Chapter 9

Composite Ion Exchangers as New Age Photocatalyst

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Abstract

The innovation of different technologies and emphasis on development of new techniques is indispensable to improve the quality of water globally. Photocatalysis is one of the major techniques explored now a days for the exclusion of water impurities using solar light. Different types of photocatalysts have been employed for the removal of dyes, heavy metals, pesticides from aqueous system. During the last few years, nanocomposite ion exchangers were used as a photocatalyst for the removal of organic pollutants. This chapter includes detailed information about introduction of pollutants into the water system, nanocomposite ion exchangers and photocatalysis removal. Nanocomposite ion exchangers effectively degrade various pollutants present in the marine system. These nanocomposites have also been used in different areas such as fuel cell, sensor, nuclear separation and heavy metal removal etc. Therefore, nanocomposite ion exchangers are a new age photocatalyst with unique and effective properties.

Keywords

Nanocomposite, Photocatalysis, Ion Exchanger, Dyes, Heavy Metals, Photocatalyst

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1. Introduction

The incessant human activities consistently degrade the water resources all over the world. The contamination of water sources due to various industrial activities is a global issue, especially in the developing countries. The scarcity of clean water in terms of quantity and quality becomes a substantial threat to the living organisms. Some sources of industrial pollutants include mining, metal plating, fertilizer industries, tanneries, batteries, pesticides, power regeneration and electronic industries etc. A variety of toxic organic and inorganic pollutants such as heavy metals, azo dyes, anthraquinone, formazan, fertilizers and pesticides, organic pollutants and other biological impurities have been discharged into water system [1-5]. The consumption of these toxins through drinking water, food and air causes serious effects in living beings. These pollutants are highly toxic, non-biodegradable, carcinogenic and persist in the environment. Therefore, the removal of these hazardous materials from industrial waste is necessary to protect the plants, animals and human beings from their adverse effects [6-8]. Different industrial processes discharge waste products in water sources and reach humans through food, water and air as shown in Figure 1.

Figure 1: Industrial activities and their exposure to surroundings.

Among various contaminants, inorganic and organic toxins are major class of pollutants. Inorganic chemicals are one of the most important categories of water pollutants. These inorganic pollutants include heavy metals, salt and minerals etc. Among these, heavy metals are of major concern because of high toxicity even at low concentrations. These heavy metals enter in the food chain through a number of ways and cause severe problems in human beings. On the other hand, persistent organic compounds are used in agriculture, disease control, manufacturing and industrial processes [9-12]. These are bio-accumulative and resistant to degradation via chemical, biological and photolytic processes. These organic pollutants are very toxic and cause adverse health effects in humans and animals. Some common organic pollutants include dyes, phenols, pesticides, antibiotics and polychlorinated biphenyls etc. Figure 2 shows different pollutants which continuously degrade the quality of drinking water [14-20].

Figure 2: Various types of water pollutants.

1.1 Heavy metals

Industrial processes generate wastewater which contains a large amount of toxic heavy metal ions which must be removed before getting discharged [21-25]. Numerous industries including battery, paints, tanning, ceramics, electroplating, mining, glassware and photographic industries generated polluted products in wastewater. The presence of heavy metal ions such as Pb, Ni, Cd, Cr, Mo, Cu, Fe, Mn, Hg, Co and Bi in wastewater are directly associated with industrial processes. For example, metal ions Cu, Zn, Cr and Cd are generated from metal plating and presence of Cr metal ions in wastewater from tanneries waste. Also, Hg is generated by fossil fuel combustion and smelting processes. Industrial and mining sources are responsible for the production of Pb metal. The concentration of toxic heavy metal ions in wastewater is up to maximum level which is much higher than the safe limits. Therefore, these must be removed before getting mixed into the environment [26-28].

