008. Additionally, the resultant ammonium adsorbed sepiolite has the potential for use as a slow-release fertilizer like ammonium adsorbed hydrogel (Wang et al., 2014). The next best option is KU-2-8 resin due to its good removal capacity and regeneration ability, relative cost-effectiveness,
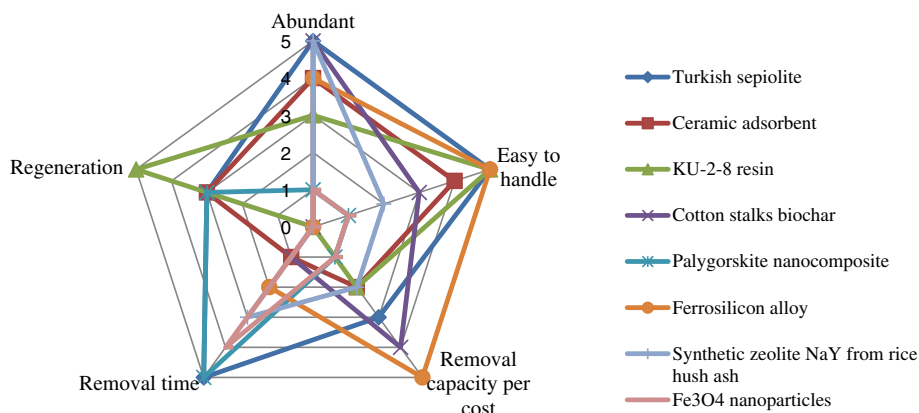

Fig. 11 – Comparison of different adsorbents.

Table 10 – Comparison of the selected adsorbents from Sections 1.1 to 1.8 and the most competitive adsorbent is highlighted in italic script (detail information see Appendix A Tables S1–S3).

Adsorbents	Abundant	Handle (preparation and application)	Removal capacity per cost (mg/$)	Removal time	Regeneration	Application in real conditions or other application (extra points)	Total score
Turkish sepiolite (Tacir)	5	5	3	5	3	–	21
Ceramic adsorbent	4	4	2	1	3	–	14
KU-2-8	3	5	2	–	5	1	16
Cotton stalks	5	3	4	1	–	–	13
Palygorskite nanocomposite	1	1	1	5	3	1	12
Ferrosilicon alloy	4	5	5	2	–	–	16
Synthesised zeolite from rice husk ash	5	2	2	3	–	–	12
Fe₃O₄ nanoparticles	1	1	1	4	–	–	7

ease of use and application under real conditions. Ferrosilicon alloy has the same ranking as KU-2-8 because of its abundance, ease of application and relatively low cost. Although information on regeneration is not provided, it can be investigated by proxy due to its similar components to zeolite. The next options are ceramic adsorbent and cotton stalks, followed by palygorskite nanocomposite and synthesised zeolite from rice husk ash. Fe_3O_4 nanoparticles are the least favoured because of its limited sources, high cost, and complicated preparation. Given the above analysis, Turkish sepiolite shows to be the most efficient, cost competitive, environmentally-friendly adsorbent for large scale commercial and wastewater treatment plants. Other suitable options are KU-2-8 resin and ceramic adsorbent.

3. Conclusion and future perspectives

Excessive ammonium in water streams and effluent can cause eutrophication in freshwater and coastal areas, leading to highly undesirable changes in ecosystem structure and function, as well as contributing to various health problems in animals and humans. Among the technologies for removing ammonium from water and wastewater, adsorption and ion exchange technique shows more advantages than other techniques because of its low-cost, ease of operation and high ammonium removal efficiency.

This review presented numerous materials that have been developed and used in ammonium removal. The study shows that various adsorbents had quite different adsorption capacities for ammonium from cotton stalks biochar (518.9 mg/g) to fly ash (0.297 mg/g). Studies have shown that most zeolites and clays have their respective adsorption capacity increased after physical and chemical treatments. However, further optimization is required to reduce overall operating costs. Polymeric ion exchangers have high absorption capacity and good chemical and mechanical stability compared to natural and synthetic zeolites. However, they are not as cost competitive as natural zeolites. Carbon-based adsorbents are also very effective at ammonium removal but their regeneration needs further testing. Hydrogels have a high adsorption capacity, high kinetics, and good regeneration. However, their preparation is complex and needs improvement. The study also presents the most suitable adsorbent for the removal of ammonium from water and wastewater, which is Turkish sepiolite due to its abundance, simplicity of use, fast removal times, and low cost. Applying Turkish sepiolite is recommended as an efficient, cost competitive, and environmental friendly adsorbent for large scale commercial and wastewater treatment plants. Additionally, other adsorbents like KU-2-8 resin and ferrosilicon alloy are excellent alternatives for removing ammonium.

