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Modified-Nano-Adsorbents for Nitrate Efficient Removal: A Review

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ABSTRACT

Excessive nitrate discharge into the aquatic environment from human activities is the main contributor to groundwater and surface water contamination. Its toxicity in water is a serious concern as it gives huge impacts on aquatic life since it damages the ecosystem and water sources around the globe. Recently, the development of nanomaterials as nano-adsorbent makes adsorption the most attractive solution among them. Nano-adsorbents pose high efficiency to remove pollutants from aqueous media. The exclusive chemical and structural properties of the developed nano-adsorbents are the determinative effects of nitrate adsorption performance. In this mini review, the state-of-the-art development of nano-adsorbents and nano-adsorbents-modified membranes for nitrate from water is discussed, and some challenges faced in this field are also highlighted.

Keywords: Nitrate removal, adsorption, nano-adsorbents, membrane, chemical modification

1.0 INTRODUCTION

Water is a basic multipurpose substance that is being utilized by a human for drinking and other daily activities. In the present era, many countries around the world are experiencing rapid growth in urbanization, industrialization and agricultural activities. The activities influence the economy decidedly, as well as inevitably contribute towards some environmental problem. One of the serious issues which arise as the shadow side of these developments is water pollution. Besides, water pollution also happened as the consequences of domestic wastes disposal that comes from human and animal excretion, food bodies and household garbage. The pollution makes the water unsuitable for desired purposes since there are changes in water quality that might harm the living organisms. The activities have introduced toxic contaminants such as oil, dyes, heavy metals, inorganic anions and synthetic organic into the aquatic environments. Among them, the discharge of inorganic anions containing waste, which has been neglected by many countries, is found to threaten the living organism even at trace concentrations [1].

Nitrate is among the most common inorganic anions found in wastewater. The ions mainly posed by the agricultural run-off containing fertilizers and pesticides alongside the untreated or undertreated disposal of domestic, aquaculture and industries [1, 2]. It is costly and difficult to remove nitrate once it seeps the soil and

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groundwater. Also, the long-term exposure to nitrate can adversely affect human health. The study on nitrate showed that consumption of food or water with high nitrate concentration may attain cancer, diabetes mellitus and methaemoglobinemia which likely to impinge young children under six months of age [3]. For these reasons, it is important to keep nitrate levels as low as possible. To get rid of the risks, the World Health Organization has set that 50 mg L-1 as the maximal admissible values for nitrate in drinking water [4].

Contemporarily, many approaches such as chemical treatments, biological treatments, adsorption and reverse osmosis have been employed for nitrate decontamination. However, energy demand, production of toxic waste and incomplete pollutant removal are the major setback to those approaches [5]. Ideally, adsorption prevails as a standout nitrate removal approach. The adsorption is an efficient process because of the flexibility in operation and produces high efficiency even at low concentration [6–9]. This review provides an overview on the recent advances of nanomaterials used as nano-adsorbents for adsorption of nitrate. The illustration on the adsorption and mechanism of ions removal are also reported. challenges which prominently limit their industrial application [1].

2.0 EXISTING TECHNOLOGIES FOR NITRATE REMOVAL

Keeping with the view that nitrate can give negative effects to human and the environment, various treatment methods have been conducted to eliminate the anions. These methods existed with their relative advantages and disadvantages [5] and the commonly used methods can be simplified into biological method, chemical method, physical treatment, adsorption and ion exchange. A brief overview of the techniques is presented in Table 1.

The costs of biological treatment are lower than that of chemical treatment, but it is usually unstable, difficult to apply and contain non-biodegrade contaminant [1, 7]. Besides, according to their studies, biological approaches consume more energy and need a lot more spaces as compared to chemical approaches. For chemical treatment, it is less complicated than biological.

Reverse osmosis (RO) is a simple and effective separation process in terms of its operation and maintenance than ion exchange [16]. In RO, the direction of water flow can be reversed by applying 750 psi pressure that is greater than the osmotic pressure. The performance dependent on membrane characteristics and water properties [17]. However, RO is a non-selective approach in which it will eliminate all ionic constituents from water. Conventional RO exhibits relatively low nitrate removal efficiency and requires an extra process for hardness removal [18]. In addition, the process generally requires further post treatment to adjust water quality.

Another commonly applied treatment method is adsorption. Adsorption through various adsorbents is a versatile and promising method among other methods for removing pollutants in wastewater. It offers relatively simple method, economic viability, easy operation and recovery [1, 19, 20]. The substances then accumulate on the adsorbent due to physical and/or chemical interactions [21]. Absorption is a process that occurred throughout the body of absorbent and allowed ions to penetrate into the absorbent’s pore. Conversely, adsorption only attracts ions to the adsorbent surfaces without penetrating into material. It is not possible for the adsorbate/absorbate to be released from the adsorbent/absorbent (oppose the adsorption/absorption process) and the phenomenon is called desorption.