1.2 Dyes

Currently, dyes are quite important materials in either industrial or domestic purposes. In 1856, synthetic dyes were invented. But now days several forms more than 8000 have been manufactured for specific purposes [29]. Dyeing, textile, paper and pulp, tannery and paint

industries are big consumers of dyes. Therefore, waste products of industries have been considered as unpleasant pollutant because they impart color in water and due to the toxic nature which affects life unfavorably [30-35].

1.3 Phenols

Like other pollutants such as dyes and metals, phenols are also measured as major pollutants due to their bad taste and odour in water [36-38]. These are very toxic in nature. Therefore, determination and deduction of these pollutants from water is very important. Phenols are produced from chemical, paint, pesticides, resin, paper and pulp, gas and coke manufacture and dyeing industries.

1.4 Pesticides

Rural activities are mainly responsible for the generation of pesticides. According to their functional properties these are classified into some categories such as molluscides, nematicides, rodenticides, pesticides, insecticides, fungicides, bactericides and herbicides [39]. Among all categories of pesticides, fungicides and insecticides are very important to human exposure in food because their time period is very short during harvesting. Significant increase in the production of herbicide is due to the gradually use of chemicals to control weeds in cultivation process. Although DDT is banned, some substitutes like malathion, heptachlor, endrin, lindane and parathion causing environmental pollution [40-42]. Different techniques have been used for the remediation of organic and inorganic pollutants including adsorption, ion exchange, membrane filtration, photocatalysis etc. Ion exchange method has been gained considerable attention due to its low cost, simplicity, and versatility. It is widely used for the removal of organic and inorganic pollutants from aqueous solutions.

The ion exchange process is a reversible process that takes place between charges. The exchanger must have an open network structure which carries the ions for the exchange. The ion exchange process takes place in both aqueous and non-aqueous solution, molten salts and with vapours. The exchange of ions between the solution and ion exchangers is a physicochemical process occurring on the basis of equivalency and principle of electro neutrality. Figure 3 shows the process of ion exchange [43-48].

Figure 3: Mechanism of ion exchange process.

2. Ion exchanger

Ion exchangers are insoluble and charged species containing loosely held ions. These ions are exchanged with other ions in the solution when come in contact with them. The ion exchangers contain either positively or negatively charged ions so called cation and anion exchangers. Ion exchange resins are water insoluble solid substances which absorb both cations and anions from an electrolyte solution and release ions of same charges into the solution. The positively charged ions such as hydrogen and sodium ions are exchanged with positively charged ions such as nickel, copper and zinc ions present in the solution. Similarly, the negative ions such as hydroxyl and chloride ions are exchanged with the negatively charged ions such as sulphate, chromate, nitrate, cyanide etc. of the solution [49-51].

Ion exchangers have been widely used due to their exclusive properties such as higher resistance and selectivity at higher temperatures. Ion exchangers have been used for selective membrane, adsorption, catalysis, drug delivery, antimicrobial action and chemical sensors. The most important application of ion exchangers was purification and demineralization of water. The characteristics of newly synthesised material are ion exchange capacity, effect of eluent concentration, elution behaviour, effect of temperature, pH titration, chemical stability, composition, structural properties and distribution studies [52-55].

2.1 Classification of ion exchangers

The ion exchanges have drawn considerable attention due to their wide range of applications. Ion exchangers are classified into three categories on the basis of chemical nature as shown in Figure 4.

Figure 4: Classification of ion exchanger on the basis of chemical nature.

2.2 Composite ion exchangers

Recently, hybrid or composite ion exchangers have been prepared due to certain limitations existed in inorganic and organic ion exchangers. The inorganic ion exchangers are non-reproducible and not suitable for column chromatography. However, the organic ion exchangers are highly responsive to immense radiation doses which lead to major changes in their chain scission, crosslinking, capacity and selectivity. The combinations of polymers and inorganic materials form hybrid ion exchange materials. The organic polymeric part of the composite material provides mechanical and chemical stability. While the inorganic part increases the ion exchange behaviour, thermal stability and electrical conductivity [56, 57].