Among the many studies examined which used the adsorption and ion exchange technique, the following was found: (a) ammonium removal capacities of different adsorbents increased with increased initial ammonium concentrations and increased amounts of adsorbents; (b) the removal rate of ammonium was initially fast, then gradually declined with increased contact time; (c) particle size, pH, competing ions and their concentrations can affect ammonium removal efficiency; (d) ammonium adsorption was spontaneous and exothermic (it is temperature dependent); and (e) the presence of organic acids can affect ammonium removal efficiency (Alshameri et al., 2014; Chen et al., 2002; Imchuen et al., 2016; Khosravi et al., 2014; Lin et al., 2013; Millar et al., 2016; Shahrooie et al., 2015; Shi et al., 2013; Widiastuti et al., 2011; Yusof et al., 2010a; Zare et al., 2016; Zhang et al., 2011c). Therefore, selecting a suitable adsorbent for effectively removing ammonium is not easy. Many experiments can provide good results under laboratory conditions but may not give very satisfactory results in the field. Some studies presented in this paper tested adsorbents in the removal of ammonium from wastewater under field conditions.

In the future, continuous testing of adsorbents in the removal of ammonium from industrial effluent under field conditions needs to be conducted. Additionally, field condition testing should be used in combination with mechanistic modelling. This would add to our understanding of adsorption mechanisms. Finally, it is important to investigate the reusability and regeneration of adsorbents. This process not only increases the number of times materials can be reused but also makes them more environmentally safe post disposal. Other applications of ammonium adsorbed materials are also encouraged, like using them as slow-release fertilizers.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2017.09.009.

REFERENCES

Alshameri, A., Ibrahim, A., Assabri, A.M., Lei, X., Wang, H., Yan, C., 2014. The investigation into the ammonium removal performance of Yemeni natural zeolite: modification, ion exchange mechanism, and thermodynamics. Powder Technol. 258, 20–31.

ANZECC, 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council/Agriculture and Resource Management Council of Australia and New Zealand, Canberra.

Augspurger, T., Keller, A.E., Black, M.C., Cope, W.G., Dwyer, F.J., 2003. Water quality guidance for protection of freshwater mussels (Unionidae) from ammonia exposure. Environ. Toxicol. Chem. 22, 2569–2575.

Badruddoza, A.Z.M., Shawon, Z.B.Z., Rahman, M.T., Hao, K.W., Hidajat, K., Uddin, M.S., 2013. Ionically modified magnetic nanomaterials for arsenic and chromium removal from water. Chem. Eng. J. 225, 607–615.

Balci, S., Dincel, Y., 2002. Ammonium ion adsorption with sepiolite: use of transient uptake method. Chem. Eng. Process. 41, 79–85.

Batley, G.E., Simpson, S.L., 2009. Development of guidelines for ammonia in estuarine and marine water systems. M. Environ. Pollut. 58, 1472–1476.

Bermejo, M., Cantero, F., Cocero, M., 2008. Supercritical water oxidation of feeds with high ammonia concentrations: Pilot plant experimental results and modeling. Chem. Eng. J. 137, 542–549.

Bernet, N., Delgenes, N., Akunna, J.C., Delgenes, J., Moletta, R., 2000. Combined anaerobic–aerobic SBR for the treatment of piggery wastewater. Water Res. 34, 611–619.

Bhatnagar, A., Sillanpaa, M., 2011. A review of emerging adsorbents for nitrate removal from water. Chem. Eng. J. 168, 493–504.

Bhatnagar, A., Hogland, W., Marques, M., Sillanpää, M., 2013. An overview of the modification methods of activated carbon for its water treatment applications. Chem. Eng. J. 219, 499–511.

Bodalo, A., Gomez, J.-L., Gomez, E., Leon, Gerardo, Tejera, M., 2005. Ammonium removal from aqueous solutions by reverse osmosis using cellulose acetate membranes. Desalination 184, 149–155.

Booker, N., Cooney, E., Priestley, A., 1996. Ammonia removal from sewage using natural Australian zeolite. Water Sci. Technol. 34, 17–24.

Boopathy, R., Karthikeyan, S., Mandal, A.B., Sekaran, G., 2013. Adsorption of ammonium ion by coconut shell-activated carbon from aqueous solution: kinetic, isotherm, and thermodynamic studies. Environ. Sci. Pollut. Res. 20, 533–542.

Britto, D.T., Kronzucker, H.J., 2002. NH4+ toxicity in higher plants: a critical review. J. Plant Physiol. 159, 567–584.

Brooks, M.A., 1999. Breakpoint Chlorination as an Alternate Means for Ammoia-Nitrogen Removal at a Water Reclamation Plant. Virginia Polytechnic Institute and State University.

Bulut, Y., Tez, Z., 2007. Removal of heavy metals from aqueous solution by sawdust adsorption. J. Environ. Sci. 19, 160–166.

Camargo, J.A., Alonso, Á., 2006. Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. Environ. Int. 32, 831–849.

Cancino-Madariaga, B., Hurtado, C.F., Ruby, R., 2011. Effect of pressure and pH in ammonium retention for nanofiltration and reverse osmosis membranes to be used in recirculation aquaculture systems (RAS). Aquac. Eng. 45, 103–108.