3.0 ADSORPTION FOR NITRATE REMOVAL

Since decades ago, adsorption has been dubbed as an effective and economically attractive technique in industries for practical wastewater treatment applications [22, 23]. Adsorption is used at several interfaces i.e. air/liquid, solid/liquid and air/solid, only solid/liquid interface will be discussed in this study. Practical application of the adsorption for removing nitrate (or other contaminants) from water is performed by combining the adsorbent with adsorbate (in a batch or fixed-bed column system). The flexibility of the batch-adsorption procedure makes adsorption applicable for water treatment application, particularly drinking water.

Upon adsorption process, a mixture of predetermined adsorbent and solution containing contaminants was agitated then separated via filtration or sedimentation after desired adsorption period. The adsorbent with the excellent properties hence adsorbs the pollutants, resulting in less polluted or non-polluted water. The adsorption process using nano-adsorbent is illustrated in Figure 1.

Wide variety of adsorbents such as silica, graphene, activated carbon, and polymers have been found efficient for the nitrate removal from wastewater. The effectiveness of this technique is based on the development of an efficient adsorbent. According to Abou Taleb *et al.* [24], high adsorption capacity and surface reactivity of nitrate depends on the affinity and specific active sites of adsorbent. The specific surface, porosity, pore size, structure, distribution, and affinity of the adsorbate are among dominant factors influencing adsorption [26]. Therefore, the selection of adsorbent is very crucial to dictate its performance.

4.0 DEVELOPMENT OF NANO-MATERIALS AS NANO-ADSORBENTS

Nano-adsorbents are developed from various nanomaterials that have ability and affinity to adsorb certain substances especially from wastewater. Nanomaterials are produced by nanotechnology technique that engineered nanoparticles with size less than 100 nm [27]. Nanomaterials are known to be used for centuries in many industries because of the superior and unique properties that cannot be found

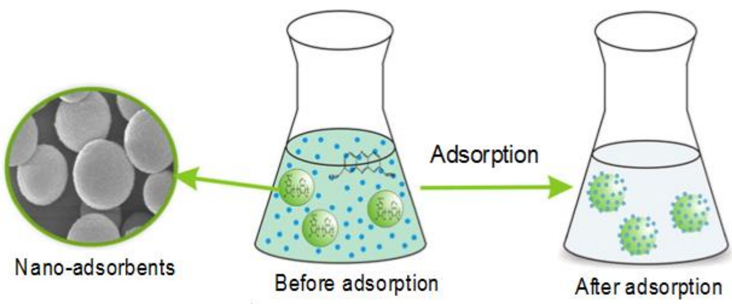

Figure 1 Diagrammatic representations of adsorption process for the nitrate using nano-adsorbent [24]

in their bulk materials. They also have the ability to be tuned with different chemical species to increase their functionality toward specific targets.

Besides innovating incredible new products, scientists also use nanomaterials to work towards cleaning water. The introduction of nanomaterials has led to changes in wastewater treatment approaches. Surface area, active sites, selectivity and the adsorption rate usually limits the efficiency of conventional adsorbents [28]. Nano-adsorbents offer more promising applications in wastewater treatment because of their desirable properties like high specific surface area, desired surface charge, and tunable pore size that far surpass conventional adsorbents [22].

Due to an increased adsorption capacity, high selectivity, easily employed and tailored for environmental applications, the nano-adsorbents are said to receive great concerns until now. As a result, nanomaterials have been well studied for heavy metals, organic impurities and dyes removal. Intense researches are currently focused on developing new effective and selective nano-adsorbent for nitrate removal. However, one of the significant issues in the use of nanoparticles is their aggregation that reduces colloidal stability and active surface sites. Therefore, application of bare nanoparticles in environmental remediation is still challenging.

The need for increasing affinity of this kind of adsorbent towards specific contaminants has led to surface modifications studies in order to draw firm conclusions about the performance. Surface modifications e.g. physical and chemical provide new functional groups that increase the surface positive charges and hence, favour nitrate adsorption. However, recent progress had shown chemical modifications receive great attentions compared to physical modification which is heat treatment. Chemical modifications used to enhance nitrate removal are classified in Figure 2.

4.1 Acid and Alkaline Activation

Among chemical modifications, acid or alkaline modification on adsorbents had proved that it was able to improve the potential of adsorbents to remove nitrate. Acid treatment was done to cause the protonation because, upon acid treatment, more OH groups were introduced on the adsorbent surface. Protonated adsorbents increased the net positive charge (H^+ ions), thereby enhancing its binding potential for negative ions nitrate ions via electrostatic attraction. Meanwhile, treating adsorbents with alkaline was

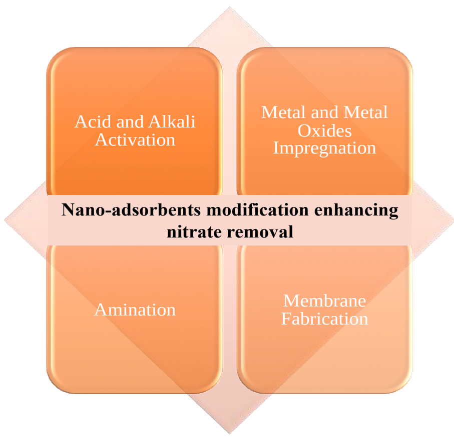

Figure 2 Modification on nano-adsorbents used for nitrate removal

found to generate more microspore and smooth the surface of adsorbents. It may be related to the dissolution of some components by alkali solution [29]. Equation of the protonated adsorbent surface and nitrate adsorption are given as follow [30].

