Chapter 13
Date Palm Assisted Nanocomposite Materials for the Removal of Nitrate and Phosphate from Aqueous Medium

Mirna Habuda-Stanić, Marija Nujic, Blanca Magdalena Gonzalez Silva, Sveinung Sægrov, Stein Wold Østerhus, and Mario Šiljeg

Abstract Nitrate and phosphate are naturally occurring nutrients in the environment, both essential for plants and animals. However, during the past decades, due to extended usage of fertilizers and detergents, as well as due to impropriate disposal of human and animal waste, the presence of nitrate and phosphate in the aquatic ecosystems became serious environmental and human health issues. Namely, the excessive loading of streams, rivers, lakes, bays and coastal waters with nitrate and phosphate can causes excessive algae growth, deteriorating water quality and severely reduce or eliminate oxygen in the water which, at the end, results with illnesses or death of large numbers of fish. Some algae also produce harmful toxins, which can be accumulated in fish and shellfish if they are grown at polluted aquatic environment. Numerous evidence also confirmed negative effect of elevated nitrate and phosphate concentrations in drinking water on human health. Ingested via drinking water, nitrates can cause life-threatening methemoglobinemia for infants. Some epidemiological studies also associated long-term exposure to high nitrate concentration in drinking water with the occurrence of diabetes, certain cancers and reproductive problems, while the chronical exposure to high phosphate concentration was related with incidence of renal disease, damage of blood vessels and induce of aging processes.

To prevent further environment loading with nitrate and phosphate compounds, as well to reduce the risk for population health, various techniques were used for their phosphate removal from drinking and wastewater. This review presents the

M. Habuda-Stanić (✉) · M. Nujic
Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Osijek, Croatia
e-mail: mirna.habuda-stanic@ptfos.hr

B. M. G. Silva · S. Sægrov · S. W. Østerhus
Department of Civil and Environmental Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

M. Šiljeg
Faculty of Geotechnical Engineering, University of Zagreb, Varaždin, Croatia

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_13

results of studies which tested the possibility of nitrate and phosphate removal from aqueous solutions using the date palm assisted nanocomposite materials.

Keywords Date palm · Nanocomposite materials · Nitrate removal · Phosphate removal · Water

13.1 Introduction

Population growth, anthropogenic activities, industrialisation, urbanisation, climate change and global warming strongly affect natural water bodies worsening water quality in physical, chemical and microbiological aspects (Alam et al. 2013, 2014). The International Food Policy Research Institute (IFPRI) and Veolia recently published the results of global study on water quality and water quantity. Due to the results of that comprehensive study, the water quality in many countries is in rapid and incontinent decrease, and over 30% of world population will be exposed to a high risk of water pollution by 2050 (IFPRI and Veolia 2014). The IFPRI and Veolia study also emphasized that the main reason for such dramatic decrease of surface waters quality will be caused by increasing amounts of nitrogen and phosphorous in water bodies and increasing values of biochemical oxygen demand (BOD).

Nitrogen and phosphorous are naturally occurring nutrients in the environment, but during the past decades their concentrations in water bodies significantly increased. Increase of nutrients in water bodies is primarily caused by human activities such as extensive usage of detergents, agricultural fertilizers and manure, livestock waste disposal, discharge of domestic and industrial wastewaters in the environment without appropriate wastewater treatment and leaching from sanitary landfills and garbage dumps. Elevated concentrations of nitrogen and phosphorous have been determined in numerous aquatic ecosystem all over the world causing its eutrophication (Kundu et al. 2015; Pandey and Yadav 2017; Álvarez et al. 2017).

Eutrophication (hypertrophication) is the process of excessive growth of plants and algae caused by elevated concentrations of nutrients (primarily nitrates and phosphates) in surface water bodies. Oxygen depletion, extensive increase of phytoplankton, and, overall, negative effects on biodiversity usually accompany this process. A natural processes or anthropogenic activities can cause eutrophication phenomenon. Natural eutrophication occurs due to ageing of water body and a slow accumulation of organic material, which cause increasing of nutrients during long period. Human-induced eutrophication occurrences more intensively as the result of frequent usage of fertilizers and discharge of nitrogen- and phosphorus-rich industrial and domestic waste waters into terrestrial, freshwater and marine ecosystems (Serrano et al. 2017; Ménesguen and Lacroix 2018).

Besides mentioned negative effect on ecosystem, elevated concentration of nitrates and phosphates can also have harmful effects to human health. Ingested via drinking water nitrates can cause methemoglobinemia (hemoglobin of the red blood cells forming methemoglobin unable to transmit oxygen in the body) in the case of acute exposure, or the occurrence of cancer in the case of chronical exposure, while the ingestion of phosphate can cause incidence of renal disease, damage of blood vessels and induce aging processes (Sadeq et al. 2008; Espejo-Herrera et al. 2015; Rojas Fabro et al. 2015; Zhai et al. 2017).

Having global negative trends in water quality and fragility of ecosystems, regulations and scientists' effort are generally focused on improvement of current drinking water and waste water technology efficiencies in order to reduce energy requirements and environmental impacts. Following those imperatives, the conception of water treatments is moving towards a circular economy approach and environmental sustainability. One of possibility to meet those criteria is usage of adsorption as easy-to-use, economically acceptable, flexible and efficient water purification technology (Sadeq et al. 2008). Adsorption was primarily used due to effective removal of organic compounds that are causing unwanted taste and odors of drinking water. But, with development of science and technology, over the last two decades, conventional adsorbents were modified and the numerous new porous materials were synthesized with aim of their effective application in various contaminants removal. Such adsorbents are nanocomposites (Figoli et al. 2017).