Carlson, J.C., Anderson, J.C., Low, J.E., Cardinal, P., MacKenzie, S.D., Beattie, S.A., et al., 2013. Presence and hazards of nutrients and emerging organic micropollutants from sewage lagoon discharges into Dead Horse Creek, Manitoba, Canada. Sci. Total Environ. 445–446, 64–78.

CCME, 2007. Canadian Water Quality Guidelines for the Protection of Aquatic Life. Canadian Council of Ministers of the Environment, Canada.

Charrois, J.W., Hrudey, S.E., 2007. Breakpoint chlorination and free-chlorine contact time: implications for drinking water N-nitrosodimethylamine concentrations. Water Res. 41, 674–682.

Chen, P.J., Chua, M.L., Zhang, B., 2002. Effects of competitive ions, humic acid, and pH on removal of ammonium and phosphorous from the synthetic industrial effluent by ion exchange resins. Waste Manag. 22, 711–719.

Cheng, Y., Huang, T., Shi, X., Wen, G., Sun, Y., 2017. Removal of ammonium ion from water by Na-rich birnessite: performance and mechanisms. J. Environ. Sci. 57, 402–410.

Clark, R.N., Swayze, G.A., Gallagher, A.J., King, T.V., Calvin, W.M., 1993. The US Geological Survey, Digital Spectral Library: Version 1 (0.2 to 3.0 um). Geological Survey (US).

Darvishi Cheshmeh Soltani, R., Safari, M., Rezaee, A., Godini, H., 2015. Application of a compound containing silica for removing ammonium in aqueous media. Environ. Prog. Sustain. Energy 34, 105–111.

Du, X., Zhang, R., Gan, Z., Bi, J., 2013. Treatment of high strength coking wastewater by supercritical water oxidation. Fuel 104, 77–82.

Erdoğan, B.C., Ülkü, S., 2011. Ammonium sorption by Gördes clinoptilolite rich mineral specimen. Appl. Clay Sci. 54, 217–225.

EU, 2006. Directive 2006/44/EC of the European Parliament and of the Council on the Quality of Fresh Waters Needing Protection or Improvement in Order to Support Fish Life. Off. J. Eur. Union 20–31.

Feng, S., Xie, S., Zhang, X., Yang, Z., Ding, W., Liao, X., et al., 2012. Ammonium removal pathways and microbial community in GAC-sand dual media filter in drinking water treatment. J. Environ. Sci. 24, 1587–1593.

Gao, F., Xue, Y., Deng, P., Cheng, X., Yang, K., 2015. Removal of aqueous ammonium by biochars derived from agricultural residuals at different pyrolysis temperatures. Chem. Speciat. Bioavailab. 27, 92–97.

Green, M., Mels, A., Lahav, O., Tarre, S., 1996. Biological-ion exchange process for ammonium removal from secondary effluent. Water Sci. Technol. 34, 449–458.

Guo, J., 2016. Adsorption characteristics and mechanisms of high-levels of ammonium from swine wastewater using natural and MgO modified zeolites. Desalin. Water Treat. 57, 5452–5463.

Guo, X., Zeng, L., Jin, X., 2013. Advanced regeneration and fixed-bed study of ammonium and potassium removal from anaerobic digested wastewater by natural zeolite. J. Environ. Sci. 25, 954–961.

Gupta, V.K., Ali, I., Saleh, T.A., Siddiqui, M., Agarwal, S., 2013a. Chromium removal from water by activated carbon developed from waste rubber tires. Environ. Sci. Pollut. Res. 20, 1261–1268.

Gupta, V.K., Kumar, R., Nayak, A., Saleh, T.A., Barakat, M., 2013b. Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. Adv. Colloid Interf. Sci. 193, 24–34.

Gupta, V., Sadegh, H., Yari, M., Shahryari Ghoshekandi, R., Maazinejad, B., Chahardori, M., 2015. Removal of ammonium

ions from wastewater: a short review in development of efficient methods. Glob. J. Environ. Sci. Manag. 1, 149–158.

Guštin, S., Marinšek-Logar, R., 2011. Effect of pH, temperature and air flow rate on the continuous ammonia stripping of the anaerobic digestion effluent. Process. Saf. Environ. Prot. 89, 61–66.

Hale, S.E., Alling, V., Martinsen, V., Mulder, J., Breedveld, G.D., Cornelissen, G., 2013. The sorption and desorption of phosphate-P, ammonium-N and nitrate-N in cacao shell and corn cob biochars. Chemosphere 91, 1612–1619.

Halim, M.T., Latif, A.I., 2013. Ammonia removal from aqueous solution using organic acid modified activated carbon. World Appl. Sci. J. 24, 1–6.

Halim, A.A., Aziz, H.A., Johari, M.A.M., Ariffin, K.S., 2010. Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment. Desalination 262, 31–35.

Halling-Sørensen, B., Jorgensen, S.E., 1993. The removal of nitrogen compounds from wastewater. Elsevier.