Acid activation:

$$X-OH + H^{+} \rightarrow X-OH_2^{+} \quad (1)$$

Nitrate adsorption:

$$X-OH_2^{+} + NO_3^{-} \rightarrow X-OH_2^{+} \cdots NO_3^{-} \quad (2)$$

$$X-OH_2^{+} + NO_3^{-} \rightarrow X-NO_3^{-} + H_2O \quad (3)$$

$X = raw\ adsorbent$

Researcher modified carbon nanotubes (CNTs) to assess their productivity for the removal of different contaminants [31]. Surface oxidation of CNT sheets was done by using concentrated acid, HNO_3 and liquid ammonia (oxygen and nitrogen-containing functional groups) to enhance the surface properties [32]. Synthesizing CNT sheets by chemical vapor deposition method resulting in easier synthesizing processes due to high flexibility and strong CNT sheets. Nitrate reacts with the functional groups that have been introduced onto the CNT sidewalls and thus, led to high nitrate sorption capacity. The acid treatment produced positives sites on CNT sheets which in turn increased electrostatic adsorption of anions.

As depicted in Figure 3, the idea of treating activated carbon (AC) with alkaline was found to generate more microspore and smooth the surface of AC. It may be attributed to the dissolution of some components by alkali solution. Two-steps treatment, alkaline treatment (NaOH) followed by cationic surfactant treatment on commercial granular AC was investigated to increase nitrate removal efficiency [29].

Successful NaOH treatment upfront was said to dissolve most organic components and hence, these couldn't pass to the solution and interfere with nitrate adsorption [33]. Large surface area and porous structure of AC did not play significant role, instead, the increment in the number of functional groups after cationic surfactant treatment seems to boost the nitrate uptake [29]. In overall, it can be deduced that acid or alkaline treatment is a simple alternative technique to promote the adsorption capacity.

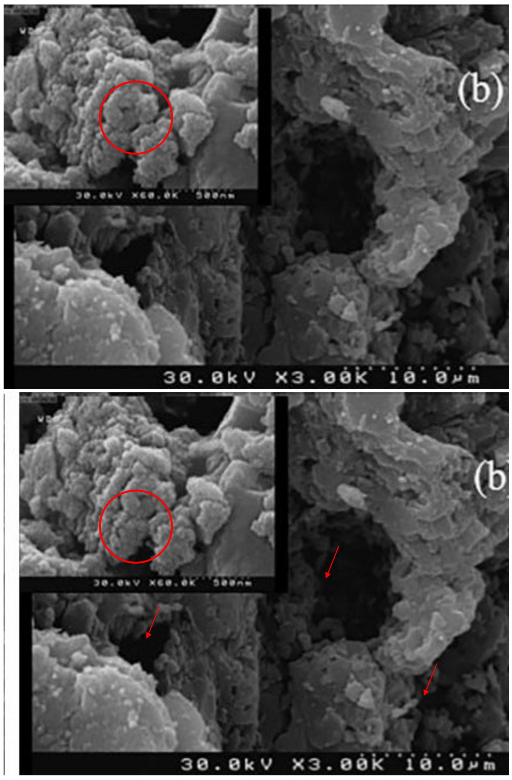

Figure 3 Micrographs of (a) AC and (b) alkaline treated AC [29]

4.2 Metal and Metal Oxides Impregnation

Having fast kinetic, large surface area, specific affinity for the adsorbate and give minimal environmental impact making metal-based nanomaterials technologically and economically advantageous [22]. Metal alloys and metal oxides have wide applications as adsorbents because of multifunctional behaviour e.g. short intraparticle diffusion distance, high adsorptivity, superparamagnetic (some of them) and easily regenerated [28].

To date, a number of metal oxides, i.e. ferric oxides, magnesium oxides, titanium oxides, zinc oxides, lanthanum oxides and zirconium oxides were used to remove the anions in water. These oxides have shown high affinity towards nitrate ions where the sorption is mainly controlled by complexation of hydroxide in solution and subsequent acidic dissociation at the solid solution interface that creates positively charged surface sites on the adsorbent, and hence, adsorb the nitrate ions [34]. The reaction occurred during modification and adsorption process could be elucidated by Eq.(4) and Eq. (5) [30].

