**Highlights**

* Surface modification of adsorbents enhanced nitrate adsorption
* Modification increased positive charges and added new functional groups on the surface
* Surface protonation, amination, and coatings with metal, metal oxide, organic compounds

**Enhanced removal of nitrate from water using surface modification of adsorbents – a review**

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**Abstract**

Elevated concentration of nitrate results in eutrophication of natural water bodies affecting the aquatic environment and reduces the quality of drinking water. This in turn causes harm to people’s health, especially that of infants and livestock. Adsorbents with the high capacity to selectively adsorb nitrate are required to effectively remove nitrate from water. Surface modifications of adsorbents have been reported to enhance their adsorption of nitrate. The major techniques of surface modification are: protonation, impregnation of metals and metal oxides, grafting of amine groups, organic compounds including surfactant coating of aluminosilicate minerals, and heat treatment. This paper reviews current information on these techniques, compares the enhanced nitrate adsorption capacities achieved by the modifications, and the mechanisms of adsorption, and presents advantages and drawbacks of the techniques. Most studies on this subject have been conducted in batch experiments. These studies need to include continuous mode column trials which have more relevance to real operating systems and pilot-plant trials. Reusability of adsorbents is important for economic reasons and practical treatment applications. However, only limited information is available on the regeneration of surface modified adsorbents.

**Graphical abstract**

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|  |  |  | Surface modification technique | | |  |  |  |
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|  |  | Chemical | | |  |  | Physical | |
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| Protonation (acid treatment) |  | Metals or metal oxides impregnation |  | Grafting amine groups |  | Organic modification of aluminosilicate minerals |  | Heat treatment |

**Keywords**: nitrate, adsorption, surfactants, aluminosilicates, water treatment, adsorbent modification

**1. Introduction**

Nitrate is a major nutrient required for plant growth and nitrogenous fertilisers are routinely applied to agricultural lands worldwide to increase crop production. However, elevated concentrations of nitrate in surface and ground waters, as a result of firstly, excessive use of nitrogenous fertilisers, and secondly, disposal of untreated municipal and industrial wastes, is a serious global environmental problem. It causes eutrophication of water bodies such as bays, inland seas, lakes and ponds. It also endangers humans and animals drinking these waters. Eutrophication stimulates the growth of algae and aquatic plants, which in turn, can endanger fish and other aquatic life and water quality (Camargo and Alonso 2006). Drinking water high in nitrate concentration can potentially cause health problems in people such as blue-baby syndrome or methemoglobinaemia in infants (Fewtrell 2004) and stomach cancer in adults (Pennington 1998; Camargo and Alonso 2006; Chiu et al. 2007). Excessive nitrate in water has also caused health problems in livestock (Canter 1997). Symptoms of nitrate poisoning in livestock include cyanosis in and about the non-pigmented areas (mouth and eyes), shortening of breath, rapid heartbeat, staggered gout, frequent urination and collapse (Canter 1997). In severe cases, coma and death may result within a few hours.

Because of the link between health problems and excessive concentration of nitrate in drinking water, the World Health Organisation (WHO) and regulatory agencies in various countries have stipulated nitrate concentration limits. The nitrate concentration limit recommended by WHO and the European Union is 50 mg NO3-/L (WHO 2011) while the US Environmental Protection Agency has stipulated 44 mg NO3-/L (EPA 2009). In Australia, the recommended limit is 50 mg NO3-/L for infants up to 3 months old and 100 mg NO3-/L for adults and children over the age of 3 months (National Health and Medical Research Council 2011). South Africa stipulates a much lower permissible level of 20 mg NO3-/L (Masukume et al. 2011).

Due to its high stability and solubility, nitrate has a low tendency for precipitation and adsorption, and therefore it is difficult to remove this ion from water using conventional water treatment technologies (Islam et al. 2010). Several physicochemical and biological methods have been tried to remove excessive nitrate from water. These include adsorption (Bhatnagar and Sillanpää 2011), ion exchange (Oztürk and Bektaş 2004; Zhan et al. 2011), reverse osmosis (Schoeman and Steyn 2003), electrodialysis (Abou-Shady et al. 2012), denitrification (Soares 2000), algae growth and disposal of the harvest (Canter 1997) and a combination of ozonation and sand/ activated carbon filtration (Canter 1997). Of these processes, adsorption is generally considered to be the most attractive due to its convenience, ease of operation, simplicity of design, and economic considerations if low-cost adsorbents amenable for easy regeneration are used (Bhatnagar and Sillanpää 2011; Khan et al. 2011).

Several adsorbents including those which are carbon-based, naturally occurring, agricultural wastes, industrial wastes, biosorbents, ion exchange resins, and other synthetic organic and inorganic compounds have been used to remove nitrate from water (Canter 1997; Kapoor et al. 1997; Dubey et al. 2009; Bhatnagar and Sillanpää 2011). Most of these adsorbents’ effectiveness is not high because of their low to medium adsorption capacities. During the last decade, more attempts have been made to physically and chemically modify the surface characteristics of adsorbents so that their adsorption capacities improved. Bhatnagar and Sillanpää (2011) reported some of these adsorbents where the adsorption capacity for nitrate increased after surface modification. This paper reviews the current information on various techniques concerning adsorbents’ surface modification for enhancing nitrate removal from water. Furthermore it presents the magnitude of the enhancement, and characteristics, efficiency in the presence of co-anions and adsorption mechanisms of the modified adsorbents. The techniques’ advantages and drawbacks are also discussed.

**2. Surface modification techniques**

Surface modification includes a number of chemical and physical methods (Fig. 1). The chemical methods involved are protonation, metals or metal oxides impregnation, grafting of amine groups, and organic modification of aluminosilicates (Fig. 2, black box in the figure denote unmodified adsorbent). The physical method deals with thermal treatment of the adsorbent, thereby increasing its surface area and porosity and where impurities are removed to expose surface functional groups that were not accessible to the adsorbate earlier. Enhanced nitrate removal by surface chemical modification of adsorbents is primarily due to: firstly, an increase in surface positive charges; or secondly, providing new surface functional groups having a higher affinity for nitrate. The latter method also includes the recently developed technique of coating nitrate-selective ion exchange materials on carbon electrodes and applying electric potentials on the electrodes to create positive charges on the electrodes for nitrate adsorption (Biesheuvel et al. 2011; Lee et al. 2011; Kim and Choi 2012). A comparison of the adsorption capacities of surface modified and unmodified adsorbents is presented in the supplementary material to this article (Appendix Table S1).

*2.1. Surface protonation*

One method of enhancing the adsorption of nitrate is by treating the adsorbents with acids to cause protonation of the adsorbent surface, thereby increasing the positive surface charge density. The elevated number of positive charges will adsorb more negatively charged nitrate anions through electrostatic attraction. Protonation by acid treatment is simple and an established technique for removing other contaminants as well (Yin et al. 2007). Generally this method of modification is performed on adsorbents derived from agricultural and industrial wastes, which are low-cost materials. Therefore this method of surface modification is cost-effective and attractive.

*2.1.1. Sepiolite*

Sepiolite is a fibrous magnesium silicate mineral (Mg4Si8O15(OH)2.6H2O) having a high surface area (516 m2/g, Oztürk and Bektaş 2004). Oztürk and Bektaş (2004) reported that waste sepiolite (10 g) treated with 400 mL of 0.75 M HCl adsorbed three times the amount of nitrate (10 mg/g) compared to unacidulated sepiolite (3.5 mg/g) from a solution containing 100 mg NO3-/L and 0.5 g adsorbent. The adsorption data at different concentrations of nitrate fitted to the Freundlich adsorption isotherm with Freundlich capacity and intensity constants much higher for acid-treated sepiolite than for the unaciduated sepiolite (Supplementary Appendix S Table 1). Only the data for the acid-treated sepiolite fitted the Langmuir adsorption isotherm giving an adsorption capacity of 38 mg NO3-/g. The mechanism of nitrate adsorption on the acid-treated sepiolite was reported to be ion exchange between the nitrate anions in solution and chloride anions attached to the positively charged surface H+ sites produced by the acid treatment. The nitrate adsorption from a solution containing 100 mg NO3-/L decreased from 100% to 31.4% and 21.1% in the presence of a lower concentration of 10 mg/L sulphate and phosphate, respectively. This was due to the higher ionic charge of the latter ions competing effectively with nitrate that was adsorbed electrostatically.

*2.1.2. Red mud*

Red mud is a waste by-product formed during alkaline-leaching of bauxite in the Bayer process. It is commonly activated by thermal or acid treatment to increase the adsorption capacity of anions, cations and organics (Wang et al. 2008). Increased adsorption capacity is considered to be due to the removal of surface impurities, and an increase in the red mud’s surface area and pore volume. Cengeloglu et al. (2006) used HCl-treated red mud to remove nitrate from an aqueous solution and found that the Langmuir nitrate saturation capacity increased from the original red mud’s value of 114 mg NO3-/g to 363 mg NO3-/g. The increased adsorption capacity was caused by the increased specific surface area and point of zero charge (PZC). The specific surface area and PZC of the acid-treated red mud were 20.7 m2/g and pH 8.5, respectively; the corresponding values for the original red mud were 14.2 m2/g and pH 8.2, respectively. The higher PZC resulted in more positive charges at a specific pH, and therefore increased the number of nitrates adsorbed by electrostatic attraction.

*2.1.3. Activated carbon cloth*

Activated carbon cloth (ACC) has increasingly become an attractive adsorbent for removing water and gaseous contaminants (Faur-Brasquet et al. 2002; Rengel-Mendez and Streat 2002; Le Cloirec 2012). It is produced from synthetic raw materials such as rayon (viscose) by carbonation at temperatures ranging between 800 and 1000oC in order to remove the volatile components and to develop a graphitic structure having high surface area and pore volume (Le Cloirec 2012). The high adsorption capacity of ACC is explained by its large specific surface area (2500 m2/g, Afkami et al. 2007; 1000-2100 m2/g, Rengel-Mendez and Streat 2002; 969-2311 m2/g, Le Cloirec 2012) and the availability of a large number of oxygen-containing surface functional groups. Afkhami et al. (2007) compared the nitrate adsorption capacity of 4 M H2SO4-treated carbon cloth to distilled water-treated carbon cloth and discovered that the Langmuir adsorption capacity for the two adsorbents was 126 mg/g and 24 mg/g, respectively. The dramatic increase in the adsorption capacity of carbon cloth as a result of acid treatment was due to the strong electrostatic interaction between the negative charges of the nitrate anions and positive charges created by the acid treatment on the carbon cloth surface. The energy of adsorption was also much higher for the acid-treated carbon cloth. In the presence of an equal concentration of other anions, sulphate and chloride did not interfere with nitrate adsorption but carbonate and phosphate did.