Häyrynen, K., Pongrácz, E., Väisänen, V., Pap, N., Mänttäri, M., Langwaldt, J., Keiski, R.L., 2009. Concentration of ammonium and nitrate from mine water by reverse osmosis and nanofiltration. Desalination 240, 280–289.

Hou, J., Huang, L., Yang, Z., Zhao, Y., Deng, C., Chen, Y., Li, X., 2016. Adsorption of ammonium on biochar prepared from giant reed. Environ. Sci. Pollut. Res. 1–9.

Huang, H., Huang, L., Zhang, Q., Jiang, Y., Ding, L., 2015a. Chlorination decomposition of struvite and recycling of its product for the removal of ammonium–nitrogen from landfill leachate. Chemosphere 136, 289–296.

Huang, H., Yang, L., Xue, Q., Liu, J., Hou, L., Ding, L., 2015b. Removal of ammonium from swine wastewater by zeolite combined with chlorination for regeneration. J. Environ. Manag. 160, 333–341.

Imchuen, N., Lubphoo, Y., Chyan, J.-M., Padungthon, S., Liao, C.-H., 2016. Using cation exchange resin for ammonium removal as part of sequential process for nitrate reduction by nanoiron. Sustain. Environ. Res. 26, 156–160.

Irani, M., Ismail, H., Ahmad, Z., Fan, M., 2015. Synthesis of linear low-density polyethylene-g-poly (acrylic acid)-co-starch/organo-montmorillonite hydrogel composite as an adsorbent for removal of Pb(II) from aqueous solutions. J. Environ. Sci. 27, 9–20.

Ismadji, S., Tong, D.S., Soetaredjo, F.E., Ayucitra, A., Yu, W.H., Zhou, C.H., 2016. Bentonite hydrochar composite for removal of ammonium from Koi fish tank. Appl. Clay Sci. 119, 146–154.

Jorgemsen, T.C., Weatherley, L.R., 2003. Ammonia removal from wastewater by ion exchange in the presence of organic contaminants. Water Res. 37, 1723–1728.

Juan, R., Hernández, S., Andrés, J.M., Ruiz, C., 2009. Ion exchange uptake of ammonium in wastewater from a Sewage Treatment Plant by zeolitic materials from fly ash. J. Hazard. Mater. 161, 781–786.

Kang, D., Yu, X., Ge, M., Xiao, F., Xu, H., 2017. Novel Al-doped carbon nanotubes with adsorption and coagulation promotion for organic pollutant removal. J. Environ. Sci. 54, 1–12.

Karadag, D., Tok, S., Akgul, E., Turan, M., Ozturk, M., Demir, A., 2008. Ammonium removal from sanitary landfill leachate using natural Gördes clinoptilolite. J. Hazard. Mater. 153, 60–66.

Kaušpėdienė, D., Snukiškis, J., 2006. Sorption kinetics of ammonia and ammonium ions on gel and macroporous sulphonic acid cation exchangers. Sep. Purif. Technol. 50, 347–353.

Khosravi, A., Esmhosseini, M., Khezri, S., 2014. Removal of ammonium ion from aqueous solutions using natural zeolite: kinetic, equilibrium and thermodynamic studies. Res. Chem. Intermed. 40, 2905–2917.

Kizito, S., Wu, S., Kipkemoi Kirui, W., Lei, M., Lu, Q., Bah, H., Dong, R., 2015. Evaluation of slow pyrolyzed wood and rice husks biochar for adsorption of ammonium nitrogen from piggery

manure anaerobic digestate slurry. Sci. Total Environ. 505, 102–112.

Kritzer, P., Dinjus, E., 2001. An assessment of supercritical water oxidation (SCWO): existing problems, possible solutions and new reactor concepts. Chem. Eng. J. 83, 207–214.

Kuokkanen, E., Repo, E., Warchoł, J.K., Sillanpää, M., 2016. Ammonium adsorption from synthetic and real mining wastewaters by eight-clay based adsorbents. Desalin. Water Treat. 57, 8289–8301.

La Cour Jansen, J., Spliid, H., Hansen, T.L., Svärd, Å., Christensen, T.H., 2004. Assessment of sampling and chemical analysis of source-separated organic household waste. Waste Manag. 24, 541–549.

Lei, L., Li, X., Zhang, X., 2008. Ammonium removal from aqueous solutions using microwave-treated natural Chinese zeolite. Sep. Purif. Technol. 58, 359–366.

Li, L., Quinlivan, P.A., Knappe, D.R.U., 2002. Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. Carbon 40, 2085–2100.

Lian, F., Chang, C., Du, Y., Zhu, L., Xing, B., Liu, C., 2012. Adsorptive removal of hydrophobic organic compounds by carbonaceous adsorbents: a comparative study of waste-polymer-based, coal-based activated carbon, and carbon nanotubes. J. Environ. Sci. 24, 1549–1558.