Metal impregnation:

$$\mathrm{X} + \mathrm{Me}^{a+} \rightarrow \mathrm{X} - \mathrm{Me}^{(a-1)+} \tag{4}$$

Nitrate adsorption:

$$\mathrm{X} - \mathrm{Me}^{(a-1)+} + \mathrm{NO_3^-} \rightarrow \mathrm{XMe}^{(a-1)+} \cdots \mathrm{NO_3^-} \tag{5}$$

$X = raw\ adsorbent, Me = metal,$
$a = charge\ of\ metal$

Lanthanum, La is one of the best metal cation for dispersion on adsorbent to boost adsorption efficiency for as much as La^{3+} ions exhibited high sorption affinity towards nitrate [35]. Lanthanum compounds e.g. La_2O_3 binds strongly to anions that they can remove nitrate ions from aqueous solution by forming lanthanum nitrate. Up to now, numbers of nanomaterials have been used to combine with La. Karthikeyan *et al*. [36] however incorporated La(III) with chitosan nano-membrane, La@CS. The nano-membrane was reported as effective separation technology for various contaminants such as dyes, heavy metals etc. The advantages of nano-membrane over others include the quality of water, effective disinfection and small space requirement for plant [37]. La@CS effectively adsorbed nitrate by multiple adsorption mechanisms, ion exchange membrane and electrostatic attraction between positively charged membrane and nitrate ions. Importantly, the field analysis verified the applicability of La@CS membrane on nitrate contaminated water.

Yang *et al*. [38] stated that the metal oxides impregnation enhanced the good features of steel slag such as high density and porosity strength and hence, increase the removal efficiency of nitrate. They successfully synthesized cost-effective adsorbent by surface modified-steel slag with $Al(OH)_3$ (MSS) and the removal performance was analysed. The removal efficiency and adsorption capacity were significantly enhanced using MSS that is incomparable with original steel slag (OSS). The pores size expansion, high porosity formation and aluminium content of MSS would provide a large number of active adsorption sites for nitrate removal. As a result, the removal efficiency of nitrate using MSS was approximately 1.9 times that of the OSS at the different contact time (pH= 4, dosage= 1 g/mL, initial concentration= 20 mg/L). Further studies on MSS anyhow need to be done in the follow-up experiments for the treatment of actual wastewater.

Biochar derived from variety of feedstock is one the versatile adsorbent for the removal of water contaminants since it possesses multifunctional characteristics; porous structure, compositional structure and surface [39]. Like most charcoal, biochar is made from biomass via pyrolysis. However, the ability of pristine biochar to adsorb anions like nitrate was limited by functionalities and poor mechanical strength [40]. Compared to other metal ions, Zr^{4+} ions with higher positive charge has greater tendency to remove the anions. Banu *et al*. [41] developed complex and novel nitrate adsorbent by embedding Zr^{4+} ions on chitosan–soya bean husk activated bio-char composite beads (Zr-CS-SAC). Thus, higher porosity and abundant active sites of Zr-CS-SAC composite beads resulted in great adsorption capacities. The results were best described by Freundlich isotherm and pseudo-second-order model for nitrate ions. Zr-CS-SAC allowed for effective adsorption of ions via ligand electrostatic adsorption, ion exchange, and also by hydrogen bonding of nitrate with hydroxyl groups of chitosan.

In other work, AC and nano zero-valent iron (nFe) composite (nFe-AC) were synthesized to remove nitrate [42]. The nFe° particles have drawn substantial attention in wastewater treatment due to its good sorptivity and reactivity towards wider range contaminants. Over time, however, it is necessary to modify nFe° as an aggregation of nanosized iron plagues its effectiveness. Additionally, direct application of nFe can lead to iron contamination due to rapid loss of its fine particles, hence AC was used to composite with nFe. AC was also undergoing thermal treatment to enhance AC surface chemistry and charge to attract nitrate ions which in turn eased the reaction with nFe. The outcomes showed nFe-AC successfully increased the removal efficiency of nitrate by 50% from their aqueous solutions. Although the removal of nitrate is sensitive to interference ions especially phosphate (shown in bar chart), this finding denoted that nFe°-AC with further optimization has the potential to be applied as reagent for wastewater treatment Figure 4 below summarizes the removal mechanisms took place in this study.