Nanocomposites are new generation, multiphase materials. They are usually produced as the solid base material with combination of a bulk matrix and nano-dimensional phase(s) by in situ polymerization, solvent-assisted methods, and, in the most cases, melt homogenization and tested for possible application in water purification processes (Singh et al. 2015). Nanocomposites can be also produced in the form of colloids, gels, or copolymers with structure characterized by nano-scale repeat distances between the different phases and dimensions of less than 100 nanometers. Since their structures contains various materials, properties of nanocomposites are defined by the same factors which characterize each nanocomposite component making the nanocomposite complex adsorbents with very large interfacial area and high adsorption capacities for different pollutants (Singh et al. 2015; Figoli et al. 2017). That makes nanocomposites the adsorbents with a high potential for application in drinking water and wastewater treatments.

In order to make nanocomposite adsorbent cheap and environmentally friendly, various types of organic materials i.e. agriculture waste were used as a base material for nanocomposites green synthesis. The agriculture waste is characterized by presence of variety functional groups and high amount of hemicellulose, hydrocarbons, proteins, lipids, lignin, simple sugars, water, and starch (Bhatnagar and Sillanpää 2010). Several studies reported successful nanocomposite synthesis using remains of wheat straw, chitosan as well as remains of *Imperata cylindrical*, *Moringa oleifera*, *Adansonia Digitata*, *Vitex trifolia*, and *Tabernaemontana divaricate, Callistemon viminalis, Calotropis gigantean* and *Theobroma cacao* (Rahimi et al. 2015; Dai et al. 2018; Ding et al. 2018). Several studies also reported good adsorption capacities of date palm-based nanocomposites (Bhatnagar et al. 2010; Ahmad et al. 2012; Yadav et al. 2014; Rahimi et al. 2015; Logam and Kumbahan 2018; Yulizar et al. 2018).

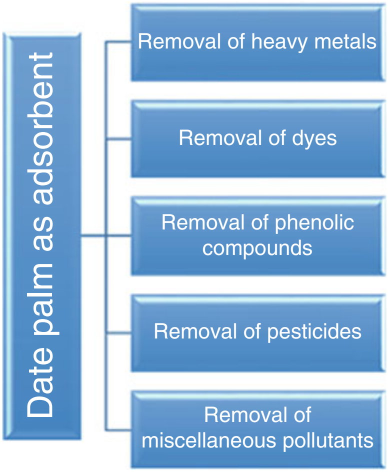

Fig. 13.1 Application of date palm as adsorbent. (According to Ahmad et al. 2012)

The date palm (*Phoenix dactylifera L.*) tree is dominant agricultural plant in East and North Africa grown for providing staple food for local population and basic material for production of palm oil. During exploitation of date palms, large amount of agricultural waste have been produced in the form of dry leaves, stems, pits and seeds. Those remains are usually transform into activated carbons which gained popularity over the last decades due to its separation performances in water purification processes and efficient removal of both organic and inorganic trace contaminants (Ahmad et al. 2012). Additionally, due to date-palm fibres, leaf fibres in the peduncle, baste fibres in the stem, wood fibres in the trunk and surface fibres around the trunk, date palm waste have been tested in raw form as adsorbent for removal of heavy metal ions, dyes, pesticides, miscellaneous pollutants and oils (Riahi et al. 2009a; Ahmad et al. 2012, Alghamdi 2016; Hussin et al. 2016; Abdelwahab et al. 2017; Ghazali et al. 2018; Logam and Kumbahan 2018). Figure 13.1 present main usage of date palm adsorbents.

This chapter present the overview of the studies conducted with the aim to remove of nitrate and phosphate from aqueous solutions using nanocomposite materials.

13.2 Nitrate Removal from Water by Palm Biomass–Based Adsorbents

Nitrogen as a major constituent, which is present in the biosphere as ammonia, nitrite and nitrate. Nitrate in environment is usually product of nitrogen denitrification and it is a highly soluble nutrient, essential for living beings. However, as the results of uncontrolled and excessive usage in various anthropogenic activities, nitrate concentrations in natural waters become a worldwide environmental problem and threat to human's health (Khan et al. 2016; Naushad et al. 2014). Due to high solubility and stability in water, conventional water treatment techniques as coagulation with flocculation and lime softening, bout followed by filtration, does not remove nitrate enough efficiently.

As efficient nitrate removal techniques following methods have been used: reverse osmosis, biological and chemical denitrification, electrodialysis, functionalized graphene nanostructured membrane, ion exchange and adsorption (Bhatnagar and Sillanpää 2011; Loganathan et al. 2013; Nur et al. 2015; Kalaruban et al. 2016a; Jahanshahi et al. 2018; Kalaruban et al. 2018). Among water treatments that efficiently removes nitrate, adsorption shows significant benefits: easy-to-use and easy-to-operate technique, cost-effective, low space requiring, high efficiency and easy upgrade water treatment. Various materials have been tested for nitrate removal showing good adsorption capacities: synthetic adsorbents, agricultural waste, fly ash, surfactant-modified zeolite, carbon nanotube, alunite and cement (Bhatnagar and Sillanpää 2011; Hu et al. 2015; Nur et al. 2015).