Liao, P.H., Chen, A., Lo, K.V., 1995. Removal of nitrogen from swine manure wastewaters by ammonia stripping. Bioresour. Technol. 54, 17–20.

Liao, Z.L., Chen, H., Zhu, B.R., Li, H.Z., 2015. Combination of powdered activated carbon and powdered zeolite for enhancing ammonium removal in micro-polluted raw water. Chemosphere 134, 127–132.

Lin, L., Chen, J., Xu, Z., Yuan, S., Cao, M., Liu, H., Lu, X., 2009. Removal of ammonia nitrogen in wastewater by microwave radiation: a pilot-scale study. J. Hazard. Mater. 168, 862–867.

Lin, L., Lei, Z., Wang, L., Liu, X., Zhang, Y., Wan, C., et al., 2013. Adsorption mechanisms of high-levels of ammonium onto natural and NaCl-modified zeolites. Sep. Purif. Technol. 103, 15–20.

Liu, H., Dong, Y., Liu, Y., Wang, H., 2010a. Screening of novel low-cost adsorbents from agricultural residues to remove ammonia nitrogen from aqueous solution. J. Hazard. Mater. 178, 1132–1136.

Liu, H., Dong, Y., Wang, H., Liu, Y., 2010b. Adsorption behavior of ammonium by a bioadsorbent — Boston ivy leaf powder. J. Environ. Sci. 22, 1513–1518.

Liu, H.B., Peng, S.C., Shu, L., Chen, T.H., Bao, T., Frost, R.L., 2013a. Effect of Fe_3O_4 addition on removal of ammonium by zeolite NaA. J. Colloid Interface Sci. 390, 204–210.

Liu, J., Su, Y., Li, Q., Yue, Q.Y., Gao, B.Y., 2013b. Preparation of wheat straw based superabsorbent resins and their applications as adsorbents for ammonium and phosphate removal. Bioresour. Technol. 143, 32–39.

Liu, Z., Xue, Y., Gao, F., Cheng, X., Yang, K., 2016. Removal of ammonium from aqueous solutions using alkali-modified biochars. Chem. Speciat. Bioavailab. 28, 26–32.

Luukkonen, T., Sarkkinen, M., Kemppainen, K., Rämö, J., Lassi, U., 2016. Metakaolin geopolymer characterization and application for ammonium removal from model solutions and landfill leachate. Appl. Clay Sci. 119 (Part 2), 266–276.

Malovanyy, A., Sakalova, H., Yatchyshyn, Y., Plaza, E., Malovanyy, M., 2013. Concentration of ammonium from municipal wastewater using ion exchange process. Desalination 329, 93–102.

Malovanyy, A., Plaza, E., Trela, J., Malovanyy, M., 2014. Combination of ion exchange and partial nitritation/Anammox process for ammonium removal from mainstream municipal wastewater. Water Sci. Technol. 70, 144–151.

Marañón, E., Ulmanu, M., Fernández, Y., Anger, I., Castrillón, L., 2006. Removal of ammonium from aqueous solutions with volcanic tuff. J. Hazard. Mater. 137, 1402–1409.

Marrone, P.A., Hodes, M., Smith, K.A., Tester, J.W., 2004. Salt precipitation and scale control in supercritical water oxidation—Part B: commercial/full-scale applications. J. Supercrit. Fluids 29, 289–312.

Mazloomi, F., Jalali, M., 2016. Ammonium removal from aqueous solutions by natural Iranian zeolite in the presence of organic acids, cations and anions. J. Environ. Chem. Eng. 4, 240–249.

Millar, G.J., Winnett, A., Thompson, T., Couperthwaite, S.J., 2016. Equilibrium studies of ammonium exchange with Australian natural zeolites. J. Water Process Eng. 9, 47–57.

Moradi, O., 2016. Applicability comparison of different models for ammonium ion adsorption by multi-walled carbon nanotube. Arab. J. Chem. 9, S1170–S1176.

Moradi, O., Zare, K., 2013. Adsorption of ammonium ion by multi-walled carbon nanotube: kinetics and thermodynamic studies. Fullerenes, Nanotubes, Carbon Nanostruct. 21, 449–459.

Mubarak, N.M., Sahu, J.N., Abdullah, E.C., Jayakumar, N.S., 2016. Rapid adsorption of toxic Pb(II) ions from aqueous solution using multiwall carbon nanotubes synthesized by microwave chemical vapor deposition technique. J. Environ. Sci. 45, 143–155.

Nolan, B.T., Hitt, K.J., 2006. Vulnerability of shallow groundwater and drinking-water wells to nitrate in the United States. Environ. Sci. Technol. 40, 7834–7840.

Nollet, L.M.L., 2013. Handbook of water analysis. CRC Press Inc.

Noworyta, A., Koziol, T., Trusek-Holownia, A., 2003. A system for cleaning condensates containing ammonium nitrate by the reverse osmosis method. Desalination 156, 397–402.