The hybrid ion exchangers with controlled functionality and hydrophobicity have opened new possibilities in different areas like catalysis, organometallic chemistry, organic host guest chemistry, hydrometallurgy, water treatment, pollution control, antibiotic purification, separation of radioactive isotopes and analytical chemistry [58-60]. The hybrid ion exchangers have been utilised in the field of chemistry, biochemistry, engineering and material science.

The composite ion exchange materials possess superior properties such as mechanical, chemical and radiation stability. The multifunctional nature of composite materials makes them potentially useful in different fields such as fabrication of selective membranes, chemical sensors, potentiometric sensors, electro-deionization, storage batteries, chromatography, electrodialysis, fuel cells and ion exchange [61-63]. The composite or hybrid materials have been prepared by sol-gel method universally. These materials are generally granular in nature and suitable for column operations. The composite materials with nano-scale dimensions have been widely used due to their multifunctionality, specificity and selectivity.

Nanocomposite materials are more effective due to greater surface area and volume ratio of nanoparticles. The nano-ranged materials find vast applicability in different fields such as drug delivery, chromatography, photocatalysis, ion selective electrode and environmental remediation. In recent years, bio-polymer based composite materials have been studied due to their low cost and renewable nature. The organic polymers such as polyaniline, polypyrrole, starch, polystyrene, chitosan, cellulose, alginate, gelatin, and polyacrylonitrile have been used for the fabrication of composite materials.

2.3 Preparative methods for nanocomposites

Polymeric nanocomposites have been usually synthesized through solution route and because of this a large amount of organic solvents has been required and this may pollute the environment. Hence green synthetic methods have attracted much attention. Polymer or inorganic filler nanocomposites have been synthesized in three different ways such as

1. Direct mixing or blending of the polymer
2. In-situ polymerization of monomers in the presence of fillers
3. Sol-gel process

2.3.1 Solution and melt processing

In this method, the layered silicates have been dispersed in a solvent in which the polymer is soluble. On evaporation of the solvent, the silicate sheets have been introduced into the polymer to make a multi-layered and ordered structure as shown in Figure 5. This process is also known as exfoliation or adsorption process. While in melt processing, layered silicate has been mixed to the polymer in the molten state. If the layer's surfaces are compatible with the polymer it results in the formation of nanocomposites by the insertion of selected polymer into interlayer space. There is no requirement of solvent in this method [64].

Figure 5: Preparation of nanocomposite by solution/melt processing.

2.3.2 In-situ polymerization

In this case monomer units with initiators have been taken and allowed to polymerize in presence of clays. The growth of polymer units separate clays and enter into the interlayer space [65]. The formation of polymer clay nanocomposite has been shown in Figure 6.

Figure 6: In-situ polymerization for the synthesis of nanocomposite.

2.3.3 Sol-gel method

Sol-gel method has been tremendously explored for the fabrication of nanostructure materials like nano-powders, nanocomposites etc. Composites have been synthesized by combining different types of materials (organic and inorganic) using the sol-gel method as shown in Figure 7. In this method, two methodologies can be used such as metal alkoxides hydrolysis and polycondensation of hydrolyzed intermediates. Transparent films of organic-inorganic composite materials have been made by co-hydrolysis and polycondensation of alkyltrimethoxy silane - tetramethoxysilane mixtures [66].

Figure 7: *Synthesis of nanocomposites using sol-gel method.*

3. Methods for the removal of pollutants

Different methods including ion exchange, adsorption, membrane filtration and photocatalysis have been developed for the removal of organic and inorganic impurities from wastewater. Photocatalysis is a relatively simple and very effective technique for the exclusion of toxic contaminants using solar radiations. Photocatalytic process is attaining more attention in the field of wastewater treatment to obtain complete mineralization of the pollutant achieved under mild conditions of temperature and pressure [67-70].