Rashidi Nodeh *et al*. [43] designed a novel nanocomposite adsorbent by hybridizing graphene with magnetic nanoparticles and La^{3+}-hydrate. The nanosized La hydrous with high positive charge was doped on magnetic reduced graphene oxide (MG@La) and its removal efficiency was evaluated. The procedure of the synthesis MG@La is given in Figure 5. The MG@La

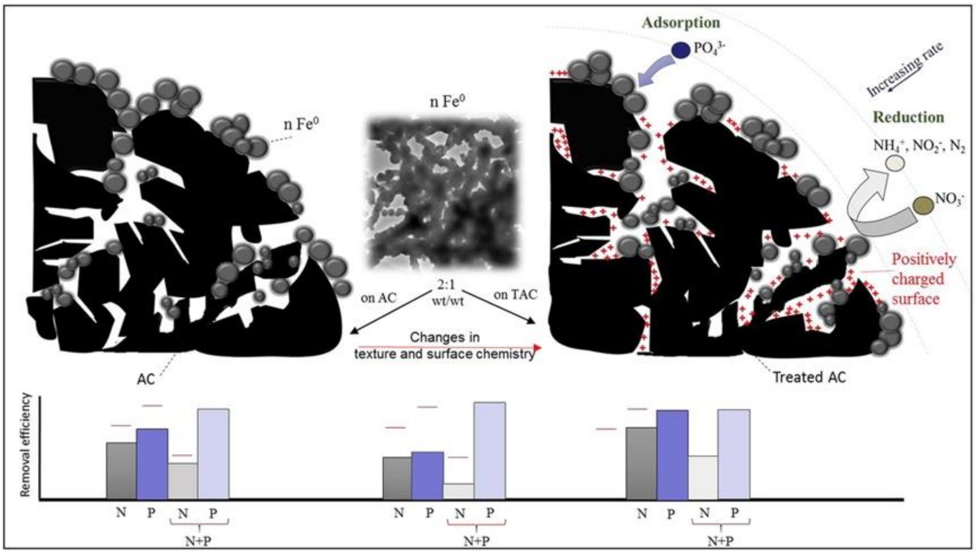

Figure 4 Schematic diagram summarizing the removal mechanism and results of batch studies [42]

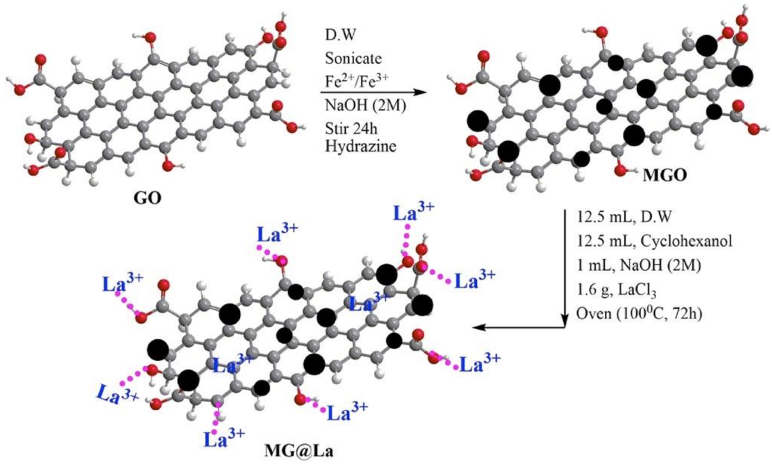

Figure 5 Graphical procedure for the synthesis of MG@La [43]

demonstrated superior adsorption capability to that of reported in previous studies. Electrostatic attraction of anions on MG@La involved was conceived as main adsorption mechanism. Also, chemical and physical adsorption result from efficient ion exchange of La to oxy donor and π-π interaction between graphene π-staking and N=O. Field application of MG@La indicates satisfactory removal of nitrate up to 74% in sewage water and 83% in river, respectively. The ferromagnetic behaviour, allowing efficient magnetic separation and repeated use of adsorbent. MG@La was found to exhibit high removal efficiency at laboratory and real field, suggesting their potential application in advanced water treatment.

Owing to the selective sorption capacities, non-toxicity, availability, and cost effective, application of zeolite has also received great attention in environment remediation [44]. $Fe(OH)_3$/Cp nano-adsorbent was produced by encapsulating $Fe(OH)_3$ with natural zeolite, clinoptilolite (Cp) that act as a stabilizer to prevent iron from supplementation and accumulation [45]. Cp with its porous structure was reported to adsorb nitrate in itself thus helps to remove them from water. The synthesized nano-adsorbent with 44.2 nm pore diameter was evidenced to be potentially useful materials to remove nitrate through adsorption and anion-exchange mechanism in acidic environments. Ease of magnetic separation, $Fe(OH)_3$ for this nanocomposite enables both the reusability of sorbent as well as nitrate recovery.

The application of $Fe(OH)_3$/Cp represents a possible perspective use in the removal of nitrate from polluted water environment. Overall, although numerous studies available on the application of magnetic-based nano-adsorbents, there are still exists knowledge gaps that need to be addressed. For example, the detailed assessment of magnetic-based nano-adsorbents against multi pollutant solutions.

4.3 Amination

In addition to metal and acid modification, amino group functionalization is another commonly applied modification and it has been demonstrated as a facile and effective modification to increase the adsorption. Adsorbent consists of amine (primary, secondary and tertiary) as active functional groups exhibit weak basic is known as weakly basic anion exchange.

Generally, silica, clays, carbon and agro solid-waste were modified using this technique to removed desired contaminants. At present, there are various ways of utilizing wastes or by-products, especially agro waste to increase their economic values.