*2.1.4. Chitosan*

Protonated cross-linked chitosan gel beads have been used to effectively remove nitrate from water. Chitosan is a natural product derived from deacetylation of the polysaccharide chitin (Jaafari et al. 2004). Chitin is found in the exo-skeletons of shrimp, crab, and other shellfish and it can be extracted in high concentrations from the waste produced after processing the edible parts. Chitosan consists of amino groups which favour the adsorption of anions. To improve anion adsorption capacity, several chemical modifications, such as chemical cross-linking and protonation of the amino groups in the chitosan molecules have been used (Jaafari et al. 2001, 2004; Chatterjee et al. 2009).

Chitosan gel beads used for nitrate adsorption are made by dissolving chitosan powder in acetic acid and pumping the solution through a hypodermic needle allowing drops to fall into an alkaline coagulating solution. Cross-linked gel beads were obtained by reaction with glutaraldehyde (Jaafari et al. 2001; Arora et al. 2010) or epichlorohydrin (Chatterjee et al. 2009). Protonation was achieved by reaction with HCl or H2SO4 (Jaafari et al. 2001; Arora et al. 2010) or NaHSO3 (Chatterjee et al. 2009).

Jaafari et al. (2004) found that the adsorption capacity of protonated cross-linked chitosan at pH 6.2 increased linearly with equilibrium nitrate concentration. At an equilibrium concentration of 30 mg/L the adsorption capacity was 0.1 mg nitrate/g. The adsorption capacity was influenced by pH in the range 2-7, and reached its maximum at pH 3-5. Chatterjee et al. (2009), on the other hand, reported a much higher adsorption capacity of 104 mg/g for a protonated cross-linked chitosan produced by them. The adsorption capacity reached its maximum at pH 3-5 which was also reported by Jaafari et al. (2004) and fell above pH 5 up to the highest pH 8 tested. The decreased adsorption at high pH was attributed to decreased positive charges on the adsorbent surface, which caused less attraction of the negatively charged nitrate anions. Furthermore increased concentration of OH- ions may have competed with nitrate for adsorption sites. The difference in the adsorption capacities in the two studies may be due to the difference in the methods of preparing the protonated cross-linked chitosan and adsorption method used. Chatterjee et al. (2009) found that cross-linking or protonation of chitosan beads significantly increased the zeta potential of chitosan, suggesting that the increased adsorption of nitrate caused by the treatments was due to more positive charges.

The review revealed that increased adsorption capacity caused by protonation varies widely (38-363 mg/g) with maximum adsorption generally in the acidic pH range (pH 3-5) where the adsorbents have more positive charges than at higher pH values. Protonation is a simple and established technique mostly performed on agricultural and industrial by products, therefore the cost of adsorbents is low and they have potential. However, nitrate adsorption on protonated materials is generally electrostatic and therefore it is not selective and other anions in water can compete for adsorption. Consequently, this method of surface modification has less potential when other anions are present in larger concentrations than nitrate concentration in water. Because nitrate adsorption is not selective the adsorbent can be regenerated easily by desorption of adsorbed nitrate using simple salts. Alternatively, when agricultural wastes are used for protonation, the exhausted adsorbent can be disposed of on agricultural lands where it can provide nitrate fertility and improve the physical, chemical and biological condition of soils.

*2.2. Surface impregnation of metals and metal oxides*

Impregnation of metals or metal oxides onto the adsorbent surface has a similar effect as surface protonation. The majority of metals, especially heavy metals, can strongly adsorb on adsorbents electrostatically by the attractive forces between the positively charged metallic ions and negatively charged surface and/or by ligand exchange mechanism (Loganathan et al. 2012). The positive charges on the adsorbed metallic ions attract and adsorb anions such as nitrate. Adding metal can also increase the surface area and pore volume of adsorbents which in turn increase their adsorption capacity of adsorbates (Namasivayam and Sangeetha 2005; Demiral and Gündüzoğlu 2010).

*2.2.1. Zinc chloride*

Namasivayam and Sangeetha (2005, 2008) reported that treating coconut coir pith with ZnCl2 at a weight ratio of 2:1 followed by heating to 700oC increased the surface area and total pore volume of the coir pith to 910 m2/g and 0.363 mL/g, respectively. This was comparable to 167 m2/g and 0.122 mL/g for untreated coir pith, respectively. The nitrate adsorption capacity of activated coir pith without ZnCl2 treatment was negligible but when treated with ZnCl2 it had a Langmuir adsorption capacity of 10.3 mg/g. Nitrate adsorption was highest in the pH range 2-11. The reason for nitrate adsorption not decreasing above the ZPC pH 3.2 of ZnCl2-treated coir pith despite the increase in surface negative charges which repel the negatively charged nitrate was explained by the chemisorption of nitrate, possibly as surface complex formation with Zn2+. Consistent with the surface complexation explanation, desorption of nitrate by water was negligible within the pH range 2-11. However, > 60% nitrate was desorbed at pH 2 and 11, due to nitrate competing for adsorption with Cl- and OH- that were used in HCl and NaOH for the adjustment of pH in the acidic and alkaline pH, respectively.

Enhanced nitrate adsorption by AC after ZnCl2 treatment and thermal activation was also reported by Demiral and Gündüzoğlu (2010) for sugar beet bagasse AC and by Khan et al. (2011) for lignite granular AC (LGAC). The method of activation was similar to that of Namasivayam and Sangeetha (2005), where the AC was initially mixed with ZnCl2 followed by heating to high temperature. However, Demiral and Gündüzoğlu (2010) and Khan et al. (2011) tested the adsorption capacity at different temperatures of heating and different weight ratios of AC to ZnCl2. Demiral and Gündüzoğlu (2010) reported that surface area of the ZnCl2-treated AC increased from 1191 to 1826 m2/g with increase in activation temperature from 500 to 700oC, respectively. The total pore volume also increased from 0.666 to 0.966 cm2/g when the temperature rose. The carbon content fell from 65% to 25% as the activation temperature rose due to evolution of volatile compounds, leading to an increase in pore development. The surface area and total pore volume also increased as the ratios of ZnCl2 to AC rose. Increasing the amounts of ZnCl2 enhanced the suppression of tar formation and the release of volatiles. Langmuir nitrate adsorption capacity at pH 6.58 and 25oC for the ZnCl2-treated bagasse AC at the impregnation ratio of 3:1 and activation temperature of 700oC was 9.14 mg/g. The capacity increased to 27.6 mg/g at 45oC.

Khan et al. (2011) reported that among the activation temperatures of 400, 500, and 600oC and impregnation weight ratios of 1:1, 2:1, and 3:1 (ZnCl2 to LGAC), the modified LGAC with a ratio of 2:1 and 500oC heating had the highest adsorption capacity for nitrate (9.5 mg/g compared to 6 mg/g for unmodified LGAC), at a 200 mg/L initial nitrate concentration. At the lower temperature (400oC), the heat supply was not sufficient for the complete evolution of the volatile matter from the LGAC. The decline in nitrate adsorption at 600oC was considered to be due to sintering effects, followed by shrinkage of char and realignment of the carbon structure which reduced the pore volume. The surface area of Zn-treated LGAC was less than that of untreated LGAC, probably due to a blockage of narrow pores by the Zn surface complex. Fourier transform infrared spectroscopic studies indicated that Zn adsorbed to the LGAC surface was responsible for the enhanced adsorption of nitrate.

Effect of different weight ratios of ZnCl2 to activated carbon and heating temperature on nitrate adsorption was also studied by Bhatnagar et al. (2008). In their study, coconut granulated activated carbon (GAC) was treated with ZnCl2 at weight ratios of 1:1, 2:1, and 3:1 (GAC to ZnCl2) and heated to 400, 500, and 600oC. Highest nitrate adsorption was observed for the weight ratio of 2:1 and 500oC. Using scanning electron microscopy and X-ray diffraction analyses the authors reported that the untreated GAC had macro-, meso-, and micropores whereas the treated GAC had mainly micropores with mesopores and macropores occupied by Zn oxide. The ZnCl2 treatment decreased the surface area from 1144 to 893 m2/g. This finding is different to that reported by Namasivayam and Sangeetha (2005) and Demiral and Gündüzoğlu (2010), where ZnCl2 treatment increased surface area of the coir pith and sugar beet bagasse, respectively. These studies’ contrasting results could be due to the difference in the method of treating ZnCl2. In the studies by Namasivayam and Sangeetha (2005) and Demiral and Gündüzoğlu (2010), thermal activation was performed after mixing the ZnCl2 with coir pith or bagasse, whereas Bhatnagar et al. (2008) ensured the individual components were activated before mixing the two components. Despite a reduction in surface area on treatment of GAC with ZnCl2, Bhatnagar et al. (2008) found a larger amount of nitrate adsorption for the ZnCl2-treated GAC. The Langmuir adsorption maximum at 25oC and pH 6.0-6.4 was 10.2 mg NO3-/g for ZnCl2-treated GAC compared to 1.7 mg NO3-/g for the untreated GAC. The higher adsorption capacity of ZnCl2-treated GAC was explained by the higher microporosity and presence of Zn oxide which acted as an additional adsorbent for nitrate in the ZnCl2-treated GAC. Similar to the findings of Namasivayam and Sangeetha (2005), highest nitrate adsorption capacity was reported at pH 4-11.