3.1 Photocatalysis

Heterogeneous photocatalysis has been used for the removal and recovery of heavy metals and organic impurities. The semiconductor particles are illuminated by ultraviolet light with energy greater than the band gap energy of the photocatalyst, electron-hole pairs are generated. In this method, light energy is used to stimulate the semiconductor material to produce electron-hole pairs which results in detoxification of pollutants. The degradation of pollutants is due to reactive oxidising species (O_2^* , OH^*) generated by two simultaneous reactions.

When sunlight in the visible region falls on a semiconductor, electrons get promoted from valence band to conduction band with the formation of e^- - h^+ pairs. These photogenerated holes oxidize the dissociated adsorbed water. The excited electrons move towards the surface of semiconductor and transferred to surface of adsorbed oxygen where it forms O_2^*

radicals. These free radicals react with water and produce OH^* [71-75]. The proposed mechanism of photocatalysis is shown in Figure 8.

Figure 8: Mechanism of photocatalysis.

3.2 Oxidation and reduction mechanism

The absorbed water is oxidized by positive holes produced in the valence band due to the electrons shifting to the conduction band. Due to irradiation of light, there was formation of hydroxyl (OH^*) and these hydroxyl radicals react with organic matter present in the dyes. If oxygen is present, the intermediate radicals in the organic compounds along with the oxygen molecules and experience radical chain reactions [76-78]. The organic matter decomposes at the end of the day becoming carbon dioxide and water. Organic compounds can react directly with positive holes resulting in oxidative decomposition as shown in Figure 9.

Figure 9: Mechanism for oxidation process.

On the other hand, reduction of oxygen takes place as an alternative to hydrogen generation because oxygen is an easily reducible substance. The conduction band electrons react with dissolved oxygen species to form superoxide anions. These superoxide anions attach to the intermediate products in the oxidative reaction and form peroxide or changing to H_2O_2 and then into water as shown in Figure 10. The reduction occurs more easily in organic matter as compared to water. Therefore, the higher concentration of organic matter tends to increase the number of positive holes and reduces the carrier recombination and improves photocatalytic activity [79, 80].

Figure 10: Mechanism for reduction process.

Different types of nanocomposites have been synthesised for the removal of dyes, pesticides, heavy metals, phenols and other pollutants using photocatalysis. In the last few decades, nanocomposites were also explored for the photocatalytic degradation of different dyes in water systems. It has been found that these nanocomposite ion exchangers

effectively degraded dyes in lesser time. Different nanocomposites have been employed for the degradation of different dyes including methylene blue, malachite green, methyl orange, fast green, methyl violet etc. as shown in Table 1.

Table 1: Different nanocomposite ion exchangers explored for photocatalytic activity

S.No.	Nanocomposite	Target Pollutant	References
1.	Polyaniline Zr(IV) selenotungstophosphate	Methylene blue and malachite green	[81]
2.	Polyacrylamide@Zr(IV) vanadophosphate nanocomposite	Congo red	[82]
3.	Pectin @ zirconium (IV) silicophosphate nanocomposite	Methylene blue	[83]
4.	Polyaniline zirconium (IV) silicophosphate nanocomposite	Methylene blue	[84]
5.	Pectin–thorium (IV) tungstomolybdate nanocomposite	Methylene blue	[85]
6.	Polyaniline zirconium(IV) silicophosphate	Methylene blue	[86]
7.	Pectin Zr(IV) selenotungstophosphate	Methylene blue and malachite green	[87]
8.	Polyacrylamide Ce(IV) silicophosphate	Methylene blue	[88]
9.	Cellulose acetate–zirconium (IV) phosphate nano-composite	Congo red	[89]
10.	Gelatin-Zr(IV) phosphate nanocomposite	Fast green and methylene blue	[90]
11.	Cellulose acetate–tin (IV) phosphate nanocomposite	Methylene blue	[91]
12.	Pectin thorium(IV) tungstomolybdate	Malachite green	[92]
13.	Styrene–tin (IV) phosphate nanocomposite	Methylene blue	[93]
14.	Alginate-Zr (IV) phosphate nanocomposite	Fast green and methylene blue	[94]
15.	lactic acid–Zr(IV) phosphate nanocomposite	Methylene blue	[95]