Tyagi et al. (2018) emphasized that efficient removal of nitrate imply its reduction to nitrogen gas and nitrogen monoxide. Following reagents shown good nitrate-reducing performances: active metals, ammonia, iron, hydrazine, borohydride, hydroxylamine, hydrogen, and formate, as well as so-called "energy methods" such as electrochemical, thermal, or photocatalytic reactions. Nitrate reduction also can be effective in the presence of powerful catalysts. Therefore, todays researches are focused on synthesis of new materials which should small surface area, high catalytic properties and excellent reducing potential, i.e. to enable nitrate reduction to ammonia (NH_3), nitrogen gas (N_2), nitrite (NO_2^-) or ammonium (NH_4^+), depending on used nanocomposite material (Tyagi et al. 2018).

Drinking water is generally produced from surface waters (river and lakes) or groundwaters. Occurrence of nitrogen in surface waters is mostly the result of excessive use of inorganic fertilizers and discharges of untreated wastewaters, while nitrate occurrence in groundwaters can be caused by the same reasons and geological composition of the aquifer (Singh et al. 2005; Bonometto et al. 2017).

Nitrate presence in drinking water is sensorially undetectable and present the health hazard. Namely, ingested by drinking water in heightened concentration, nitrate is transformed to nitrite. Transformation begin in the digestive system and nitrite enters the circulatory system where nitrite oxidizes the iron in the hemoglobin and form methemoglobin. Methemoglobin does not have the oxygen-carrying ability which causing an abrupt drop in blood oxygen and appearance of blue skin. The overall reduced ability of the red blood cell to release oxygen to tissues results with hypoxemia and the condition known as methemoglobinemia ("blue baby syndrome"). Most humans over 1 year of age have the ability to rapidly convert methemoglobin back to oxyhemoglobin, but methemoglobinemia can be fatal for infants under 6 months of age (Afzal 2006; Sadeq et al. 2008). Besides methemoglobinemia, transformation of nitrate ions from nitrite also causes a subsequent generation of carcinogenic nitrosamine (Meghdadi 2018). Therefore, the primer reason for nitrate removal from drinking water is public health.

Table 13.1 Agro-industrial waste materials for nitrate removal from aqueous solutions

Adsorbent	q_{max}	References
Chitin	200 mg g^{-1}	Morghi et al. (2015)
Wheat straw anion exchanger (WS-AE)	58.8 mg g^{-1}	Xu et al. (2010)
Coconut granular activated carbon	1.7 mg g^{-1}	Bhatnagar et al. (2008)
Red mud (unmodified)	1.859 mmol g^{-1}	Cengeloglu et al. (2006)
Red mud (modified)	5.858 mmol g^{-1}	Cengeloglu et al. (2006)
Quaternized Chinese reed	7.55 mg g^{-1}	Namasivayam and Sangeetha (2006)
Activated carom from coconut shells	$2.66 \cdot 10^{-1}$ mmol g^{-1}	Ohe et al. (2003)
Activated carbon from bamboo	$1.04 \cdot 10^{-1}$ mmol g^{-1}	Ohe et al. (2003)
Rice hull	1.32 mmol g^{-1}	Orlando et al. (2002)
Sugarcane bagasse	1.41 mmol g^{-1}	Orlando et al. (2002)
Pure alkaline lignin	1.8 mmol g^{-1}	Orlando et al. (2002)
Pure cellulose	1.34 mmol g^{-1}	Orlando et al. (2002)

Following materials have been tested as adsorbent for nitrate removal from drinking water: carbon-based materials (powder activated carbon, carbon cloth, carbon nanotubes, commercial activated carbon, $ZnCl_2$ treated granular activated carbon, iron oxide-dispersed activated carbon fibers), natural adsorbents (clay, zeolite, sepiolite) agriculture wastes (sugarcane bagasse, rice hull, coconut shells, wheat residues, almond shell, sugar beet pulp), industrial waste (fly ash, red mud, slag), biosorbents (chitosan, bamboo powder, Chinese reed) and miscellaneous adsorbents (layered-double hydroxides/hydrotalcite-like compounds/ hydroxyapetite, nano-alumina, mesoporous silica, cement paste), Nanoscale Zero Valent Iron (NZVI), nanotubes, nanofibres etc. (Bhatnagar and Sillanpää 2011; Olgun et al. 2013; Motamedi et al. 2014; Hu et al. 2015; Kalaruban et al. 2016a, b; Dai et al. 2018; He et al. 2018; Meghdadi 2018; Tyagi et al. 2018).

To obtain maximum adsorption capacities, various adsorbents demands various conditions and efficiency of adsorbent is mainly defined by adsorbent type, initial nitrate concentration in raw water, pH and temperature (Singh et al. 2018).

Due to its loose and porous structures, abundantly of functional groups such as the carboxyl- and hydroxyl- groups, renewability and low cost, various agriculture and industrial waste were tested as adsorbents for nitrate removal from water. Agro-industrial waste materials and their maximum capacities for nitrate adsorption are presented in Table 13.1.

Various palm biomass–based adsorbents were tested as potential low-cost adsorbents. Ohe et al. (2003) used coconut shells to prepare activated carbon for nitrate removal. Obtained activated carbon was ground up and sieved to obtain adsorbent with the size of particles in the range from 0.3 to 0.5 mm. Authors tested obtained adsorbents for nitrate removal as a function of contact time, pH, temperature and initial nitrate concentration. Prepared palm biomass–based adsorbents shown high selectivity for nitrate anions and inversely proportional of adsorption capacity and temperature. As highest capacity of coconut shells based activated carbon, authors reported 3.06 mmol g^{-1} noted at room temperature. They also emphasized that nitrate removal of 70% was obtained at pH 4 (Ohe et al. 2003).