Among the anions commonly present in water, Cl- competes with nitrate adsorption the most and PO43- the least. The reduction in nitrate adsorption on ZnCl2-treated coir pith AC by anions was in the order, Cl- > SO42- > PO43- (Namasivayam and Sangeetha 2005), and on ZnCl2-treated LGAC was in the order Cl- > CO32- > PO43- (Khan et al. 2011). The higher valent PO43- did not have the most impact on nitrate adsorption reduction. This may be explained by the phosphate ion predominantly existing as a monovalent H2PO4- anion at the pH 6-7 of most waters.

*2.2.2. Zirconium oxychloride*

Recently, the production of low-cost adsorbents from organic wastes to remove pollutants from water has attracted growing interest (Gupta et al. 2009). Any benefits from using them can save disposal costs, prevent environmental pollution and make available lands for alternative and productive use. However, agricultural wastes do not have the ability to remove anions due to the absence of cationic groups that can adsorb anions (Hassan et al. 2010). This problem can be overcome by loading multivalent cations onto these waste materials to induce anion exchange properties. Hassan et al. (2010) loaded tetravalent Zr (Zr4+) onto sugar beet pulp (SBP) by adding Zr oxychloride to SBP and tested its ability to remove nitrate from water. The SBP had ~ 40% pectin which reacted with Zr4+ to produce 13.3% by weight of Zr4+ loaded onto SBP. Fourier transform infrared spectroscopic studies showed that nitrate was adsorbed onto the Zr4+ loaded SBP by substituting hydroxyl ions from the coordination sphere of the Zr4+ (Fig. 3). The maximum nitrate adsorption capacity at pH 6.0 and room temperature was 63 mg/g (1.0 mmole/g). Compared to nitrate, sulphate had an adsorption capacity of 114 mg/g (1.18 mmole/g), indicating that in the presence of the both these ions in solution, sulphate is likely to reduce the adsorption of nitrate. The rise of solution pH caused by the addition of NaOH decreased adsorption capacity due to possible competition between the hydroxide ion and nitrate ion for adsorption sites. The adsorbent was regenerated by 0.01 M NaOH after its saturation with nitrate for 5 adsorption cycles without significantly losing its adsorption capacity. The stability of hydrous Zr, bound to the carboxylate groups of SBP, was able to prevent the dissolution of SBP constituents in the NaOH treatment during regeneration.

*2.2.3. Magnesium oxide*

Zhang et al. (2012) synthesised a highly porous nanocomposite material consisting of MgO nano-flakes within thebiochar matrix by heating a mixture of biochar and MgCl2 to 600oC, and used it to remove nitrate from water. Biochars were produced from biomasses such as sugar beet tailings, sugarcane bagasse, cotton woods, pine woods, and peanut shells. All materials were able to remove considerable amounts of nitrate as a result of the positive charges on the MgO surface. The zero point of charge pH is around 12 and therefore at the normal neutral pH of water MgO surface has positive charges. The remarkable effectiveness with which MgO-biochar removed nitrate was attributed to the high surface area (347 m2/g by CO2 adsorption method) and zero point of charge of MgO. Of the different MgO-biochars, the MgO incorporated peanut shell biochar had the highest nitrate adsorption capacity. The Langmuir nitrate adsorption capacity for this material was 94 mg/g, which was reported to be much higher or comparable to most commercially used adsorbents. However, the phosphate adsorption capacity was 835 mg/g, suggesting that phosphate in solution will reduce nitrate adsorption. Biochar production from organic materials has become very popular in recent times because in soil application it reduces or suppresses greenhouse gas generation (Kookana et al. 2011). Therefore, MgO-biochar adsorbents can be cost-effective when they are used for nitrate removal.

It can be concluded that surface modification of adsorbents by metals or metal oxides incorporation, significantly increases the adsorption capacity of the adsorbent. However, the adsorption capacity of the modified adsorbent remains low because the original adsorbent had very low adsorption capacity to start with. Nonetheless there are some exceptions to this, such as the incorporation of Zr and MgO, which produced adsorbents with high adsorption capacities. Most of the adsorbents used in this modification are agricultural wastes and therefore the cost of the original adsorbent is low but some modifications involving heating to high temperatures, increase the cost of modification. The presence of other anions in water reduced the adsorption of nitrate. Therefore adsorbents modified by this method, as those modified by protonation, can be effectively used only if the concentrations of other anions are low in comparison to nitrate. As stated in the case of protonation modification, the modified agricultural waste adsorbents, after their use, can be applied to agricultural lands to improve soil fertility provided that the metals in the adsorbents are not in toxic concentration.

*2.3. Grafting amine groups*

*2.3.1. Agricultural wastes*

Lignocellulosic agricultural wastes (AW) have been grafted with amine groups to produce weak-base anion exchangers for adsorbing nitrate from water. Orlando et al. (2002a) introduced epoxy and amine groups into sugarcane bagasse and rice husk containing α-cellulose and tested their effectiveness in removing nitrate. The Langmuir maximum adsorption capacities for nitrate on bagasse and rice hull modified materials at 30oC were 87 and 71 mg/g, respectively. These adsorption capacities compared well with the value of 74 mg/g reported for the commercial anion exchanger, Amberlite IRA-900 (Orlando et al. (2002b).

In another study, Orlando et al. (2002b) converted seven AW (rice husk, sugarcane bagasse, coconut husk, pine bark, persimmon tea leaf, moringa oleifera husk, and lauan sawdust) into anion exchangers (AWAE) using the amine grafting method previously employed (Orlando et al. 2002a). Nitrate adsorption by all the AWAE at 30oC fitted the Langmuir adsorption isotherm, with the AWAE from moringa oleifera husk, rice husk, sugarcane bagasse, and pine bark having the highest adsorption capacities (63-74 mg/g), which were reported to be approximately equal to that of the commercial anion exchanger, Amberlite IRA-900 (74 mg/g). Increased α-cellulose content in the AW increased the yield of the AWAE, with sugarcane bagasse having the highest α-cellulose content of 51.2%. However, the anion exchangers’ Langmuir adsorption capacity did not depend on the α-cellulose content. The selectivity of adsorption of anions by the anion exchanger made from bagasse was in the order SO42- > Br- > NO3- > NO2- > F- > PO43-. Nearly 87% of the adsorbed nitrate could be desorbed from the bagasse anion exchanger using 0.1 M NaOH. The ion exchanger’s reusability is important because it has economic implications and the practical application of the treatment process. This was tested using four adsorption-desorption cycles and it emerged that the anion exchanger did not lose much of the initial adsorption capacity.

Recently, Katal et al. (2012) reported that rice husk aminated by a method similar to that of Orlando et al. (2002b) had a Langmuir nitrate adsorption capacity of 56 mg/g at pH 7, which was slightly lower than the value of 74 mg/g reported by Orlando et al. (2002b) for another rice husk aminated product. The maximum adsorption was found to be at pH 6 in the pH range 3-11 tested. Low adsorption at low pH values was due to the dissociation of the functional groups in the adsorbent whereas at high pH the reduced adsorption was due to competition of the high OH- concentration. The presence of other anions at the same concentration as nitrate reduced nitrate adsorption only by < 25%. The order of reduction was CO32- > Cl- > H2PO4- > SO4-. However, in real waters contaminated with nitrate, the nitrate concentration is expected to be higher than the other anions and therefore competition from other anions for adsorption should be low. Katal et al. (2012) in fact observed that the adsorbent’s removal of nitrate from urban waste water in Iran was 91.8%. This was comparable to 95% under the same experimental conditions from a synthetic nitrate solution in the absence of other anions. The inability of other anions in water not able to markedly reduce nitrate adsorption by the rice aminated product is probably that most of the nitrates were strongely adsorbed. This was confirmed by the high free energy of adsorption value obtained by successful fitting of the adsorption data to the Dubinin-Radushkevich isotherm model. Based on the high free energy value, Katal et al. (2012) suggested that nitrate was adsorbed by anion exchange (possibly ligand exchange) and electrostatic attraction.

Several studies have been conducted on the use of amine grafted wheat straw products to remove nitrate from water. Wang et al. (2007a, b) prepared an anion exchanger from wheat straw (WSAE) using Orlando et al.’s (2002a) chemical treatment method, and tested its structural and adsorptive properties for nitrate removal from aqueous solutions. The yield of WSAE was 350% by weight of WS and the total anion exchange capacity as determined from the N% of the material was 2.57 meq/g (159 mg maximum nitrate adsorption/g) compared to 0.25 meq/g (16 mg maximum nitrate adsorption/g) for WS. Zeta potential meaurements were used to explain the higher anion exchange capacity of WSAE. Zeta potential is the electrical potential close to the particle surface where adsorption of ions from solution phase occurs and it is positively related to the surface charge. Higher the positive zeta potential the higher the anion exchange capacity resulting in higher amounts of anion adsorption. The zeta potential of the WS was -35 mV, whereas that of WSAE was +40 mV, indicating that the increased anion exchange capacity predicted from the increase in N content of WSAE was due to the increase in the positive charges created by the chemical treatment. Fourier transform infrared spectroscopic and scanning electron microscopic studies showed that tertiary amino groups were introduced by the chemical treatment and the adsorbed nitrate anions were aggregated on the surface of the WSAE. Consistent with the higher anion exchange capacity of the WSAE the Langmuir nitrate adsorption capacity was higher for the WSAE (129 mg/g) than that for the untreated-WS (9 mg/g). The adsorption capacity value of the WSAE was higher than that reported by Orlando et al. (2002b) for anion exchangers produced from other agricultural wastes. The adsorption capacity for nitrate was much higher than that for SO42- and HPO42-, indicating the higher adsorption selectivity of nitrate in natural waters containing these ions. About 90% of adsorbed nitrate ions could be desorbed from 0.2 g WSAE using 30 mL 0.1 M NaOH, indicating that this adsorbent had high regeneration efficiency in alkaline solutions. The adsorption-desorption cycle was repeated 12 times and it was observed that the adsorption capacity only decreased slightly at the 11th cycle.