16.	Tin (IV) phosphate/poly(gelatin-cl-alginate) nanocomposite	Methyl orange	[96]
17.	Gelatin-tin (IV) phosphate nanocomposite	Methylene blue	[97]
18.	Gelatin–zirconium(IV) tungstophosphate nanocomposite	Methyl violet	[98]
19.	Zirconium (IV) phosphate/poly(gelatin-cl-alginate) nanocomposite	Methylene blue and methylene green	[99]
20.	Gelatin-zirconium Dioxide Nanocomposite	Methylene blue	[100]
21.	Zirconium phosphoborate nanocomposite	Methylene blue	[101]

4. Other applications of nanocomposite ion exchangers

The ion exchangers possess wide range of applications in various areas such as pollution control, separation of radioisotopes, antibiotic purification, fuel cell etc. Therefore, composite ion exchangers received special attention due to stability in column operations especially for separation, pre-concentration and filtration of ionic species. The composite ion exchangers have good ion exchange capacity, reproducibility, high thermal stability and selectivity for the removal of heavy metal ions. The applications of composite ion exchangers in different fields are shown in Figure 11.

Conclusion

In recent years, various processes including population growth, unrestrained water usage, climate change and infrequent rainfall, etc. continuously affect our surroundings. Due to these activities, demand for water has been increased but there is only small percentage of water which we can use. Water pollution is one of the major causes for water dearth. Therefore, we need to develop different techniques for the removal of toxic impurities present in water. In this, we have discussed photocatalytic processes for their exclusion using nanocomposite ion exchangers. It has been observed that nanocomposite ion exchangers act as photocatalyst and effectively degraded different dyes present in the

marine system. These nanocomposites open new prospects for researchers to improve the quality of water.

Figure 11: Applications of composite or hybrid ion exchangers in different fields.

References

- [1] Q. Wang, Z. Yang, Industrial water pollution, water environment treatment, and health risks in China, *Environmental pollution*, 218 (2016) 358-365. <https://doi.org/10.1016/j.envpol.2016.07.011>
- [2] A.K. Awasthi, X. Zeng, J. Li, Environmental pollution of electronic waste recycling in India: a critical review, *Environmental pollution*, 211 (2016) 259-270. <https://doi.org/10.1016/j.envpol.2015.11.027>
- [3] L. Zhang, J. Gao, Exploring the effects of international tourism on China's economic growth, energy consumption and environmental pollution: Evidence from a regional panel analysis, *Renewable and Sustainable Energy Reviews*, 53 (2016) 225-234. <https://doi.org/10.1016/j.rser.2015.08.040>
- [4] R. Michalski, A. Ficek, Environmental pollution by chemical substances used in the shale gas extraction—a review, *Desalination and water treatment*, 57 (2015) 1336-43. <https://doi.org/10.1080/19443994.2015.1017331>