Namasivayam and Sangeetha (2006) modified coir pith in order to produce $ZnCl_2$ loaded activated carbon as adsorbents for removal of nitrate and several other contaminants. Coir pith was dried in sunlight for 5 h and then zinc chloride activated coir pith carbon was prepared by adding the coir pith in a boiling solution of zinc chloride. After filtration and drying, adsorbent was carbonized at 700 °C. After cooling, carbonized material was sieved to 250–500 μm particle size and tested as adsorbent used for adsorption studies. Authors reported more than 90% removal of nitrate at pH 6.2 and adsorbent dose of 400 mg/50 ml (Namasivayam and Sangeetha 2006).

Kalaruban et al. (2016a, b) studied nitrate removal by chemically surface-modified coconut copra. Chemical surface modification implied incorporation of amine groups with the aim to increase the surface positive charges. Authors reported that maximum nitrate adsorption capacity of 59 mg/g was obtained by modified coconut copra at pH 6.5 (Kalaruban et al. 2016a, b).

Adebayo et al. (2016) tested palm kernel shell as nitrate removal material. Preparation of adsorbent implied soak of biosorbent in warm deionized water, washing with NaOH, and rinsing with deionized water. pH neutral adsorbent was further oven-dried, ground, and sieves to obtain particles size 53-74 μm. Adsorbent particles were put in a flask for 2 h for treatment with acid solution and heated reflux (95 °C). After 2 h, adsorbent was rinsed with deionized water until neutral pH. Palm biomass–based adsorbents was than dried at 60 °C, pulverized to 0.45 mm, heated for 2 h at 200 °C, and tested for nitrate removal. The adsorption capacitiy of the adsorbent was tested by 50 mL solutions with initial nitrate concentrations ranged from 50 to 500 mg L^{-1} and 0.2 g of the adsorbents. As maximum adsorption capacity 85.73 mg g^{-1} was reported (Adebayo et al. 2016).

Bashir et al. (2018) tested low-cost bioadsorbent obtained by chemical modification of palm kernel shells. Effect of initial nitrate concentration, pH and temperature on nitrate removal was tested. Authors reported the maximum adsorption capacity of 54.18 mg/g and removal efficiency of 79.6%. Palm biomass–based adsorbent removed effectively nitrate in a wide range of pH 4–8 and temperature (20–40 °C) (Bashir 2018).

13.3 Phosphate Removal from Water by Palm Biomass–Based Adsorbents

Phosphate is an inorganic compound, which is considered as a non-toxic for humans. The United States Food and Drug Administration (FDA) reported that inorganic phosphates, as food ingredients, are considers as “generally safe”. FDA also quoted that average phosphate levels found in a litre of drinking water are about 100 times lower than the average phosphate levels found in the average American diet.

Table 13.2 Agriculture and industrial waste materials for phosphate removal from aqueous solutions

Adsorbent	q_{max}/mg g^{-1}	References
Alkaline residue	2.2 mg g^{-1}	Yan et al. (2014)
Granular date stones	8.7 mg g^{-1}	Ismail (2012b)
Palm surface fibres	5.5 mg g^{-1}	Ismail (2012a)
Wheat straw	8.43 mg g^{-1}	Ma et al. (2011)
Wheat straw anion exchanger (WS-AE)	45.7 mg g^{-1}	Xu et al. (2010)
Date palm fibres	4.34 mg g^{-1}	Riahi et al. (2009a)
Red mud (raw)	0.23 mg g^{-1}	Huang et al. (2008)
Red mud (HCl treated)	0.58 mg g^{-1}	Huang et al. (2008)

Phosphate in water bodies is undesirable due to a worldwide problem of eutrophication. Phosphate in water resources mainly originates from fertilizers, detergents which contains sodium tripolyphosphates and untreated wastewater. But, nowadays, wastewater has been recognized as alternative source of phosphorus, and newest trends in wastewater treatments are now focused on phosphate recovery from wastewater as a potential respond to overcome the global challenge of phosphorus scarcity (Weiner et al. 2001; Length 2012).

Various physical, biological and chemical techniques have been tested for the phosphates removal from water and wastewaters including ion exchange, chemical precipitation/coagulation and adsorption (Length 2012). Among all mentioned methods, adsorption is widely accepted as efficient phosphate removal method.

Phosphate removal by adsorption is tested by decades and adsorption capacities of numerous unmodified and modified materials have been investigated such as: activated alumina, clay, fly ash, calcite, graphene, activated carbons, iron oxide, modified zeolite, dolomite, aluminum oxide, lanthanum hydroxide hybrid material, pumice powder, nanocomposite, brucite-periclase materials etc. (Onar et al. 1996; Prochaska and Zouboulis 2006; Islam et al. 2014; Nur et al. 2014; Mehrabi et al 2015; Andrés et al. 2018). Adsorbents obtained from agriculture and industrial waste were also tested and their maximum capacities for phosphate removal are presented in Table 13.2.

The palm biomass was in the focus of several adsorption studies for phosphate removal from aqueous solutions. Riahi et al. (2009a) studied the removal of phosphate ions from domestic wastewater by date palm fibers. Date-palm fibers filter media whit diameters 0.2–0.5, 0.5–0.8 and 0.8–1.2 mm were tested in glass column. Fixed-bed up-flow filter media was between 12 and 72 mL min^{-1}. Results shown that efficiency of adsorbent depend on initial phosphate concentration, pH, and adsorbent dosage. Amount of adsorbed phosphate increased with the increase of its initial concentration, while increasing pH values had negative effect on adsorption. The highest phosphate removal (cca 57%) was obtained when filter material with smallest particle size was used. Authors emphasized that tested date-palm fibers filter most suitable for small water supply systems (Riahi et al. 2009a).