Xu et al. (2010) and Xing et al. (2011) made two modifications to the method of grafting amine groups proposed by Orlando et al. (2002 a, b). In one modification, instead of cross-linking WS with epichlorohydrin to form epoxy ethers, and then grafting amine groups onto the epoxy ethers by amination reaction, amination of epichlorohydrin was first carried out before introducing it into the wheat straw (Xu et al. 2010). The reaction time and temperature were optimised for increased efficiency of nitrate removal. The zeta potentials of the WSAE were -28.2 to +32 mV in comparison with -48 to +4.6 mV for WS in the pH range 2-12, indicating the existence of increased number of positive charges on the WSAE. NMR and infra-red spectroscopic data showed that the intense amine carbon peaks for the WSAE compared to the WS spectra as the reason for the increased number of positive charges.

Langmuir adsorption maxima for nitrate on WSAE was 52.8 mg/g, which was lower than that of the commercial anion exchange resin Amberlite IRA 400 (226 and 290 mg/g) (Chabani et al. 2007), but higher than that for activated carbon (6.8 mg/g) (Park and Na 2006), and other modified adsorbents (9.8-45.6 mg/g) (Xu et al. 2010). The adsorbent was satisfactorily regenerated by desorption of the adsorbed nitrate using 0.1 M HCl and 0.1 M NaCl. This indicates that nitrate was non-specifically adsorbed by electrostatic attraction (outer-sphere complexation) and the desorption process probably occurred through the ion exchange of nitrate by chloride, the reverse of the adsorption process (chloride by nitrate). After four adsorption-desorption cycles, only a slight loss in the initial adsorption capacity was observed, suggesting that the adsorbent can be repeatedly used to remove nitrate from waters.

The second modification method consisted of chain reactions, where the first step was to attach epichlorohydrin to the cellulose/hemicellulose chains in WS to produce epoxy cellulose/hemicellulose ethers, followed by two steps of successive amination of the ethers (Xing et al. 2011). Solid state 13CNMR and zeta potential analyses validated the existence of cross-linked amine groups in WSAE. Raman spectroscopic analysis suggested an electrostatic attraction between the adsorbed nitrate ions and positively charged amine sites, and the nitrate removal process occurred through an ion exchange of Cl- adsorbed to the amine group (R-N+(CH2CH3)3)by NO3- in solution according to the equation (1).

R-N+(CH2CH3)3....Cl- + NO3- → R-N+(CH2CH3)3….NO3- + Cl- (1)

Zeta potential of WS decreased from +2.2 mV to -46.3 mV as the initial pH of the WS suspensions in water increased from 2.0 to 12.0 (Fig. 4). In contrast, the zeta potentials of WSAE were +35.3 to -7.0 in the pH range; this indicates the presence of positively-charged surface functional groups on the WSAE.

Column adsorption capacity of WS for nitrate at pH 5.12 was negligible (0.54-0.57 mg/g), whereas that of WSAE ranged from 86 to 87 mg/g, depending on column bed height and influent nitrate concentration and flow rate (Xing et al. 2011). At the solution pH values of 2.00, 5.12, 7.08, 9.85, and 12.14, the column adsorption capacities were 62.7, 87.27, 87.45, 85.15, and 41.90 mg/g, respectively. The low adsorption capacity at pH 2 was due to nitrate ions competing with chloride ions added in HCl to reduce the pH value. At pH 12.14 the adsorption capacity was low due to less attractive or more repulsive electrostatic interaction resulting from the increased negatively charged surface sites at high pH values. This is also due to the presence of excess OH- ions competing with nitrate ions for sorption sites. Based on these results, the suitable pH range of influent water for efficient nitrate removal is 5-10; this demonstrates a potential application to most wastewaters in the field. As in the previous study of Xu et al. (2010), 0.1 M HCl demonstrated its high desorption rate for the regeneration of WSAE. The adsorption-desorption process provided an excellent regeneration capacity of the adsorbent with little loss (5.2%) in its adsorption capacity when used four times.

To regulate practical utilisation, three types of wheat residues modified by different amounts of amine groups were prepared and their costs and efficiency when removing nitrate from water were calculated by Xu et al. (2011). The weights of chemicals used for grafting amine groups on 10 g wheat residues (WS) were 11.8, 14.5, and 17.4 g, respectively, and the corresponding costs (US$) were 0.5, 1.1, and 2.0. The percentage by weight of N in the low, medium, and high cost modified WS were 2.15, 3.76, and 6.20, respectively, and the Langmuir adsorption capacities of the three modified WS were 27.5, 52.1, and 89.8 mg/g, respectively. Since the efficiency of nitrate removal depends on the cost of the modification, the water treatment professional can choose the type of modified product according to the treatment required.

*2.3.2. Plant biomass*

Xu et al. (2012) extended their study on the development of anion exchangers using wheat straw to *Arundo donax* L. reed (ADR)-based anion exchanger (ADRAE) and examined the nitrate removal properties. ADR is a naturally growing hydrophyte with high biomass productivity, can be intensely cultivated, and easily adapted to different ecological conditions. Therefore, it is a suitable low-cost material for use as an adsorbent, after grafting amine groups, to increase its nitrate adsorption properties. Langmuir adsorption capacity for nitrate on ADRAE was 44.61 mg/g. Column adsorption capacity range was 38-39 mg/g, depending on the weight of adsorbent in the column. The high adsorption capacity of ADRAE is due to the positive charges created by grafting amine groups. Amination of ADR significantly increased its zeta potential, similar to that observed for WS (Xu et al. 2011), thus illustrating the increased positively charged functional groups on the framework of the ADRAE.

*2.3.3. Mesoporous silica*

Surface modified mesoporous silica materials produced by surface functionalization via the tethering of organic functional groups are potential adsorbents that can remediate a number of important water pollutants (Hamoudi et al. 2007). Saad et al. (2008) synthesized and protonated several amino-functionalized mesoporous silica materials and successfully applied them to remove nitrate from water (Fig. 5). The amine groups were introduced into mesoporous silica at a molar ratio of 0.1:1. The amino-functionalized products were subsequently acidified in order to convert the amino groups into ammonium moieties with positive charges to enhance anion adsorption. The aminated and protonated mesoporous silica showed high adsorption capacities for nitrate reaching 46.5 mg/g compared to adsorption capacities of 0.6-2.4 mg/g for the unmodified mesoporous silica, despite the latter having a high surface area and total pore volume. The reduction in surface area and pore volume of the surface modified silica was attributed to the occupation of the pore framework by the terminal organic functional groups protruding into the internal surface of the pores. Phosphate was found to reduce nitrate adsorption, therefore the adsorption of nitrate was considered to be non-specific (outer-sphere complexation). However, special types of functionalised mesoporous silicas (SBA-15) were produced where the nitrate adsorption was less affected by phosphate. This was explained by the monovalent phosphate anion - having a larger ionic radius (0.238 nm) - was unable to enter the mesopores of silica in these materials whereas nitrate with a lower ionic radius (0.177 nm) did.

*2.3.4. Aminoclays*

Recently, Lee et al. (2012) prepared aminoclays (aminopropyl-functionalised metal phyllosilicates) by adding 3-aminopropyltroethoxysilane to solutions containing Fe, Al, or Mg chlorides. The removal of nitrate, fluoride, and phosphate from 30 mL solutions containing 30 mg/L of these ions at pH 4.65 involved aminoclays (0.25-1.25 g/L). It emerged that all clays removed 100% phosphate, 30-70% fluoride, and 10-40% nitrate. The removal mechanism was electrostatic attraction between the protonated amine (-NH3+) group in the clays and the negatively charged anions in water. Higher valency of the phosphate anions explained the preferential adsorption of phosphate. However, in most waste waters the concentration of nitrate is much higher than that of phosphate and F, and therefore these aminoclays are expected to remove a much higher percentage of nitrates than in the study by Lee et al. (2012) where equal concentrations of the three anions were used. Studies on the removal of nitrate from solutions containing realistic concentrations of anions or using real waste waters are required.

*2.3.5. Carbon nanotube sheets*

Enhanced adsorption of nitrate by protonation of activated carbon cloth was discussed previously in this paper (Afkhami et al. 2007). Tofighy and Mahammadi (2012) synthesised another type of carbon material in the form of carbon nanotube sheets (CNT) and functionalised them by protonation of surface hydroxyl groups using HNO3 oxidation (0-CNT) and amination using liquid ammonia treatment (N-CNT). They reported that the functionalised CNTs had very high nitrate adsorption capacities (pH 7 Langmuir adsorption capacities of 90.9 mg/g for 0-CNT and 142.9 mg/g for N-CNT). The adsorption capacity of N-CNT was greater than that of the activated carbon cloth (126 mg/g) reported by Afkhami et al. (2007) and most of the adsorbents reported in the literature on nitrate removal. The adsorption capacity of O-CNT was, however, slightly less than that of the activated carbon cloth. Based on the kinetic adsorption data, the higher adsorption capacity of N-CNT compared to O-CNT was due to the chemical adsorption of nitrate to the N-containing functional groups in N-CNT. In contrast the adsorption on O-CNT was physical, involving electrostatic attractive forces between the positive surface charges on the adsorbent and negatively charged nitrate. However, more than 85% nitrate was desorbed from N-CNT when the latter was dispersed in water. This suggests that nitrate adsorption on N-CNT was weaker than that expected from the chemical adsorption mechanism. Further studies are required to resolve this discrepancy.

It is evident from the review that the amine grafting technique can produce materials with very high nitrate adsorption capacity (28-143 mg/g, Supplementary Appendix Table S1). Many of the amine graftings have been made on agricultural wastes and plant biomass which are not costly. This makes the amine grafted product inexpensive. Amine grafting of mesoporous silica and carbon nanotube sheets produced the highest adsorption capacity but they are more expensive than other products. However, the high adsorption capacity compensates for the costs of these materials. With the high adsorption capacity materials, larger volumes of water can be treated with less adsorbents. Unlike the modified products made by other surface modification techniques, many of the amine grafted materials are capable of having high selectivity for nitrate adsorption. Therefore, other anions in water would not have significant competition with nitrate for adsorption.

*2.4. Organically modified aluminosilicate minerals and carbon electrodes*

Another technique of incorporating positive charges on adsorbent surfaces to enhance nitrate adsorption is by loading cationic organic compounds or exchange resins on negatively charged aluminosilicates and carbon electrodes. Common adsorbents used for this purpose are aluminosilicate minerals such as zeolites, smectites, halloysites, and kaolinites. Zeolites are the most popular aluminosilicate and surfactants are the most popular type of organic compound studied. In contrast to smectites and kaolinites, natural zeolites can occur as millimetre-long or larger particles and are free of shrink-swell behaviour (Haggerty and Bowman 1994). As a result, zeolites have superior hydraulic properties and are suitable for use in filtration-type water treatment processes.