- [5] W.A. Suk, H. Ahanchian, K.A. Asante, D.O. Carpenter, F. Diaz-Barriga, E.H. Ha, X. Huo, M. King, M. Ruchirawat, E.R. da Silva, L. Sly, Environmental pollution: an under-recognized threat to children's health, especially in low-and middle-income countries, *Environmental health perspectives*, 124 (2016) 41-50.
<https://doi.org/10.1289/ehp.1510517>
- [6] T.K. Parmar, D. Rawtani, Y.K. Agrawal. Bioindicators: the natural indicator of environmental pollution, *Frontiers in life science*, 9 (2016) 110-118.
<https://doi.org/10.1080/21553769.2016.1162753>
- [7] L. M. Chiesa, G. F. Labella, A. Giorgi, S. Panseri, R. Pavlovic, S. Bonacci, F. Arioli, The occurrence of pesticides and persistent organic pollutants in Italian organic honeys from different productive areas in relation to potential environmental pollution, *Chemosphere*, 154 (2016) 482-490.
<https://doi.org/10.1016/j.chemosphere.2016.04.004>
- [8] S. Dudka, D. C. Adriano, Environmental impacts of metal ore mining and processing: a review, *Journal of environmental quality*, 26 (1997) 590-602.
<https://doi.org/10.2134/jeq1997.00472425002600030003x>
- [9] Y. M. Hsueh, C. Y. Lee, S. N. Chien, W. J. Chen, H. S. Shiue, S. R. Huang, M. I. Lin, S. C. Mu, R. L. Hsieh, Association of blood heavy metals with developmental delays and health status in children, *Scientific reports*, 7 (2017) 43608. <https://doi.org/10.1038/srep43608> (2017)
- [10] K. Kumar, S. C. Gupta, S. K. Baidoo, Y. Chander, C. J. Rosen, Antibiotic uptake by plants from soil fertilized with animal manure, *Journal of environmental quality*, 34 (2005) 2082-5. doi:10.2134/jeq2005.0026
- [11] I. Zadnipyany, O. Tretiakova, T. P. Sataieva, W. Zukow, Experimental review of cobalt induced cardiomyopathy, *Russian Open Medical Journal*, 6 (2017) 103.
<https://doi.org/10.15275/rusomj.2017.0103>
- [12] L. Makarichi, V. Jutidamrongphan, K. A. Techato, The evolution of waste-to-energy incineration: A review, *Renewable and Sustainable Energy Reviews*, 91 (2018) 812-21. <https://doi.org/10.1016/j.rser.2018.04.088>
- [13] R. Verma, K. S. Vinoda, M. Papireddy, A. N. Gowda, Toxic pollutants from plastic waste-a review, *Procedia Environmental Sciences*, 35 (2016) 701-8.
<https://doi.org/10.1016/j.proenv.2016.07.069>

- [14] X. Wang, D. Sun, T. Yao, Climate change and global cycling of persistent organic pollutants: a critical review, *Science China Earth Sciences*, 59 (2016) 1899-911. <https://doi.org/10.1007/s11430-016-5073-0>
- [15] J. P. Bonde, E. M. Flachs, S. Rimborg, C. H. Glazer, A. Giwercman, C. H. Ramlau-Hansen, K. S. Hougaard, B. B. Høyer, K. K. Hærvig, S. B. Petersen, L. Rylander, The epidemiologic evidence linking prenatal and postnatal exposure to endocrine disrupting chemicals with male reproductive disorders: a systematic review and meta-analysis, *Human Reproduction Update*, 23 (2016) 104-25. <https://doi.org/10.1093/humupd/dmw036>
- [16] M. Brits, J. De Vos, J. M. Weiss, E. R. Rohwer, J. De Boer, Critical review of the analysis of brominated flame retardants and their environmental levels in Africa, *Chemosphere*, 164 (2016) 174-89. <https://doi.org/10.1016/j.chemosphere.2016.08.097>
- [17] D. Megson, E. J. Reiner, K. J. Jobst, F. L. Dorman, M. Robson, J. F. Focant. A review of the determination of persistent organic pollutants for environmental forensics investigations, *Analytica Chimica Acta*, 941 (2016) 10-25. <https://doi.org/10.1016/j.aca.2016.08.027>
- [18] V. Filimonova, F. Gonçalves, J. C. Marques, M. De Troch, A. M. Goncalves, Fatty acid profiling as bioindicator of chemical stress in marine organisms: a review, *Ecological indicators*, 67 (2016) 657-72. <https://doi.org/10.1016/j.ecolind.2016.03.044>
- [19] G. Cagnetta, H. Liu, K. Zhang, J. Huang, B. Wang, S. Deng, Y. Wang, G. Yu, Mechano-chemical conversion of brominated POPs into useful oxybromides: a greener approach, *Scientific reports*, 6 (2016) 28394. <https://doi.org/10.1038/srep28394>
- [20] J. Ma, H. Hung, R. W. Macdonald, The influence of global climate change on the environmental fate of persistent organic pollutants: A review with emphasis on the Northern Hemisphere and the Arctic as a receptor, *Global and Planetary Change*, 146 (2016) 89-108. <https://doi.org/10.1016/j.gloplacha.2016.09.011>
- [21] M. K. Uddin, A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade, *Chemical Engineering Journal*, 308 (2017) 438-62. <https://doi.org/10.1016/j.cej.2016.09.029>
- [22] Y. Zhao, G. Mao, H. Hongxia, L. Gao, Effects of EDTA and EDDS on heavy metal activation and accumulation of metals by soybean in alkaline soil, *Soil and Sediment Contamination: An International Journal*, 24(4) (2015) 353-67. <https://doi.org/10.1080/15320383.2015.962125>