Agro solid-wastes pose great properties in terms of surface, porosity, mechanical and chemical strength. Hence, a wide array of waste like rice husk (RH), corncob, sugarcane bagasse etc have been explored concerning the use of cost-effective adsorbents. They are often used for the immobilization of heavy metals, dyes, oils and nutrients anions. Unfortunately, the adsorption performance of raw waste on nitrate somehow was not that great. The researcher now paying much attention to enhance the adsorption capacity of cultivated waste through modification like amine grafting. The modification and adsorption are portrayed in Eq. (6) and Eq. (7) [30].

Amine grafting:

$$X + RN^{+} \rightarrow X - RN^{+} \qquad (6)$$

Nitrate adsorption:

$$X - RN^{+} + NO_3^{-} \rightarrow X - RN^{+} \cdots NO_3^{-} \quad (7)$$

$X = raw\ adsorbent$
$R = organic\ molecule$

A few recent studies reported on agro-waste can be referred for other possible adsorbents for the removal of nitrate. In the year 2019, a study by Qiao *et al*. [46] proves that the feasibility of utilizing tea waste (TW) crosslinked with amine groups (ACTW) to remove inorganic ions e.g. nitrate, phosphate. TW is found to have the ability to adsorb ions to a certain extent due to its multifunctional characteristics; porous and network structure, high surface area and large composition of cellulose. The removal of nitrate by both TW and ACTW were compared through a set of experiments. ACTW demonstrated good applicability in removing nitrate over a wide pH range (3 to 10). Adsorption equilibrium analysis showed that Langmuir isotherm and pseudo-second-order model best fit the experimental data nitrate with the adsorption capacity obtained, q_m=136.43 mg/g.

Likewise, Wu *et al*. [47] fabricated a novel adsorbent by modifying aluminium-manganese bi-metal oxide with organic solvent (50% dimethylamine) (OABO) introduce new active amine sites for remarkable of coadsorption nitrate. OABO changed its structural from nanoparticles to nanoplatelets, flake-like sheets. The infrared analysis further confirmed the presence of amine on OABO. Also, the analysis suggests that nitrate was adsorbed exclusively via electrostatic interactions between two groups of opposite charge (amine groups and nitrate) as well as ligand exchange with chloride ions. Furthermore, $NaHCO_3$ solution was used to regenerate OABO using for repeated use. The good adsorption capability and reusability imply that OABO holds good potential in enhancing the removal of nitrate.

Silica is often applied in the past for wastewater treatment, owing to its good adsorptive properties due to its functional groups, i.e. silanol (Si-OH) and siloxane (Si-O-Si). The most widely reported silica for anions removal are MCM-41, MCM-48 and SBA-15 [43–45]. Despite possess high porosity and tremendous surface area, mesoporous silica has a less adsorptivity and selectivity towards nitrate [49–51]. Since modification on nano-silica can bring out high performance, several methods have been devised on silica includes amino groups functionalization [52,53] via post-synthesis grafting or co-condensation process.

On the other hand, a strong basic anion exchange resin, new polymeric adsorbent (NDQ) has been evidenced to demonstrate higher selective adsorption ability toward nitrate in aqueous solution [54]. The NDQ with average pore size of 46.59 nm was modified with amine groups to enhance the adsorption capacity. The synthesis process of NDQ is presented in Figure 6. NDQ showed a high amount of sorbed nitrate, q_m=221.8 mg/g in comparison to other resins [55]. This probably due to the several mechanisms occurred not only ion-exchange mechanism but also by hydrogen bonding from the amino and hydroxyl groups. Modified adsorbent also highly selective to nitrate in the aqueous solutions containing other ions, HCO_3^- and Cl^-. In all, this adsorbent has the potential to be practically used in the purification of water resources owing to its good adsorption capacity and reusability.

4.4 Membrane for Nitrate Removal

In recent days, development of membrane incorporated with nanomaterials have been receiving considerable interest due to its high efficient operation. Previous membrane application via RO demonstrated that nitrate and other ions are rejected because of larger size than the membrane pore size [56]. Fabrication of nanocomposite membrane serves as an alternative to address current limitations and enhance the performance of membranes in nitrate decontamination. The prominent criterions of membranes fabricated from nanomaterials to remove ions from wastewater includes; (1) non-toxic, (2) possesses high adsorption capacity and selectivity, (3) easy separation and (4) recyclable [57]. In this process, microfiltration (MF) or ultrafiltration (UF) membranes coupled with adsorption technology are used to treat the nitrate contaminated water. Nitrate ions are usually adsorbed to the functional groups of the membrane or to the sorbent incorporated in the support membrane as illustrated in Figure 7 [58].