The same year (2009b) Riahi et al. published result of similar study conducted with the aim to test natural fibers from the surface of *P. dactylifera* L. date palm for phosphate removal. Used date palm surface fibers had 0.2–0.8 mm diameter. Prior usage, date palm fibers were washed with distilled water and dried at 105 °C for 24 h. Adsorption tests were preformed with various initial phosphate concentrations and contact time at room temperature. Obtained results shown that pH, initial phosphate concentration and adsorbent dosage were key factor for effective removal.

With initial pH in range 5–8, about 4.35 mg of phosphate was adsorbed on 1 g of adsorbent (Riahi et al. 2009b).

In the year of 2017, Riahi et al. published the results of a kinetic modeling study of phosphate adsorption onto *Phoenix dactylifera* L. date palm fibers conducted in batch mode in order to define the mechanisms and kinetic model for phosphate sorption. Test were performed by the solutions with initial phosphate concentration in the range from 30 to 110 mg/L. Using seven statistical functions, authors estimated that Elovich equation and pseudo second-order equation provide the best fit to experimental data. Authors emphasized that adsorption in time dependent. They reported that over 88% of phosphate was adsorbed within 30 minutes in the test performed when solution with initial phosphate concentration of 110 mg/L was used (Riahi et al. 2017).

Ismail (2012) tested palm fibres and the granular date stones obtained from the trunk surface of a *Phoenix dactylifera* L. date palm for phosphate removal. The effects of contact time, initial phosphate concentrations, sorbent dosage and pH were examined. Author reported that increase of adsorbents dosages from 1 to 10 g L^{-1} increased efficiencies of phosphate removal from 25% to 85%, although maximum adsorption capacities were obtained after the adsorbent amount exceeded 5 g L^{-1}. Tested palm-based adsorbents untaken more phosphate with decreasing the pH. Ismail reported that maximum adsorption capacity of granular date stones were 8.70 mg P g^{-1}, and maximum adsorption capacity of palm surface fibres 8.50 mg P g^{-1} (Ismail 2012).

13.4 Conclusions

Industrialisation, population growth and agriculture activities are the main factors that significantly interrupted the quality of aquatic ecosystems during the last decades. Although various water bodies are characterized by different chemism, anthropogenic eutrophication driven by general increasing of phosphate and nitrate in surface water becomes global environmental and health issue. Therefore, significant efforts are daily given by many scientists all over the world for finding the most cost-benefit solutions for nitrates and phosphates removal from drinking water and wastewater in order to prevent further nitrate and phosphate loading of the environment.

One of the eco-friendly solution for nitrate and phosphate removals is water treatment by biosorbents i.e. adsorbents obtained from biomass which is, in the most cases, classified as agriculture waste. Using biosorbents for nitrate and phosphate removal contribute to achievement of circular economy goals. The other benefit of biosorbents usage is that after their saturation with nutrients they can be used organic fertilizers i.e. source of bioavailable nitrogen and phosphorous for crops.

The palm biomass-based adsorbents have been tested, with or without prior modification, as adsorbents for nitrate and phosphate removal from water. Authors of adsorption studies reported good performances and adsorption capacities of raw palm-based adsorbents which were additionally improved by chemical modifications of materials.

Effective removal of nitrate and phosphate, as well as guidelines for agriculture waste management are the main reasons which will keep palm biomass as attractive base material for further research and applications in water treatments.

References

Abdelwahab O, Nasr SM, Thabet WM (2017) Palm fibers and modified palm fibers adsorbents for different oils. Alex Eng J 56(4):749–755. https://doi.org/10.1016/j.aej.2016.11.020

Adebayo OL, Adaramodu AA, Ajayi MG, Olasehinde FE, Oyetunde JG (2016) Purification of nitrate contaminated aqueous solution using modified and unmodified palmkernel shell. Int Lett Chem Phys Astron 71:11–18. https://doi.org/10.18052/www.scipress.com/ILCPA.71.11

Afzal BM (2006) Drinking water and women's health. J Midwifery Women's Health 51(1):12–18. https://doi.org/10.1016/j.jmwh.2005.08.014

Ahmad T, Danish M, Rafatullah M, Ghazali A, Sulaiman O, Hashim R, Ibrahim MNM (2012) The use of date palm as a potential adsorbent for wastewater treatment: a review. Environ Sci Pollut Res 19(5):1464–1484. https://doi.org/10.1007/s11356-011-0709-8

Alam MM, ALOthman ZA, Naushad M (2013) Analytical and environmental applications of polyaniline Sn(IV) tungstoarsenate and polypyrrole polyantimonic acid composite cation-exchangers. J Ind Eng Chem 19:1973–1980. https://doi.org/10.1016/j.jiec.2013.03.006

Alam MM, ALOthman ZA, Naushad M, Aouak T (2014) Evaluation of heavy metal kinetics through pyridine based Th(IV) phosphate composite cation exchanger using particle diffusion controlled ion exchange phenomenon. J Ind Eng Chem 20:705–709. https://doi.org/10.1016/j.jiec.2013.05.036

Alghamdi AA (2016) An investigation on the use of date palm fibers and coir pith as adsorbents for Pb(II) ions from its aqueous solution. Desalin Water Treat 57(26):12216–12226. https://doi.org/10.1080/19443994.2015.1048743