Panic, V.V., Madzarevic, Z.P., Volkov-Husovic, T., Velickovic, S.J., 2013. Poly (methacrylic acid) based hydrogels as sorbents for removal of cationic dye basic yellow 28: kinetics, equilibrium study and image analysis. Chem. Eng. J. 217, 192–204.

Park, S.J., Kim, B.J., 2005. Ammonia removal of activated carbon fibers produced by oxyfluorination. J. Colloid Interface Sci. 291, 579–599.

Pressley, T.A., Bishop, D.F., Roan, S.G., 1972. Ammonia-nitrogen removal by breakpoint chlorination. Environ. Sci. Technol. 6, 622–628.

Qu, X., Alvarez, P.J.J., Li, Q., 2013. Applications of nanotechnology in water and wastewater treatment. Water Res. 47, 3931–3946.

Quan, X., Liu, X., Bo, L., Chen, S., Zhao, Y., Cui, X., 2004. Regeneration of acid orange 7-exhausted granular activated carbons with microwave irradiation. Water Res. 38, 4484–4490.

Rabah, F.K., Darwish, M.S., 2013. Using microwave energy for the removal of ammonia from municipal wastewater: continuous flow lab-scale system. Environ. Nat. Resour. Res. 3, 24.

Rickerby, D.G., Morrison, M., 2007. Nanotechnology and the environment: a European perspective. Sci. Technol. Adv. Mater. 8, 19–24.

Ruiz, R., Blanco, C., Pesquera, C., González, F., Benito, I., López, J.L., 1997. Zeolitization of a bentonite and its application to the removal of ammonium ion from waste water. Appl. Clay Sci. 12, 73–83.

Sadegh, H., Shahryari-ghoshekandi, R., Kazemi, M., 2014. Study in synthesis and characterization of carbon nanotubes decorated by magnetic iron oxide nanoparticles. Int. Nano Lett. 4, 129–135.

Saltali, K., Sari, A., Aydin, M., 2007. Removal of ammonium ion from aqueous solution by natural Turkish (Yıldızeli) zeolite for environmental quality. J. Hazard. Mater. 141, 258–263.

Shahrooie, B., Rajabi, L., Derakhshan, A.A., Keyhani, M., 2015. Fabrication, characterization and statistical investigation of a new starch-based hydrogel nanocomposite for ammonium adsorption. J. Taiwan Inst. Chem. Eng. 51, 201–215.

Shi, M., Wang, Z., Zheng, Z., 2013. Effect of Na$^+$ impregnated activated carbon on the adsorption of NH^{+4}-N from aqueous solution. J. Environ. Sci. 25, 1501–1510.

Shigemoto, N., Hayashi, H., Miyaura, K., 1993. Selective formation of Na-X zeolite from coal fly ash by fusion with sodium hydroxide prior to hydrothermal reaction. J. Mater. Sci. 28, 4781–4786.

Sica, M., Duta, A., Teodosiu, C., Draghici, C., 2014. Thermodynamic and kinetic study on ammonium removal from a synthetic water solution using ion exchange resin. Clean Technol. Environ. 16, 351–359.

Siegrist, H., 1996. Nitrogen removal from digester supernatant-comparison of chemical and biological methods. Water Sci. Technol. 34, 399–406.

Smith, V.H., Tilman, G.D., Nekola, J.C., 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environ. Pollut. 100, 179–196.

Soetardji, J.P., Claudia, J.C., Ju, Y.-H., Hriljac, J.A., Chen, T.-Y., Soetaredjo, F.E., Santoso, S.P., Kurniawan, A., Ismadji, S., 2015. Ammonia removal from water using sodium hydroxide modified zeolite mordenite. RSC Adv. 5, 83689–83699.

Sperling, L.H., 1984. Interpenetrating polymer networks and related materials. Polymer 18, 3593–3595.

Splettstoesser, T., 2016. The microporous molecular structure of ZSM-5 zeolite.

Thornton, A., Pearce, P., Parsons, S.A., 2007. Ammonium removal from solution using ion exchange on to MesoLite, an equilibrium study. J. Hazard. Mater. 147, 883–889.

Turan, M., 2016. Application of Nanoporous Zeolites for the Removal of Ammonium from Wastewaters: A Review, Low-Dimensional and Nanostructured Materials and Devices. Springer, pp. 477–504.

Uğurlu, M., Karaoğlu, M.H., 2011. Adsorption of ammonium from an aqueous solution by fly ash and sepiolite: isotherm, kinetic and thermodynamic analysis. Microporous Mesoporous Mater. 139, 173–178.

Uludag-Demirer, S., Demirer, G., Chen, S., 2005. Ammonia removal from anaerobically digested dairy manure by struvite precipitation. Process Biochem. 40, 3667–3674.

USEPA, 1999. Update of Ambient Water Quality Criteria for Ammonia. US Environmental Protection Agency Office of Water, Washington, DC, USA.

USEPA, 2006. National Recommended Water Quality Criteria. United States Environmental Protection Agency.