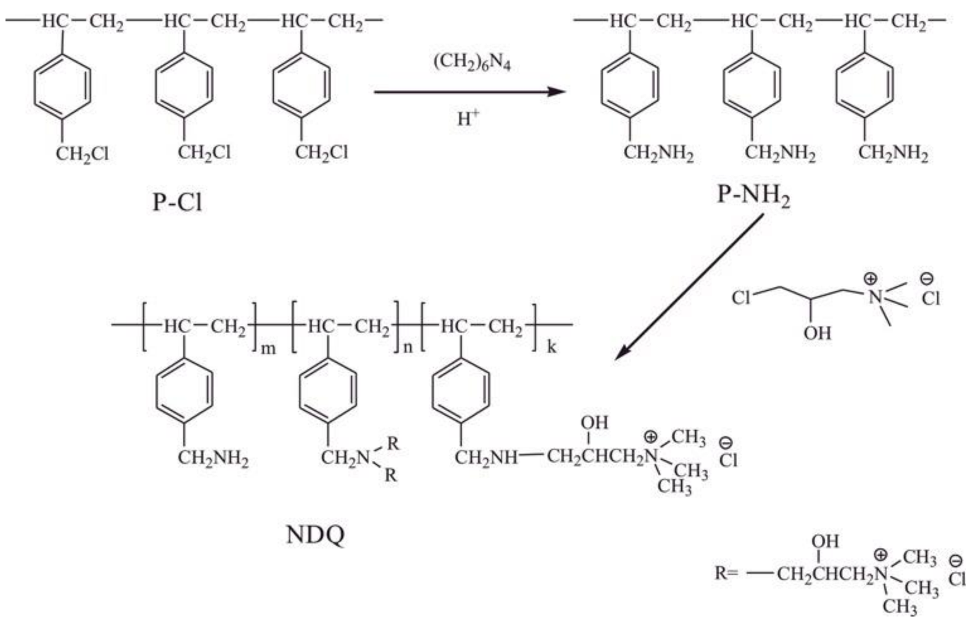

Figure 6 Schematic diagram showing preparation process of NDQ [54]

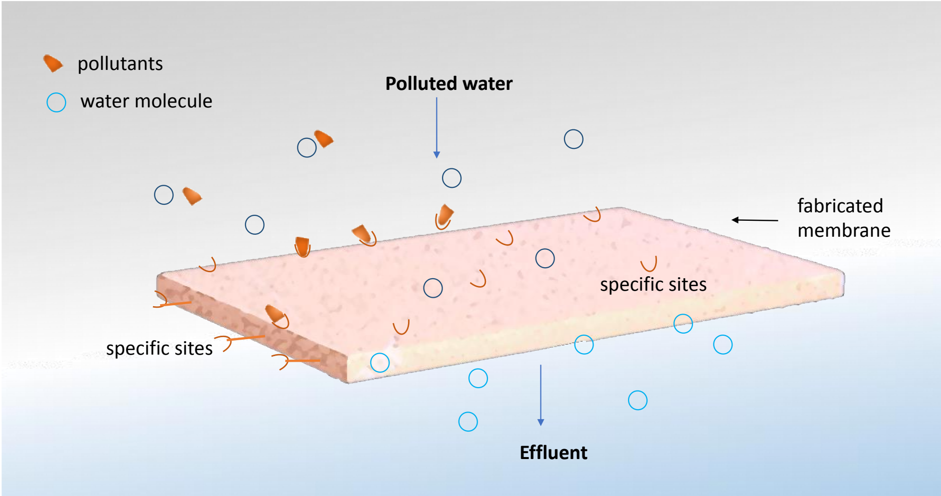

Figure 7 Illustration of membrane application for nitrate removal

High selectivity of the process is usually explained in terms of several factors e.g. pore size, charge of adsorptive sites, as well as solubility of solutes [59]. In this regard, Bahmani et la. developed a novel UF mixed matrix membrane by impregnating α-Fe_2O_3 nanoparticles in a porous membrane containing polyacrylonitrile (PAN) via facile and inexpensive preparation process [60]. The elemental analyses confirmed the presence of nanoparticles in the PAN membrane matrix that proved to be useful in the improvement of surface hydrophilicity, fouling resistance, and removal efficiency. The batch adsorption experiments indicated that the maximum adsorption capacity of the membrane was 47.7 mg/g in a pH range of 3–4 and equilibrium time of 120 min. Additionally, the application of membrane for groundwater sample showed significant nitrate removal, implying the effectiveness of membrane for real water environments. The negligible leakage of α-Fe_2O_3 from the membrane matrix confirms the safety used of membrane in water treatment.

Recently, Ghaemi *et al.* [61] discovered a new fabricated membrane that demonstrated high nitrate removal efficiency from water. Different amount of chitosan nanoparticles (CS) was embedded into the polyethersulfone (PES) membrane matrix by phase inversion method. Comparing the SEM micrographs (Figure 8a), increment in the number and straight alignment of macro-voids of the support layer can be seen in PES/CS1 and PES/CS2 due to the presence of hydrophilic nanoparticles. Besides improving membrane permeability, PES/CS1 and PES/CS2 showed an enhancement of porosity and hydrophilicity. High addition of nanoparticles (>0.4 wt.%) however, shrank the chitosan biopolymer, hence a compact and dense membrane (PES/CS3) was produced. The nitrate removal capability of modified membrane increased significantly owing to the adsorptive property of chitosan nanoparticles, which enhance the interaction of nitrate with membrane surface. Considering acceptable flux and nitrate removal, PES/CS2 membrane was identified as the optimum sample with stable water permeability and good nitrate removal at neutral pH (Figure 8b).