*2.4.1. Surfactant modified zeolite*

Bowman et al. (2003) reviewed the literature on pollutants removed from water by surfactant modified zeolites. When a surfactant is mixed with a zeolite, it is adsorbed by selectively exchanging with inorganic cations on the zeolite. At low concentrations (< critical micelle concentration (CMC)) the surfactant forms a monolayer or ‘hemimicelle’ at the solid-solution interface (Haggerty and Bowman 1994; Zhan et al. 2011). Inorganic anions such as nitrate are adsorbed on the positively charged hydrophilic head segments of the surfactant which are attached to the zeolite (Fig. 2d). At high concentrations (> CMC), the hydrophobic tails of the surfactant molecules link to form a bilayer or ‘admicelle’ through a tail-tail interaction (hydrophobic bonding by van der Waals forces) of two surfactant molecules allowing the positively charged head segments to extend into the solution (Fig. 2 d) (Haggerty and Bowman 1994; Guan et al. 2010; Schick et al. 2010). This creates a positively charged solid-solution interface, providing sites for the adsorption of anions. Evidence for the charge reversal of the zeolite from negative to positive as a result of surfactant adsorption was produced by zeta potential measurements (Schick et al. 2010). Fourier transform infrared (FTIR) spectroscopy analysis of the zeolite indicated that new peaks similar to those of the surfactant were produced when the zeolite was loaded with the surfactant. Nitrate adsorption on the surfactant-modified zeolite reduced the intensity of these peaks (Masukume et al. 2011), suggesting that the active sites created by the surfactant were responsible for nitrate adsorption.

Hexadecyltrimethylammonium (HDTMA) is a major cationic surfactant used to modify the surface properties of zeolite to enhance the removal of non-ionic organic solutes and inorganic oxyanions (Haggerty and Bowman 1994). It is a tetrasubstituted ammonium cation with permanently-charged pentavalent nitrogen and a long straight alkyl chain, which produces a high degree of hydrophobicity. Because HDTMA is too large to enter into the internal pores of the zeolite it is adsorbed only on the external surface. Also, HDTMA-modified surface is stable when exposed to extreme pH, ionic strength, and organic solvents (Haggerty and Bowman 1994). These properties of HDTMA make it a useful surfactant for modifying the zeolite surface to enhance nitrate removal.

Li (2003) reported that the adsorption capacity of an HDTMA-modified zeolite (effective cation exchange capacity (ECEC), 100 mmole/kg) increased with the dose of HDTMA added to the zeolite. At an equilibrium nitrate concentration of 310-620 mg/L, the HDTMA-modified zeolite at an HDTMA dose equivalent to 25% ECEC of zeolite removed < 0.3 mg nitrate/g, whereas at the dose equivalent to 150-200% ECEC the nitrate removal increased to 5.0 mg/g. The Langmuir adsorption capacity for nitrate at 100% ECEC was 4.0 mg/g, but at 150-200% ECEC, it was 5.6-6.6 mg/g. The increased nitrate removal at 150-200% ECEC was attributed to the surfactant forming a bilayer on the zeolite creating large number of positive charges on the surface, whereas at < 100% ECEC, the surfactant formed a monolayer producing a limited number of positive charges to adsorb nitrate. A column leaching study showed that when zeolite was blended with 3.8 mg/g of nitrate and leached with water, initial effluent nitrate concentration (at 0.2 pore volume) was 22.3-22.8 g/L. In contrast, the initial effluent nitrate concentration was only 1.2 g/L when HDTMA-modified zeolite with the same nitrate load was leached, indicating the enhanced adsorption capacity of zeolite by surface modification with HDTMA.

Four natural zeolites, from the USA, Croatia, Australia, and China were treated with HDTMA-Br and tested for nitrate adsorption by Guan et al. (2010). Thermo-gravimetric analysis revealed that although the amount of HDTMA-Br mixed with unit weight of zeolite was the same, the first and second layer loadings of HDTMA on the zeolites were different. Thin section examination of the zeolites with a polarisation microscope indicated that intra-grain surface porosity of the different zeolites was the reason for the difference in the loading characteristics. Zeolites having total loadings of 219, 133, 137, and 75 mmole HDTMA/kg had Langmuir adsorption capacities of 3.5, 2.8, 1.5, and 1.5 mg nitrate/g, respectively. The unmodified zeolite tested for nitrate adsorption had a Langmuir adsorption capacity of 0.2 mg nitrate/g.

Schick et al. (2010) found that a zeolite modified by HDTMA to a level equivalent to 120% of its ECEC had a Langmuir adsorption capacity of 87 mmole nitrate/kg (5.4 mg/g) in contrast to no affinity for nitrate by the raw zeolite. The presence of competing anions did not influence the adsorption of nitrate by the zeolite-HDTMA, but slowed down the adsorption kinetics. The affinity of the anions towards the adsorbent was in the order Cl- << HCO3-, SO42- < NO3-. In a fixed-bed column study the affinity order for this adsorbent was Cl- << HCO3- < SO42- < NO3- (Schick et al. 2011). The fixed-bed column study also showed that during nitrate adsorption, some leaching of HDTMA occurred, whose concentration exceeded the ecotoxic levels. Filtration through an activated carbon bed was required to reduce the concentration of HDTMA in the leachate to values less than the ecotoxic levels.

For an adsorbent to be cost-effective in water treatment operations it should be capable of efficient regeneration and reuse for a long period of time. Complete desorption of the adsorbed nitrate and recovery of the adsorption capacity of the used adsorbent is a requirement for reuse. Masukume et al. (2011) reported that about 93% of the adsorbed nitrate on HDTMA-loaded zeolite (7.82 mg nitrate/g) was desorbed by leaching with NaOH at pH 12.2, but when the adsorbent was reused, it adsorbed only 2.97 mg nitrate/g. This suggests that the adsorbent can only be used once. However, the nitrate loaded adsorbent can be used as a slow release nitrogen fertiliser for crops (Li 2003).

Cetylpyridinium bromide (CPB) is another cationic surfactant used to modify aluminosilicate minerals to enhance nitrate adsorption. Zhan et al. (2011) investigated the adsorption behaviour of nitrate on a CPB modified natural zeolite at different loading rates of CPB with a maximum rate equivalent to a bilayer configuration (409 mmole/ kg zeolite). The adsorption of nitrate was due to exchange of the electrostatically bonded Br- on positively charged bilayers of Cetylpyridinium (CP) adsorbed to the zeolite by NO3- in solution as shown in equation (2).

Zeolite-CP-CP+…Br- + NO3- = Zeolite-CP-CP+…NO3- + Br- (2)

When the number of moles of CPB loaded onto zeolite was equal to the number of moles of Br- released to solution, a monolayer of CPB was considered to be formed on the zeolite. When the CPB loading was twice that of the moles of Br- released, a bilayer had formed. Between these two loading rates a patchy bilayer was formed. Unmodified zeolite and modified zeolite with monolayer coverage had negligible nitrate adsorption (< 2% removal efficiency). The patchy bilayer and full bilayer coverages were more efficient in removing nitrate (5-30% and 32%, respectively). The unmodified zeolite had a negative surface charge and monolayer coverage neutralised this negative charge, but did not produce any positive charges for nitrate adsorption, and therefore nitrate removal was very low. On the other hand, the patchy and full bilayer coverage produced positive charges for enhanced nitrate adsorption. The Langmuir adsorption capacity of the bilayer covered zeolite at pH 6 and 15oC for nitrate was 9.68 mg/g. The adsorption capacity fell slightly when the temperature increased, indicating that the adsorption was an exothermic process. Negative standard Gibb’s free energy values were obtained, which indicated that the adsorption process was spontaneous.

*2.4.2. Surfactant modified kaolinite, halloysite, and smectite*

Other aluminosilicate minerals such as kaolinite, halloysite, and smectite have been used as adsorbents on which HDTMA was loaded to enhance nitrate adsorption. The mechanism of adsorption of oxyanions on these adsorbents is similar to that of HDTMA-loaded zeolite. HDTMA loading equal to or higher than twice the CEC of these aluminosilicates was used to ensure bilayer formation of HDTMA, in order for a large amount of nitrate adsorption to be achieved (Li and Bowman 2001; Xi et al. 2010). Li and Bowman (2001) loaded HDTMA onto kaolinite at rates equal to twice the CEC of kaolinite (CEC 60 mmole/kg) and tested its capacity to adsorb nitrate, chromate and arsenate. The respective Langmuir adsorption capacities for these anions’ adsorption by the adsorbent were 1.5, 0.8, and 0.4 mg/g. The corresponding values for the unmodified kaolinite were 0.012, 0.018, and < 0.002 mg/g. Because the release of Br- originally present in the HDTMA to the solution was chemically equivalent to the amount of nitrate adsorbed at all concentrations of nitrate, anion exchange was considered to be the mechanism of adsorption.

Xi et al. (2010) loaded HDTMA onto three aluminosilicates, namely smectite (bentonite) (CEC 66.7 meg/100g, specific surface area (SSA) 20.1 m2/g), kaolinite (CEC 9.8 meg/100g, SSA 30.9 m2/g), and halloysite (CEC 10.0 meq/100g, SSA 26.5 m2/g) at 2 and 4 times the CEC. They compared their nitrate adsorption capacities using 100 mg nitrate/L solution, finding that the untreated aluminosilicates were inefficient in adsorbing nitrate (0-0.5 mg nitrate/g). However, when modified with HDTMA, their adsorption capacities greatly increased (smectite 13-15 mg nitrate/g; kaolinite and halloysite 2-5 mg nitrate/g). The higher adsorption capacities of smectite were due to more HDTMA molecules being adsorbed to this aluminosilicate which had higher CEC. The percentages of HDTMA in smectite, kaolinite and halloysite were 30-43, 5-9, and 2, respectively. These aluminosilicates’ specific surface areas did not constitute a key factor for controlling the adsorption because smectite - having the lowest specific surface area - adsorbed the largest amount of HDTMA leading to the highest nitrate adsorption. Generally, there was no significant difference between the two HDTMA loading rates on any of the aluminosilicates, suggesting that once a bilayer of the surfactant is formed at a loading rate equivalent to twice the CEC of the aluminosilicate, further increase in loading rate will not greatly influence the anion adsorption capacity ((Haggerty and Bowman 1994). Xi et al. (2010) suggest that adsorbents with higher CEC have greater potential for use in cationic surfactant modification to enhance nitrate adsorption.