Álvarez X, Valero E, Santos RMB, Varandas SGP, Sanches Fernandes LF, Pacheco FAL (2017) Anthropogenic nutrients and eutrophication in multiple land use watersheds: best management practices and policies for the protection of water resources. Land Use Policy 69(August):1–11. https://doi.org/10.1016/j.landusepol.2017.08.028

Andrés E, Araya F, Vera I, Pozo G, Vidal G (2018) Phosphate removal using zeolite in treatment wetlands under different oxidation-reduction potentials. Ecol Eng 117(March):18–27. https://doi.org/10.1016/j.ecoleng.2018.03.008

Bashir MT (2018) A sustainable approach of nitrate adsorption from water using palm oil agricultural waste. Asian J Microbiol Biotechnol Environ Sci 20(2):451–457

Bashir MT, Ali S, Azni I, Harun AR (2018) A sustainable approach of nitrate adsorption from water using palm oil agricultural waste. Asian J Microbiol Biotechnol Environ Sci 20(2):451–457

Bhatnagar A, Sillanpää M (2010) Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment – a review. Chem Eng J 157:277–296. https://doi.org/10.1016/j.cej.2010.01.007

Bhatnagar A, Sillanpää M (2011) A review of emerging adsorbents for nitrate removal from water. Chem Eng J 168(3):493–504. https://doi.org/10.1016/j.cej.2011.01.103

Bhatnagar A, Ji M, Choi Y, Jung W, Lee S, Kim S et al (2008) Removal of nitrate from water by adsorption onto zinc chloride treated activated carbon. Sep Sci Technol 43(4):886–907. https://doi.org/10.1080/01496390701787461

Bhatnagar A, Vilar VJP, Botelho CMS, Boaventura RAR (2010) Coconut-based biosorbents for water treatment – a review of the recent literature. Adv Colloid Int Sci 160:1–15. https://doi.org/10.1016/j.cis.2010.06.011

Bonometto A, Giordani G, Ponis E, Facca C, Boscolo Brusà R, Sfriso A, Viaroli P (2017) Assessing eutrophication in transitional waters: a performance analysis of the Transitional Water Quality Index (TWQI) under seasonal fluctuations. Estuar Coast Shelf Sci. https://doi.org/10.1016/j.ecss.2017.08.008

Cengeloglu Y, Tor A, Ersoz M, Arslan G (2006) Removal of nitrate from aqueous solution by using red mud. Sep Purif Technol 51(3):374–378. https://doi.org/10.1016/j.seppur.2006.02.020

Dai Y, Sun Q, Wang W, Lu L, Liu M, Li J, . . . Zhang Y (2018) AC SC. https://doi.org/10.1016/j.chemosphere.2018.06.179

Ding J, Li Q, Xu X, Zhang X, Su Y, Yue Q, Gao B (2018) SC. Carbohydrate polymers. Elsevier. https://doi.org/10.1016/j.carbpol.2018.02.032

Espejo-Herrera N, Cantor KP, Malats N, Silverman DT (2015) Nitrate in drinking water and bladder cancer risk in Spain. Environ Res 137:299–307. https://doi.org/10.1016/j.envres.2014.10.034

Figoli A, Saeed M, Dorraji S, Amani-ghadim AR (2017) 4 – Application of nanotechnology in drinking water purification. Elsevier, New York. https://doi.org/10.1016/B978-0-12-804300-4/00004-6

Ghazali A, Shirani M, Semnani A, Zare-shahabadi V, Nekoeinia M (2018) Optimization of crystal violet adsorption onto Date palm leaves as a potent biosorbent from aqueous solutions using response surface methodology and ant colony. Biochem Pharmacol 6:3942–3950. https://doi.org/10.1016/j.jece.2018.05.043

He Y, Lin H, Dong Y, Li B, Wang L, Chu S et al (2018) Zeolite supported Fe/Ni bimetallic nanoparticles for simultaneous removal of nitrate and phosphate: synergistic effect and mechanism. Chem Eng J 347:669–681. https://doi.org/10.1016/j.cej.2018.04.088

Hu Q, Chen N, Feng C, Hu W (2015) Nitrate adsorption from aqueous solution using granular chitosan-Fe3+ complex. Appl Surf Sci 347:1–9. https://doi.org/10.1016/j.apsusc.2015.04.049

Huang W, Wang S, Zhu Z, Li L, Yao X, Rudolph V, Haghseresht F (2008) Phosphate removal from wastewater using red mud. J Hazard Mater 158(1):35–42. https://doi.org/10.1016/j.jhazmat.2008.01.061

Hussin MH, Aqilah N, Garba ZN, Kassim MJ, Abdul A, Brosse N et al (2016) International journal of biological macromolecules physicochemical of microcrystalline cellulose from oil palm fronds as potential methylene blue adsorbents. Int J Biol Macromol 92:11–19. https://doi.org/10.1016/j.ijbiomac.2016.06.094

International Food Policy Research Institute (IFPRI) and Veolia (2014) The murky future of global water quality. https://espas.secure.europarl.europa.eu/orbis/sites/default/files/generated/document/en/IFPRI_Veolia_H2OQual_WP.pdf

Islam M, Mishra S, Swain SK, Patel R, Dey RK, Naushad M (2014) Evaluation of phosphate removal efficiency from aqueous solution by polypyrrole/BOF Slag nanocomposite. Sep Sci Technol 49(13):2668–2680. https://doi.org/10.1080/01496395.2014.933981