Vassileva, P., Tzvetkova, P., Nickolov, R., 2009. Removal of ammonium ions from aqueous solutions with coal-based activated carbons modified by oxidation. Fuel 88, 387–390.

Wahab, M.A., Jellali, S., Jedidi, N., 2010. Effect of temperature and pH on the biosorption of ammonium onto Posidonia oceanica fibers: Equilibrium, and kinetic modeling studies. Bioresour. Technol. 101, 8606–8615.

Wajima, T., Munakata, K., 2011. Material conversion from paper sludge ash in NaOH solution to synthesize adsorbent for removal of Pb^{2+}, NH^{4+} and PO$_4^{3-}$ from aqueous solution. J. Environ. Sci. 23, 718–724.

Wang, Y., Liu, S., Xu, Z., Han, T., Chuan, S., Zhu, T., 2006. Ammonia removal from leachate solution using natural Chinese clinoptilolite. J. Hazard. Mater. 136, 735–740.

Wang, Y.F., Lin, F., Pang, W.Q., 2007. Ammonium exchange in aqueous solution using Chinese natural clinoptilolite and modified zeolite. J. Hazard. Mater. 142, 160–164.

Wang, X., Lü, S., Gao, C., Xu, X., Zhang, X., Bai, X., et al., 2014. Highly efficient adsorption of ammonium onto palygorskite nanocomposite and evaluation of its recovery as a multifunctional slow-release fertilizer. Chem. Eng. J. 252, 404–414.

Wang, Z., Guo, H., Shen, F., Yang, G., Zhang, Y., Zeng, Y., et al., 2015a. Biochar produced from oak sawdust by Lanthanum (La)-involved pyrolysis for adsorption of ammonium (NH4+), nitrate (NO3−), and phosphate (PO43−). Chemosphere 119, 646–653.

Wang, B., Lehmann, J., Hanley, K., Hesrin, R., Enders, A., 2015b. Adsorption and desorption of ammonium by maple wood biochar as a function of oxidation and pH. Chemosphere 138, 120–126.

Wang, X.L., Qiao, B., Li, S.M., Li, J.S., 2016. Using natural Chinese zeolite to remove ammonium from rainfall runoff following

urea fertilization of a paddy rice field. Environ. Sci. Pollut. Res. 23, 5342–5351.

Weatherley, L.R., Miladinovic, N.D., 2004. Comparison of the ion exchange uptake of ammonium ion onto New Zealand clinoptilolite and mordenite. Water Res. 38, 4305–4312.

Widiastuti, N., Wu, H., Ang, H.M., Zhang, D., 2011. Removal of ammonium from greywater using natural zeolite. Desalination 277, 15–23.

Wu, D.Y., Zhang, B.H., Li, C.J., Zhang, Z.J., Kong, H.N., 2006. Simultaneous removal of ammonium and phosphate by zeolite synthesized from fly ash as influenced by salt treatment. J. Colloid Interface Sci. 304, 300–306.

Xue, R., Donovan, A., Zhang, H., Ma, Y., Adams, C., Yang, J., et al., 2017. Simultaneous removal of ammonia and N-nitrosamine precursors from high ammonia water by zeolite and powdered activated carbon. J. Environ. Sci. https://doi.org/10.1016/j.jes.2017.02.010.

Yagub, M.T., Sen, T.K., Afroze, S., Ang, H.M., 2014. Dye and its removal from aqueous solution by adsorption: a review. Adv. Colloid Interf. Sci. 209, 172–184.

Yang, X., Chen, C., Li, J., Zhao, G., Ren, X., Wang, X., 2012. Graphene oxide-iron oxide and reduced graphene oxide–iron oxide hybrid materials for the removal of organic and inorganic pollutants. RSC Adv. 2, 8821–8826.

Yang, J., Zeng, Q., Peng, L., Lei, M., Song, H., Tie, B., Gu, J., 2013. La-EDTA coated Fe3O4 nanomaterial: preparation and application in removal of phosphate from water. J. Environ. Sci. 25, 413–418.

Yao, Y., Gao, B., Chen, J., Zhang, M., Inyang, M., Li, Y., et al., 2013. Engineered carbon (biochar) prepared by direct pyrolysis of Mg-accumulated tomato tissues: characterization and phosphate removal potential. Bioresour. Technol. 138, 8–13.

Yin, C.Y., Aroua, M.K., Daud, W.M.A.W., 2007. Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. Sep. Purif. Technol. 52, 403–415.

Yunnen, C., Changshi, X., Jinxia, N., 2016. Removal of ammonia nitrogen from wastewater using modified activated sludge. Pol. J. Environ. Stud. 25.

Yusof, A.M., Keat, L.K., Ibrahim, Z., Majid, Z.A., Nizam, N.A., 2010a. Kinetic and equilibrium studies of the removal of ammonium ions from aqueous solution by rice husk ash-synthesized zeolite Y and powdered and granulated forms of mordenite. J. Hazard. Mater. 174, 380–385.