*2.4.3. Chitosan modified zeolite*

Chitosan beads are a promising material for nitrate adsorption with adsorption capacities reported to be 104 mg nitrate/g (Chatterjee et al. 2009). However, they are not mechanically strong and this causes particle breaking that alters the hydraulic conductivity (Arora et al. 2010). To increase mechanical strength, chitosan has been used to coat other stable materials such as zeolite. Arora et al. (2010) coated a natural zeolite with chitosan followed by protonation of the chitosan coating with acid treatment (Ch-Z) and tested the material for nitrate removal from water. The surface area of the Ch-Z (4.74 m2/g) was lower than that of the acid washed zeolite (10.15 m2/g) due to partial and/or full blockage of the zeolite pores, but it had a nitrate adsorption capacity comparable to other weak-base anion exchangers. Unmodified zeolite, on the other hand, had very small or no capacity to adsorb nitrate. The maximum nitrate adsorption capacity of the Ch-Z at 20oC was 37-46 mg/g. The Ch-Z did not favour nitrate adsorption when compared to Cl- and SO42- with the selectivity series being SO42- > Cl- > NO3-. Therefore, Ch-Z can be effectively used only in waters having low concentrations of Cl- and SO42-.

*2.4.4. Anion exchange resin coated carbon electrode*

Carbon electrodes have been used to remove cations and anions from water through the capacitive deionisation process (Biesheuvel et al. 2011; Lee et al. 2011; Kim and Choi 2012). Here an electrode potential is applied to porous carbon electrodes for the removal of ions by adsorption onto the electrodes. The adsorption of ions is improved by coating cation and anion exchange membranes or polymers onto the positively charged electrodes (Lee et al. 2011). However, this process removes all types of anions at the positively charged electrode coated with the anion exchanger.

Recently, Kim and Choi (2012) fabricated a novel composite carbon electrode in a capacitive deionisation set-up to selectivity remove nitrate in the presence of excess chloride ions by coating a nitrate selective anion exchange resin onto a carbon electrode. Nitrate adsorption was expected to be improved due to initial adsorption of large amounts of these ions onto the anion exchanger before migrating to the electrode surface. After the adsorption the electrode is regenerated by desorption of the adsorbed nitrate by applying zero electrode potential. When a carbon electrode coated with an anion exchange polymer that was not selective for nitrate was used, 7.8 and 17 mmoles/m2 of nitrate and chloride were removed from a 300 mL solution containing 2.0 and 5 mM concentrations of these ions, respectively. In contrast, when the carbon electrode was coated with a nitrate-selective anion exchanger, the amounts of nitrate and chloride removed were 19 and 15 mmoles/m2, respectively. This constituted a 2.3 times increase in nitrate adsorption when using a nitrate-non-selective anion exchanger. This is a promising technique for removing nitrate and therefore more studies on this method are required. They will need to use larger volumes of solution in the presence of a series of anions commonly found in waste water in long-term trials.

It is evident from the review that aluminosilicates’ ability to adsorb nitrate is negligible because of their negative surface charges. Even after surface modification with surfactant to provide positive surface charges, they did not demonstrate appreciable nitrate adsorption capacity (1.5-9.7 mg/g Langmuir adsorption capacity, Supplementary Appendix Table S1). Furthermore the adsorption capacity for nitrate decreased in the presence of other anions. Therefore they are not very good in removing nitrate from water. However, aluminosilicates are low-cost natural materials and have good physical properties (hydraulic conductivity) for practical use. Instead of surfactants, other organic materials like chitosan can be used for coating aluminosilicates to provide them with good adsorption capacities. Recently, an electrochemical method using carbon electrodes coated with nitrate-selective anion exchange resin was found to have good potential for nitrate removal. However, they require more research to test their practicality.

*2.5. Heat treatment*

Heat treatment can increase the surface area and porosity of some adsorbents providing increased number of sites for adsorption of pollutants. Heat activation of carbon produced from many biological materials has been shown to increase the adsorption capacity of many pollutants, especially dissolved organic compounds (Yin et al. 2007; Gupta et al. 2009). Similarly, heat activation of alumina and red mud has been shown to increase the adsorption capacity of phosphate and heavy metals (Li et al. 2006; Bhatnagar et al. 2011). For nitrate adsorption, heating layered double hydroxides (LDH) up to 400oC have increased the surface area and porosity of LDH, but the adsorption capacity increased at 200oC and then decreased with further heating (Islam and Patel 2009, 2010, 2011). The rise in surface area and porosity was due to the loss of physically adsorbed water and loosely bonded water in the interlayer spaces of LDH (Islam and Patel 2011). The decreased adsorption at temperatures above 200oC was attributed to structural deformation at these high temperatures (Islam and Patel 2009, 2010, 2011). The cost of heating should be considered in tandem with the beneficial effect of heating to increase the nitrate adsorption capacity, particularly when making decisions on employing this technique of surface modification.

Socías-Viciana et al. (2008) reported that heating LDH to 500oC and 650oC increased surface area, whereas heating to 850oC decreased surface area. However, the nitrate adsorption capacity increased from 62 to 105 mg/g when temperature increased from 550oC to 850oC (Supplementary Appendix Table S1). Nitrate has difficulty in exchanging with interlayer CO32- in LDH, but when LDH is heated to temperatures above 550oC, the CO32- is decomposed into CO2 and NO3- is adsorbed on the sites that CO32- occupied earlier. This reason was suggested by Socías-Viciana et al. (2008) for the increased NO3- adsorption. Furthermore, heating LDH to 500oC and 650oC produced amorphous Mg-Al mixed oxides with higher surface areas with increased number of adsorption sites; this led to greater nitrate adsorption. Heating to 850oC reduced surface area in relation to the sample heated to 650oC due to the formation of spinal-like crystalline oxides. The samples heated to 500oC and 650oC regained the initial layered structure of LDH when rehydrated by incorporation of NO3- in interlayer spaces, whereas the sample heated to 850oC, only partially recovered the initial structure and consequently demonstrated less nitrate adsorption.

The above studies provided information on the effect of heating LDH on nitrate adsorption at low (< 400oC) and high (550-850oC) ranges of temperatures with mixed results. Further studies are required to determine the effect of heating within a wider temperature range. Heat treatment of adsorbents, though increased surface area and porosity, had no significant impact on adsorption capacity, unlike in the case of heating ZnCl2 treated activated carbon (see section 2.2.1) where the adsorption capacity increased by more than 100%. Not only the calcining process has no significant effect on nitrate removal but also the heat energy required for the activation of the adsorbents can be expensive and therefore this process of surface modification may not be attractive. Even without excessive heating, LDHs have appreciable nitrate adsorption capacity (Supplementary Appendix Table S1), because they have net positive charges unlike the other aluminosilicates discussed in section 2.4 that have net negative charges.

**3. Conclusions**

For an adsorbent to be effective in a plant-scale water treatment system, it should have the following characteristics: large nitrate adsorption capacity, high nitrate selectivity in the presence of other ions, low cost, capable of efficient regeneration for multiple re-use of the adsorbent, and good hydraulic conductivity when used in fixed-bed columns. The value of the adsorbent in simultaneously removing other contaminants in water should also be considered when selecting adsorbents. Many of the surface modified adsorbents have comparable or higher adsorption capacities than most of the unmodified adsorbents. The enhanced nitrate removal by surface chemical modification of adsorbents is primarily due to an increase in surface positive charges or providing new surface functional groups having a greater affinity for nitrate.

Of the surface modification methods, protonation and amine grafting of adsorbents produced the highest increase in adsorption capacity (Langmuir nitrate adsorption capacity upto 363 mg/g for protonation and upto 125 mg/g for amination, 3 and 14 times the values for the unmodified adsorbents, respectively). Heat treatment of adsorbents, while they increased surface area and porosity, led to no significant increase in adsorption capacity. The heat energy required for activating the adsorbents can also be expensive and therefore this process of surface modification must be treated with caution. Protonation by acid treatment is simple and an established technique for other contaminants removal as well. Generally this method of modification is performed on adsorbents produced from agricultural and industrial wastes, which are low-cost materials. Therefore this method of surface modification does have potential.

Organic compounds added to aluminosilicates had the lowest adsorption capacity (Langmuir nitrate adsorption capacity generally < 10 mg/g), because aluminosilicates have negligible adsorption capacity for nitrate to start with. However, adsorbents, especially zeolite, modified by this method have good physical properties such as mechanical strength and hydraulic conductivity that are suited for fixed-bed columns filtration system. Furthermore, the aluminosilicates are natural inexpensive materials which keep the treatment costs low.

Limited data is available on nitrate selectivity of adsorption in the presence of other ions in water. Some amine grafted adsorbents and surfactant modified adsorbents have been reported as having high selectivity for nitrate. On the other hand, metals and metal oxide modified adsorbents generally have low selectivity for nitrate.

Only a limited amount of data is available on the regeneration of adsorbents. Generally, NaOH is used to desorb the nitrate adsorbed. Disposal of the used alkaline solution is a problem. If inexpensive materials such as agricultural and industrial wastes are used as adsorbents, they need not be regenerated for reuse. Instead they can be applied to agricultural lands after only a short period of use, as a nitrate fertiliser and soil amendment to improve the physical and chemical properties of soils. This is possible as long as they do not contain excessive concentrations of contaminants.

**Acknowledgements**

This work was funded by Australian Research Council Discovery Research Project (DP 1092603). We thank Phil Thomas for proof reading the paper.