The interest of using UF for nitrate ions concentration reduction has been demonstrated by adding surfactant to enhance the process. PAN membrane

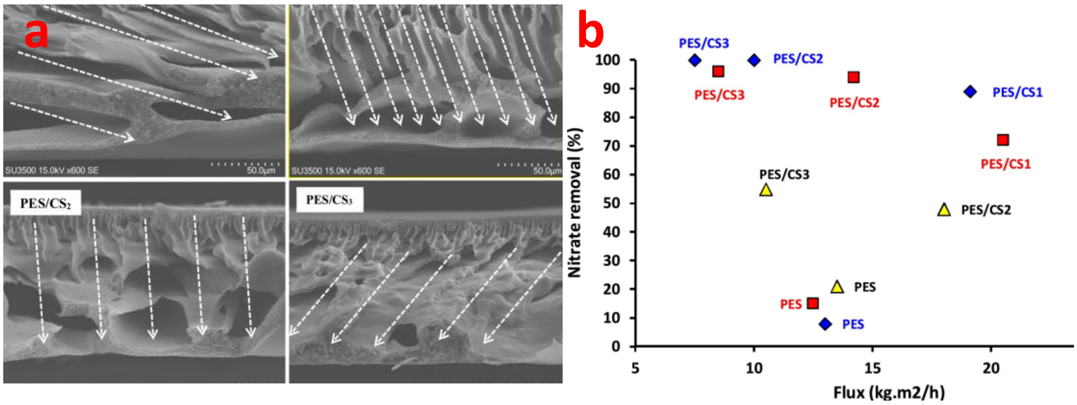

Figure 8 (a) SEM cross-section images of PES membrane at different CS; (b) Nitrate removal versus flux of PES, PES/CS1, PES/CS2 and PES/CS3 under various solution pH [61]

and cationic surfactant, cetylpyridinium chloride was then prepared using phase inversion method [62]. Above the critical micelle concentration (CMC), the solution formed spherical micelles, which are larger than the membrane pore [41, 42]. The concentration of surfactant significantly affects the performance where removal efficiency was progressively increased (0.3% to 90.5%) with increasing surfactant from 0.1 to 5 mM. The presence of positively charged head micelles bound electrostatically with the nitrate ions which resulted in high removal. At the same time, the permeate flux reduced from 54.2 to 33.3 L/m^2/h due to gel layer of surfactant and low concentration polarization. Accordingly, micellar-enhanced UF has been an effectively used as inorganic pollutants separation from the aqueous phase.

5.0 CONCLUDING REMARKS AND FUTURE PROSPECT

The progress in nanoscale science and technology has brought a drastic positive change to the environmental remediation and world. Nanotechnology has proven an incredible potential to address various environmental problems as well as offering leapfrogging opportunities for solving water crisis around the world [22,63]. Numerous materials and modification have been assessed in recent years to boost the efficiency and adsorption capacities of nitrate contaminants from wastewater. A series of recent studies indicated that as time went by, the adsorption capacity of nitrate increased, thanks to the development nano-technology that helps to combat the pollutants in water. From the comparison between the used nano-absorbents, superior results for nitrate adsorption in the aqueous solution are seen for the metal composite and membrane fabrication nano-adsorbents. Based on the review, although nano-adsorbents give better performances for nitrate adsorption, some challenges remain to be tackled for their practical industries applications e.g. wastewater treatment on a large scale, high capital cost, complex nano-adsorbents synthesis and unsatisfactory performance such as low adsorption uptake in field test. In the above context, development of more effective nano-adsorbents with higher adsorption and desorption ability is paramount. It is expected that nano-adsorbents will be widely acknowledged as an effective aqueous nitrate remediation in terms of efficiency, cost and safeness. Accordingly, more robust and simpler modifications of potential nano-adsorbents with enhanced uptake capacity and selectivity of nitrate should be continuously explored. Also, the development of some novel nano-adsorbent such as composite of MOFs, dendrimers and hyper-branched polymer can offer some desired characteristics to address the aforementioned limitations. The fabrication of nanocomposite membranes has been recognized as an emerging approach for nitrate ion wastewater treatment. Besides exploiting the nanomaterials as superior adsorbent, the effect of nanomaterials on the environment should be carefully assessed before they are used extensively for water treatment and pollution remediation. The control and recovery of these materials should be well understood to reduce the negative short-term and long-term effects of these nano-adsorbents on the ecosystem.

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