- [23] C. F. Carolin, P. S. Kumar, A. Saravanan, G. J. Joshiba, M. Naushad, Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review, *Journal of Environmental Chemical Engineering*, 5 (2017) 2782-99. <https://doi.org/10.1016/j.jece.2017.05.029>
- [24] D. L. Lake, P. W. Kirk, J. N. Lester, Fractionation, characterization and speciation of heavy metals in sewage sludge and sludge-amended soils: a review, *Journal of Environmental Quality*, 2 (1984) 175-83. <https://doi.org/10.2134/jeq1984.00472425001300020001x>
- [25] A. C. Bosch, B. O'Neill, G. O. Sigge, S. E. Kerwath, L. C. Hoffman, Heavy metals in marine fish meat and consumer health: a review, *Journal of the Science of Food and Agriculture*. 96 (2016) 32-48. <https://doi.org/10.1002/jsfa.7360>
- [26] S. H. Liu, G. M. Zeng, Q. Y. Niu, Y. Liu, L. Zhou, L. H. Jiang, X. F. Tan, P. Xu, C. Zhang, M. Cheng, Bioremediation mechanisms of combined pollution of PAHs and heavy metals by bacteria and fungi: A mini review, *Bioresource technology*. 224 (2017) 25-33. <https://doi.org/10.1016/j.biortech.2016.11.095>
- [27] E. Da'na, Adsorption of heavy metals on functionalized-mesoporous silica: A review, *Microporous and Mesoporous Materials*, 247 (2017) 145-57. <https://doi.org/10.1016/j.micromeso.2017.03.050>
- [28] M. Abtahi, Y. Fakhri, G. Oliveri Conti, H. Keramati, Y. Zandsalimi, Z. Bahmani, R. HosseiniPouya, M. Sarkhosh, B. Moradi, N. Amanidaz, S. M. Ghasemi, Heavy metals (As, Cr, Pb, Cd and Ni) concentrations in rice (*Oryzasativa*) from Iran and associated risk assessment: a systematic review, *Toxin reviews*, 36 (2017) 331-41. <https://doi.org/10.1080/15569543.2017.1354307>
- [29] G. Richhariya, A. Kumar, P. Tekasakul, B. Gupta, Natural dyes for dye sensitized solar cell: A review, *Renewable and Sustainable Energy Reviews*, 69 (2017) 705-18. <https://doi.org/10.1016/j.rser.2016.11.198>
- [30] H. A. Shindy. Fundamentals in the chemistry of cyanine dyes: A review, *Dyes and Pigments*, 145 (2017) 505-13. <https://doi.org/10.1016/j.dyepig.2017.06.029>
- [31] A. M. Ghaedi, A. Vafaei, Applications of artificial neural networks for adsorption removal of dyes from aqueous solution: a review, *Advances in colloid and interface science*, 245 (2017) 20-39. <https://doi.org/10.1016/j.cis.2017.04.015>
- [32] C. A. Martínez-Huitle, E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: a general review, *Applied Catalysis B: Environmental*, 87 (2009) 105-45. <https://doi.org/10.5772/58333>