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**Figure captions**

Fig. 1. Surface modification techniques used to enhance nitrate removal by adsorbents

Fig. 2. Schematic illustration of surface modification of adsorbents (■ represents unmodified adsorbents) for the removal of nitrate (a) surface protonation (b) surface impregnation of metal or metal oxide (c) surface grafting of amine group (d) cationic surfactant modification

Fig. 3. Schematic illustration of nitrate adsorption on Zr4+-loaded sugar cane beet pulp (redrawn from Hassan et al. 2010)

Fig. 4. Zeta potentials (related to surface charge) of wheat straw (WS) and wheat straw grafted with amine groups anion exchanger (WSAE) as a function of pH (redrawn from Xing et al. 2011)

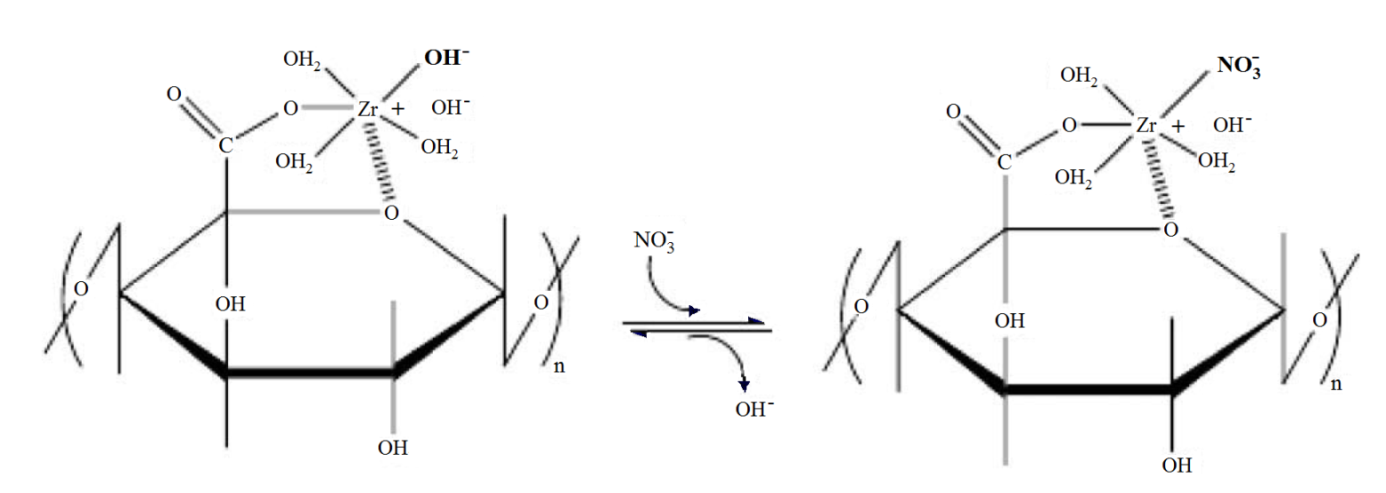
Fig. 5. Schematic illustration of (a) amine group grafting of mesoporous silica and (b) protonation of the amine group (redrawn from Saad et al. 2008)

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  | Surface modification technique | | |  |  |  |
|  |  |  |  |  |  |  |  |  |
|  |  | Chemical | | |  |  | Physical | |
|  |  |  |  |  |  |  |  |  |
| Protonation (acid treatment) |  | Metals or metal oxides impregnation |  | Grafting amine groups |  | Organic modification of aluminosilicate minerals |  | Heat treatment |

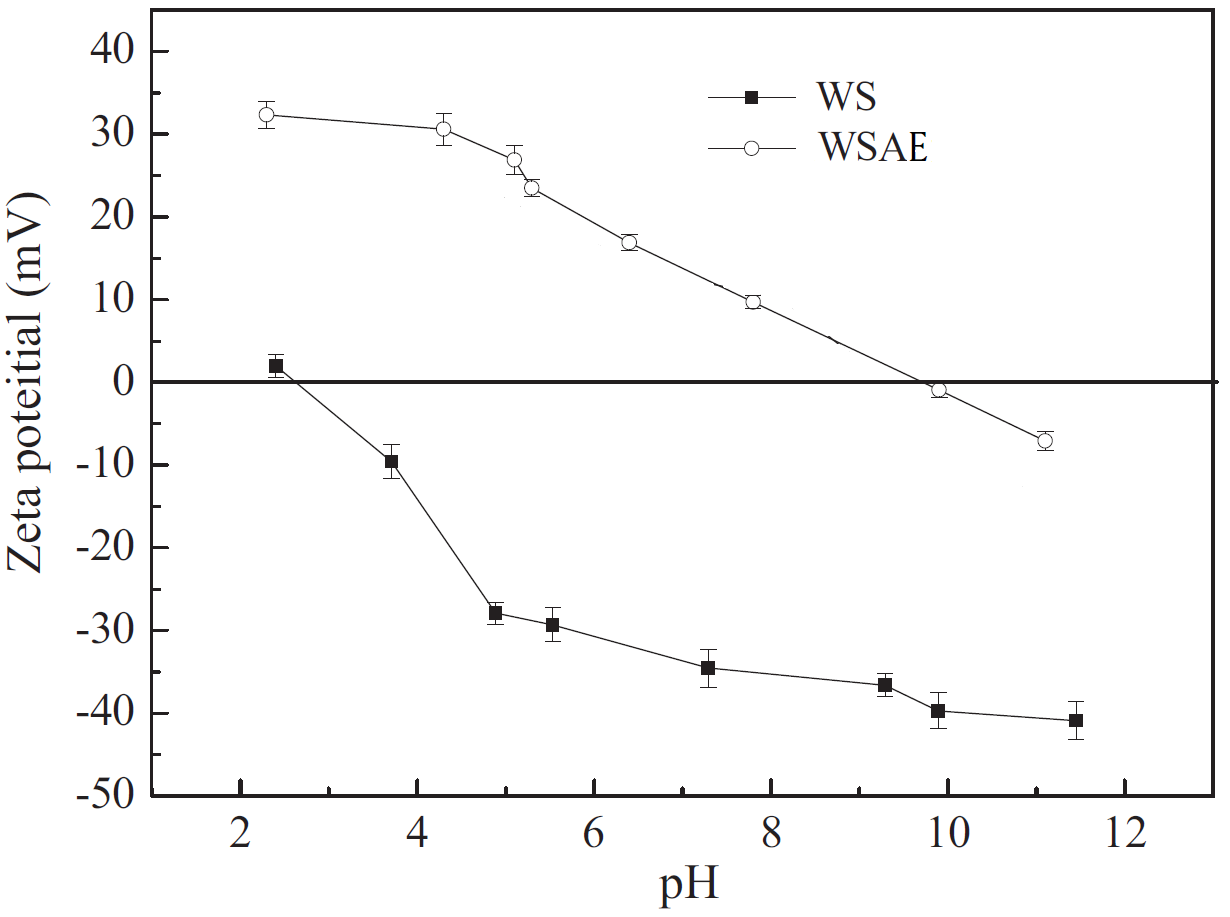
**Fig. 1.**

|  |  |  |
| --- | --- | --- |
| (a) |  | (b) |
|  |  |  |
| (c) |  | (d) |
|  |  |  |