Yusof, A.M., Nizam, N.A., Rashid, N.A.A., 2010b. Hydrothermal conversion of rice husk ash to faujasite-types and NaA-type of zeolites. J. Porous. Mater. 17, 39–47.

Zare, K., Sadegh, H., Shahryari-ghoshekandi, R., Asif, M., Tyagi, I., Agarwal, S., Gupta, V.K., 2016. Equilibrium and kinetic study of ammonium ion adsorption by Fe₃O₄ nanoparticles from aqueous solutions. J. Mol. Liq. 213, 345–350.

Zhang, B.-h., Wu, Y., Wang, C., He, S.-b., Zhang, Z.-j., Kong, H.-n., 2007. Simultaneous removal of ammonium and phosphate by zeolite synthesized from coal fly ash as influenced by acid treatment. J. Environ. Sci. 19, 540–545.

Zhang, M., Zhang, H., Xu, D., Han, L., Niu, D., Tian, B., et al., 2011a. Removal of ammonium from aqueous solutions using zeolite synthesized from fly ash by a fusion method. Desalination 271, 111–121.

Zhang, M., Zhang, H., Xu, D., Han, L., Niu, D., Zhang, L., et al., 2011b. Ammonium removal from aqueous solution by zeolites

synthesized from low-calcium and high-calcium fly ashes. Desalination 277, 46–53.

Zhang, T., Li, Q., Ding, L., Ren, H., Xu, K., Wu, Y., Sheng, D., 2011c. Modeling assessment for ammonium nitrogen recovery from wastewater by chemical precipitation. J. Environ. Sci. 23, 881–890.

Zhang, L., Zhang, H., Guo, W., Tian, Y., 2013. Sorption characteristics and mechanisms of ammonium by coal by-products: slag, honeycomb-cinder and coal gangue. Int. J. Environ. Sci. Technol. 10, 1309–1318.

Zhang, C., Cano, G.G., Braun, P.V., 2014. Linear and fast hydrogel glucose sensor materials enabled by volume resetting agents. Adv. Mater. 26, 5678–5683.

Zhang, H., Li, A., Zhang, W., Shuang, C., 2016. Combination of Na-modified zeolite and anion exchange resin for advanced treatment of a high ammonia–nitrogen content municipal effluent. J. Colloid Interface Sci. 468, 128–135.

Zhao, Y., Yang, Y., Yang, S., Wang, Q., Feng, C., Zhang, Z., 2013. Adsorption of high ammonium nitrogen from wastewater using a novel ceramic adsorbent and the evaluation of the ammonium-adsorbed-ceramic as fertilizer. J. Colloid Interface Sci. 393, 264–270.

Zhao, K., Zhang, X., Wei, J., Li, J., Zhou, X., Liu, D., et al., 2015. Calcium alginate hydrogel filtration membrane with excellent anti-fouling property and controlled separation performance. J. Membr. Sci. 492, 536–546.

Zhao, Y., Niu, Y., Hu, X., Xi, B., Peng, X., Liu, W., et al., 2016. Removal of ammonium ions from aqueous solutions using zeolite synthesized from red mud. Desalin. Water Treat. 57, 4720–4731.

Zheng, Y., Wang, A., 2009. Evaluation of ammonium removal using a chitosan-g-poly (acrylic acid)/rectorite hydrogel composite. J. Hazard. Mater. 171, 671–677.

Zheng, H., Han, L., Ma, H., Zheng, Y., Zhang, H., Liu, D., Liang, S., 2008. Adsorption characteristics of ammonium ion by zeolite 13X. J. Hazard. Mater. 158, 577–584.

Zheng, Y., Liu, Y., Wang, A., 2011. Fast removal of ammonium ion using a hydrogel optimized with response surface methodology. Chem. Eng. J. 171, 1201–1208.

Zheng, Y., Xie, Y., Wang, A., 2012. Rapid and wide pH-independent ammonium-nitrogen removal using a composite hydrogel with three-dimensional networks. Chem. Eng. J. 179, 90–98.

Zhou, Z., Yuan, J., Hu, M., 2015. Adsorption of ammonium from aqueous solutions on environmentally friendly barbecue bamboo charcoal: Characteristics and kinetic and thermodynamic studies. Environ. Prog. Sustain. Energy 34, 655–662.

Zhu, M., Zhu, G., Li, W., Zhang, Y., Zhao, L., Gu, Z., 2013. Estimation of the algal-available phosphorus pool in sediments of a large, shallow eutrophic lake (Taihu, China) using profiled SMT fractional analysis. Environ. Pollut. 173, 216–223.

Zhu, Y., Kolar, P., Shah, S.B., Cheng, J.J., Lim, P.K., 2016. Avocado seed-derived activated carbon for mitigation of aqueous ammonium. Ind. Crop. Prod. 92, 34–41.

Zieliński, M., Zielińska, M., Dębowski, M., 2016. Ammonium removal on zeolite modified by ultrasound. Desalin. Water Treat. 57, 8748–8753.