Ismail ZZ (2012) Kinetic study for phosphate removal from water by recycled date-palm wastes as agricultural by-products. Int J Environ Stud 69(1):135–149. https://doi.org/10.1080/00207233.2012.656975

Jahanshahi D, Vahid B, Azamat J (2018) Computational study on the ability of functionalized graphene nanosheet for nitrate removal from water. Chem Phys 511:20–26. https://doi.org/10.1016/j.chemphys.2018.05.018

Kalaruban M, Loganathan P, Shim WG, Kandasamy J, Naidu G, Nguyen TV, Vigneswaran S (2016a) Removing nitrate from water using iron-modified Dowex 21K XLT ion exchange resin: batch and fluidised-bed adsorption studies. Sep Purif Technol 158:62–70. https://doi.org/10.1016/j.seppur.2015.12.022

Kalaruban M, Loganathan P, Shim WG, Kandasamy J, Ngo HH, Vigneswaran S (2016b) Science of the total environment enhanced removal of nitrate from water using amine-grafted agricultural wastes. Sci Total Environ 565:503–510. https://doi.org/10.1016/j.scitotenv.2016.04.194

Kalaruban M, Loganathan P, Shim WG, Kandasamy J (2018) Applied sciences mathematical modelling of nitrate removal from water using a submerged membrane adsorption hybrid system with four adsorbents. https://doi.org/10.3390/app8020194

Khan MR, Wabaidur SM, Alothman ZA et al (2016) Method for the fast determination of bromate, nitrate and nitrite by ultra performance liquid chromatography-mass spectrometry and their monitoring in Saudi Arabian drinking water with chemometric data treatment. Talanta 152:513–520. https://doi.org/10.1016/j.talanta.2016.02.036

Kundu S, Vassanda Coumar M, Rajendiran S, Ajay, Subba Rao A (2015) Phosphates from detergents and eutrophication of surface water ecosystem in India. Curr Sci 108(7):1320–1325

Length F (2012) Phosphate pollution control in waste waters using new, 4 April, 73–85. https://doi.org/10.5897/IJWREE11.132

Logam P, Kumbahan A (2018) Removal of heavy metals from wastewater using Date Palm as a biosorbent: a comparative review. Sains Malaysiana 47(1):35–49

Loganathan P, Vigneswaran S, Kandasamy J (2013) Enhanced removal of nitrate from water using surface modification of adsorbents – a review. J Environ Manag 131:363–374. https://doi.org/10.1016/j.jenvman.2013.09.034

Ma Z, Li Q, Yue Q, Gao B, Li W, Xu X, Zhong Q (2011) Adsorption removal of ammonium and phosphate from water by fertilizer controlled release agent prepared from wheat straw. Chem Eng J 171(3):1209–1217. https://doi.org/10.1016/j.cej.2011.05.027

Meghdadi A (2018) SC. Water Res. https://doi.org/10.1016/j.watres.2018.04.063

Mehrabi N, Soleimani M, Sharififard H, Yeganeh MM (2015) Optimization of phosphate removal from drinking water with activated carbon using response surface methodology (RSM), (September). Desalin Water Treat 57(33):15613–15618. https://doi.org/10.1080/19443994.2015.1070763

Ménesguen A, Lacroix G (2018) Modelling the marine eutrophication: a review. Sci Total Environ 636:339–354. https://doi.org/10.1016/j.scitotenv.2018.04.183

Morghi M, Abidar F, Soudani A, Zerbet M, Chiban M, Kabli H, Sinan F (2015) Removal of nitrate ions from aqueous solution using chitin as natural adsorbent. Int J Res Environ Stud 2:8–20

Motamedi E, Atouei MT, Kassaee MZ (2014) Comparison of nitrate removal from water via graphene oxide coated Fe, Ni and Co nanoparticles. Mater Res Bull 54:34–40

Namasivayam C, Sangeetha D (2006) Recycling of agricultural solid waste, coir pith: removal of anions, heavy metals, organics and dyes from water by adsorption onto ZnCl 2 activated coir pith carbon, vol 135, pp 449–452. https://doi.org/10.1016/j.jhazmat.2005.11.066

Naushad M, Khan MA, ALOthman ZA, Khan MR (2014) Adsorptive removal of nitrate from synthetic and commercially available bottled water samples using De-Acidite FF-IP resin. J Ind Eng Chem 20:3400–3407. https://doi.org/10.1016/j.jiec.2013.12.026

Nur T, Johir MAH, Loganathan P, Nguyen T, Vigneswaran S, Kandasamy J (2014) Journal of industrial and engineering chemistry phosphate removal from water using an iron oxide impregnated strong base anion exchange resin. J Ind Eng Chem 20:1301–1307

Nur T, Shim WG, Loganathan P, Vigneswaran S, Kandasamy J (2015) Nitrate removal using Purolite A520E ion exchange resin: batch and fixed-bed column adsorption modelling. Int J Environ Sci Technol 12:1311–1320. https://doi.org/10.1007/s13762-014-0510-6

Ohe K, Nagae Y, Nakamura S, Baba Y (2003) Removal of nitrate anion by carbonaceous materials prepared from bamboo and coconut shell. J Chem Eng Jpn 36(4):511–515. https://doi.org/10.1252/jcej.36.511

Olgun A, Atar N, Wang S (2013) Batch and column studies of phosphate and nitrate adsorption on waste solids containing boron impurity. Chem Eng J 222:108–119. https://doi.org/10.1016/j.cej.2013.02.029

Onar AN, Balkaya N, Akyüz T (1996) Phosphate removal by adsorption. Environ Technol 17 (May):207–213. https://doi.org/10.1080/09593331708616378