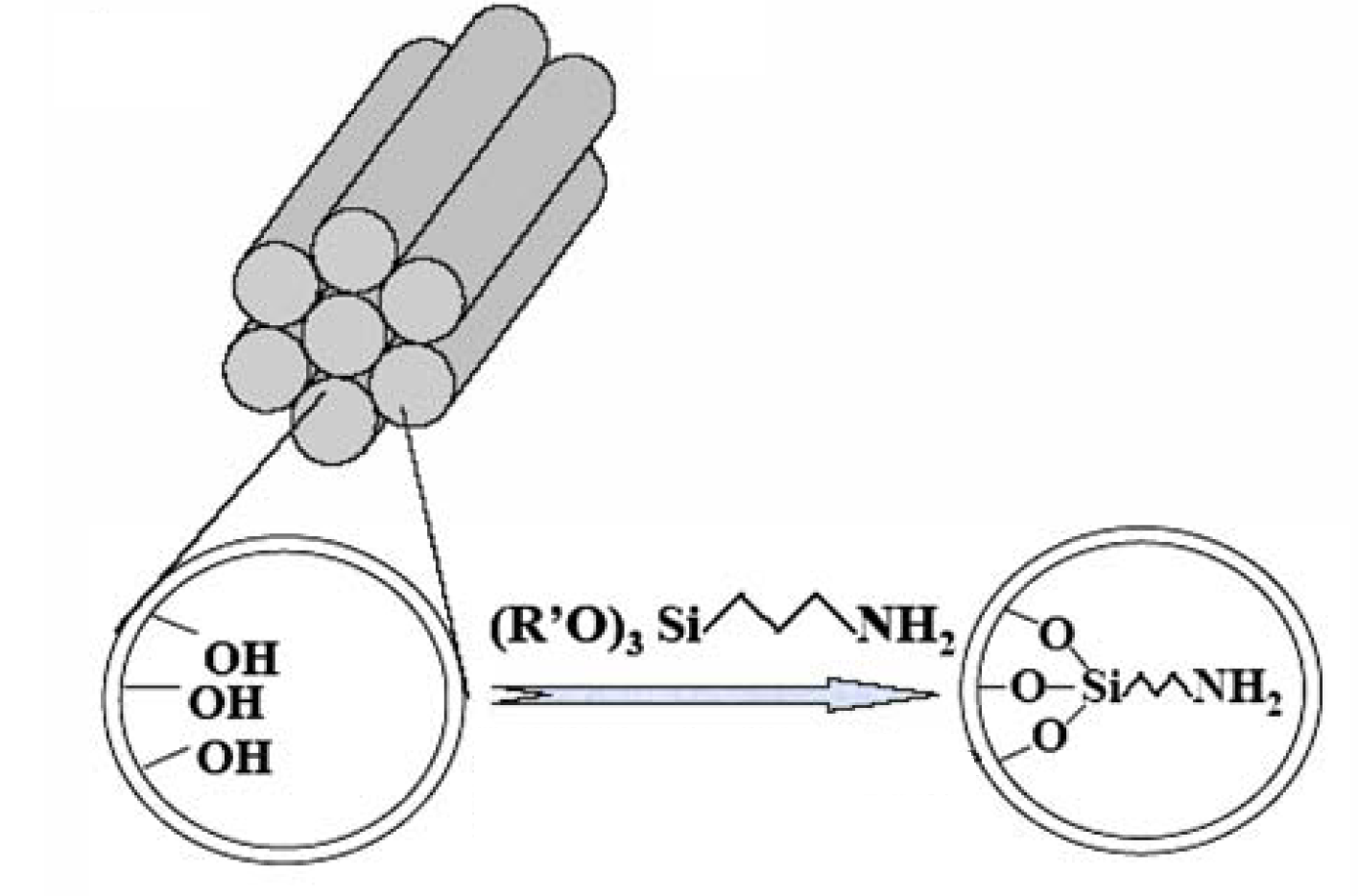
**Fig. 2.**



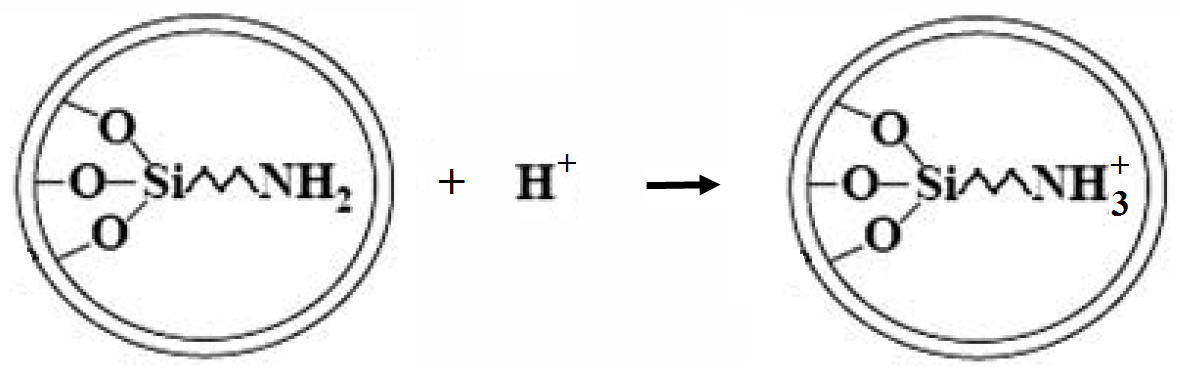
**Fig. 3.**



**Fig. 4**



a)



b)

**Fig. 5**

Supplemenary data Appendix Table S1

**Enhanced removal of nitrate from water using surface modification of adsorbents – a review**

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Table S1. Effect of surface modification of adsorbents on enhancement of nitrate adsorption (adsorption capacity unit is mg NO3-/g; Langmuir denotes Langmuir adsorption capacity; Freundlich constant related to adsorption capacity, (mg/g)(L/mg)1/n)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Adsorbent | Modification | Experimental conditions | Adsorption capacity - adsorbent | Adsorption capacity - modified adsorbent | Reference |
| Sapiolite | Protonation (HCl) | Batch, 0.5 g adsorbent, 50 mL, 100 mg NO3-/L | Freundlich  9.16 x  10-17 | Freundlich 2.49 (Langmuir 38) | Öztürk and Bektaş (2004) |
| Red mud | Protonation (HCl) | Batch, pH 6, room temp. | Langmuir 115 | Langmuir 363 | Cengeloglu et al. (2006) |
| Carbon cloth | Protonation (H2SO4, HCl) | Batch, pH 7, 25oC | Langmuir 24 | Langmuir 126 | Afkhami et al. (2007) |
| Chitosan beads | Protonation (NaHSO4),Cross-linked(CL), non-CL | Batch, 1 g adsorbent, 50 mL, 500 mg NO3-/L, 30oC | Un-protonated CL 88, non-CL 79 | Protonated  CL 93, non-CL 83 | Chatterjee et al. (2009) |
| Activated carbon (AC) (coconut coir pith) | ZnCl2 | Batch, pH 3, 35oC | negligible | Langmuir 10.3 | Namasivayam and Sangeetha (2005, 2008) |
| Granular AC (coconut) | ZnCl2 | Batch, pH 5.5, 25oC | Maximum adsorption 1.7 | Maximum adsorption 10.2 | Bhatnagar et al. (2008) |
| AC (sugar beet bagasse) | ZnCl2 | Batch, pH 6.58, 25oC, 35oC | - | 25oC, 9.1; 35oC, 15.5 | Demiral, and Gündüzoğlu, (2010) |
| Granular AC (Lignite) | ZnCl2 | Batch, 25oC | Langmuir 10 | Langmuir 12-15 | Khan et al. (2011) |
| AC fibres (cellulose based) | α-FeOOH, β-FeOOH | Column, inlet 3 mg NO3-/L, pH 6.5, 30oC, 200 g AC, at 30 min, 4 mL/min | Amount adsorbed 1.2 | Amount adsorbed, α-FeOOH-AC 2.2, β-FeOOH-AC 1.8 | Kaneko et al. (1991) |
| Sugar beet pulp | Zr (IV) (zirconium ions) | Batch, pH 6, 25oC | - | Langmuir 63 | Hassan et al. (2010) |
| Polypropylene film | Amine group grafting | Batch, pH 7.2, 200 mg NO3-/L,  Room temp. | Amount adsorbed 13 | Amount adsorbed 22-23 | Taleb et al. (2008) |
| Biochar | MgO | Batch, room temp. | - | Langmuir 94 | Zhang et al. (2012) |
| Wheat straw | Amine group grafting | Batch, pH 6.8, 23oC | Langmuir 8.9 | Langmuir 125 | Wang et al. (2007a, b) |
| Wheat straw | Amine group grafting | Batch, 20oC | - | Langmuir 53 | Xu et al. (2010) |
| Wheat straw | Amine group grafting (low, medium, high doses) | Batch, 20oC | - | Langmuir, low dose 28, medium 52, high 90 | Xu et al. (2011) |
| Wheat straw | Amine group grafting | Column, height 1-2.5 cm, flow rate 5 mL/min, pH 5.1, room temp. | negligible | Column adsorption  86-87 mg/g | Xing et al. (2011) |
| Sugarcane bagasse (BG), Rice hull(RH) | Amine group grafting | Batch, 30oC | - | Langmuir, BG 87, RH 81 | Orlando et al. (2002a) |
| Lauan saw dust,coconut husk, moringa hull, rice hull, pine bark | Amine group grafting | Batch, 30oC | - | Langmuir 47-74 | Orlando et al. (2002b) |
| Rice husk | Amine group grafting | Batch, 20oC,  pH 7 | - | Langmuir 56 | Katal et al. (2012) |
| Coconut shell powder | Ammonium quarternary salt | Batch, pH 7, 25oC | negligible | Langmuir 34 | De Lima et al. (2012) |
| kaolinite | HDTMA-Br, 200% kaolinite CEC | Batch, 25oC | Langmuir 0.01 | Langmuir 1.5 | Li and Bowman (2001) |
| Carbon nanotube sheets | Ammoniation, N-group addition | Batch, 25oC | - | Langmuir 143 | Tofighy and Mohammadi (2012) |
| Kaolinite | HDTMA-Br, 25-200% kaolinite CEC | Batch, 25oC | Langmuir  < 0.1 | Langmuir CEC 100%, 4.0; 150% 6.6, 200% 5.6 | Li (2003) |
| Kaolinite (K), halloysite (H), smectite (S) | HDTMA-Br, 200-400% kaolinite CEC | Batch, 0.2g adsorbent, 40 mL 100mg/L, pH 5.4 | Amount adsorbed K, S, < 1; H, 5 | Amount adsorbed S, 13-15; K, 2-5; H, 2-3 | Xi et al. (2010) |
| Zeolite (four countries) | HDTMA-Br,75-219 mmol/kg | Batch, 25oC | Langmuir 0.2 | Langmuir  1.5-3.5 | Guan et al. (2010) |
| Zeolite | HDTMA-Br, 120% Zeol. CEC | Batch, room temp., pH 5-6 | No affinity | Langmuir 5.4 | Schick et al. (2010) |
| Zeolite | CPB, 100-409 mmole/kg | Batch,25oC,4g/L adsorbent, pH 6, 88.6 mg NO3-/L | < 2% removal | Removal %increased with CPB load, 3-33. Langmuir 9.7maximum | Zhan et al. (2011) |
| Zeolite | Chitosan + protonation | Batch, 20oC | Low or no affinity | Maximum adsorption 46 | Arora et al. (2010) |
| Carbon electrode | Anion exchange resin | Laboratory, 2.0 mM NO3-, 5.0 mM Cl-, room temp. | 515 mg/m2 | 1176 mg/m2 | Kim and Choi (2012) |
| Layered double hydroxide (Mg-Al-CO32-, LDH) | Heating to 550, 650, 850oC for 12 h | Batch, 25oC, 0.1g LDH/50 mL, 12.7-236 mg NO3-/L | - | Langmuir: 550oC, 61.7; 650oC, 82; 850oC, 105 | Socías-Viciana et al. (2008) |
| LDH (Mg-Al-Cl) | Heating, 100, 150, 200, 300, 400oC, 8 h | Batch, 25oC, 0.1-0.8 g LDH in 100 mL, 10-100 mg NO3-/L | % removal 70.6 | % removal, 100-200oC 73-79; 300-400oC 47-65 | Islam and Patel (2009) |
| LDH (Zn-Al-Cl) | Heating, 100, 150, 200, 300, 400oC, 8 h | Batch, 25oC, 0.1-0.8 g LDH in 100 mL, 10-100 mg NO3-/L | % removal 67.8 | % removal, 100-200oC 71-76; 300-400oC 42-62, Langmuir 40 for 200oC | Islam and Patel (2010) |
| LDH (Ca-Al-Cl) | Heating, 100, 150, 200, 300, 400oC, 8 h | Batch, 25oC, 0.1-0.8 g LDH in 100 mL, 10-100 mg NO3-/L | % removal 67.8 | % removal, 100-200oC 71-76; 300-400oC 42-62 | Islam and Patel (2011) |