Orlando US, Baes AU, Nishijima W, Okada M (2002) A new procedure to produce lignocellulosic anion exchangers from agricultural waste materials. Bioresour Technol 83(3):195–198. https://doi.org/10.1016/S0960-8524(01)00220-6

Pandey J, Yadav A (2017) Alternative alert system for Ganga river eutrophication using alkaline phosphatase as a level determinant. Ecol Indic 82(January):327–343. https://doi.org/10.1016/j.ecolind.2017.06.061

Prochaska CA, Zouboulis AI (2006) Removal of phosphates by pilot vertical-flow constructed wetlands using a mixture of sand and dolomite as substrate. Ecol Eng 26:293–303. https://doi.org/10.1016/j.ecoleng.2005.10.009

Rahimi S, Moattari RM, Rajabi L, Derakhshan AA (2015) Optimization of lead removal from aqueous solution using goethite/chitosan nanocomposite by response surface methodology. Colloids Surf A Physicochem Eng Asp 484:216–225. https://doi.org/10.1016/j.colsurfa.2015.07.063

Riahi K, Mammou AB, Thayer BB (2009a) Date-palm fibers media filters as a potential technology for tertiary domestic wastewater treatment. J Hazard Mater 161(2–3):608–613. https://doi.org/10.1016/j.jhazmat.2008.04.013

Riahi K, Thayer BB, Mammou AB, Ammar AB, Jaafoura MH (2009b) Biosorption characteristics of phosphates from aqueous solution onto Phoenix dactylifera L. date palm fibers. J Hazard Mater 170(2–3):511–519. https://doi.org/10.1016/j.jhazmat.2009.05.004

Riahi K, Chaabane S, Thayer BB (2017) A kinetic modeling study of phosphate adsorption onto Phoenix dactylifera L. date palm fibers in batch mode. J Saudi Chem Soc 21(s1):s143–s152. https://doi.org/10.1016/j.jscs.2013.11.007

Rojas Fabro AY, Pacheco Ávila JG, Esteller Alberich MV, Cabrera Sansores SA, Camargo-Valero MA (2015) Spatial distribution of nitrate health risk associated with groundwater use as drinking water in Merida, Mexico. Appl Geogr 65:49–57. https://doi.org/10.1016/j.apgeog.2015.10.004

Sadeq M, Moe CL, Attarassi B, Cherkaoui I (2008) Drinking water nitrate and prevalence of methemoglobinemia among infants and children aged 1 – 7 years in Moroccan areas. Int J Hyg Environ Health 211:546–554. https://doi.org/10.1016/j.ijheh.2007.09.009

Serrano L, Reina M, Quintana XD, Romo S (2017) A new tool for the assessment of severe anthropogenic eutrophication in small shallow water bodies effect of hydroperiod on the specific richness of zooplankton view project shallow wetland lake functioning and restoration in a changing European environment view project. Ecol Indic 76:324–334. https://doi.org/10.1016/j.ecolind.2017.01.034

Singh KP, Malik A, Singh VK, Mohan D, Sinha S (2005) Chemometric analysis of groundwater quality data of alluvial aquifer of Gangetic plain, North India. Anal Chim Acta 550(1–2):82–91. https://doi.org/10.1016/j.aca.2005.06.056

Singh B, Chauhan S, Verma G (2015) Nanocomposites – a review. J Chem Cheml 5 (September):506–510

Singh NB, Nagpal G, Agrawal S (2018) Water purification by using adsorbents: a review. Environ Technol Innov 11:187–240. https://doi.org/10.1016/j.eti.2018.05.006

Tyagi S, Rawtani D, Khatri N, Tharmavaram M (2018) Journal of water process engineering strategies for nitrate removal from aqueous environment using nanotechnology: a review. J Water Process Eng 21(September 2017):84–95. https://doi.org/10.1016/j.jwpe.2017.12.005

Weiner ML, Salminen WF, Larson PR, Barter RA, Kranetz JL, Simon GS (2001) Toxicological review of inorganic phosphates. Food Chem Toxicol 39:759–786

Xu X, Gao BY, Yue QY, Zhong QQ (2010) Preparation of agricultural by-product based anion exchanger and its utilization for nitrate and phosphate removal. Bioresour Technol 101 (22):8558–8564. https://doi.org/10.1016/j.biortech.2010.06.060

Yadav SK, Sinha S, Singha DK (2014) Chromium(VI) removal from aqueous solution and industrial wastewater by modified date palm trunk. Environ Prog Sustain Energy 34(2):452–460. https://doi.org/10.1002/ep

Yan Y, Sun X, Ma F, Li J, Shen J, Han W et al (2014) Removal of phosphate from wastewater using alkaline residue. J Environ Sci (China) 26(5):970–980. https://doi.org/10.1016/S1001-0742(13)60537-9

Yulizar Y, Bakri R, Bagus Apriandanu DO, Hidayat T (2018) ZnO/CuO nanocomposite prepared in one-pot green synthesis using seed bark extract of *Theobroma cacao*. Nano-Structures & Nano-Objects 16:300–305. https://doi.org/10.1016/j.nanoso.2018.09.003

Zhai Y, Zhao X, Teng Y, Li X, Zhang J, Wu J, Zuo R (2017) Groundwater nitrate pollution and human health risk assessment by using HHRA model in an agricultural area, NE China. Ecotoxicol Environ Saf 137(December 2016):130–142. https://doi.org/10.1016/j.ecoenv.2016.11.010