- [33] G. Annadurai, R.S. Juang, D.J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, *Journal of hazardous materials*, 92(3) (2002) 263-74. [https://doi.org/10.1016/S0304-3894\(02\)00017-1](https://doi.org/10.1016/S0304-3894(02)00017-1)
- [34] I. Khurana, A. Saxena, J. M. Khurana, P. K. Rai, Removal of dyes using graphene-based composites: a review, *Water, Air & Soil Pollution*, 228 (2017) 180. <https://doi.org/10.1007/s11270-017-3361-1>
- [35] T. Robinson, G. McMullan, R. Marchant, P. Nigam, Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative, *Bioresource technology*, 77(3) (2001) 247-55. [https://doi.org/10.1016/S0960-8524\(00\)00080-8](https://doi.org/10.1016/S0960-8524(00)00080-8)
- [36] Z. Cao, J. Engelhardt, M. Dierks, M. T. Clough, G. H. Wang, E. Heracleous, A. Lappas, R. Rinaldi, F. Schüth, Catalysis meets nonthermal separation for the production of (alkyl) phenols and hydrocarbons from pyrolysis oil, *Angewandte Chemie International Edition*, 56 (2017) 2334-9. <https://doi.org/10.1002/anie.201610405>
- [37] S. D. Schimler, M. A. Cismesia, P. S. Hanley, R. D. Froese, M. J. Jansma, D. C. Bland, M. S. Sanford, Nucleophilic deoxy fluorination of phenols via aryl Fluorosulfonate intermediates, *Journal of the American Chemical Society*, 139 (2017) 1452-5. DOI: 10.1021/jacs.6b12911
- [38] J. Zhou, M. L. Wang, X. Gao, G. F. Jiang, Y. G. Zhou, Bifunctional squaramide-catalyzed synthesis of chiral dihydrocoumarins via ortho-quinonemethides generated from 2-(1-tosylalkyl) phenols, *Chemical Communications*, 53 (2017) 3531-4.
- [39] R. D. Wauchope, The pesticide content of surface water draining from agricultural fields—a review, *Journal of environmental quality*, 7 (1978) 459-72. <https://doi.org/10.2134/jeq1978.00472425000700040001x>
- [40] R. J. Hillocks, Farming with fewer pesticides: EU pesticide review and resulting challenges for UK agriculture, *Crop Protection*, 31 (2012) 85-93. <https://doi.org/10.1016/j.cropro.2011.08.008>
- [41] M. Cycoń, A. Mroziak, Z. Piotrowska-Seget, Bio augmentation as a strategy for the remediation of pesticide-polluted soil: a review, *Chemosphere*, 172 (2017) 52-71. <https://doi.org/10.1016/j.chemosphere.2016.12.129>
- [42] M. L. Xu, Y. Gao, X. X. Han, B. Zhao, Detection of pesticide residues in food using surface-enhanced Raman spectroscopy: A review, *Journal of agricultural and food chemistry*, 65 (2017) 6719-26. <https://doi.org/10.1021/acs.jafc.7b02504>

- [43] K. Khoiruddin, A. N. Hakim, I. G. Wenten, Advances in electrode ionization technology for ionic separation-A review, *Membrane Water Treatment*, 5 (2014) 87-108. <https://doi.org/10.12989/mwt.2014.5.2.087>
- [44] O. Oleksiienko, C. Wolkersdorfer, M. Sillanpää, Titanosilicates in cation adsorption and cation exchange—a review, *Chemical Engineering Journal*, 317 (2017) 570-85. <https://doi.org/10.1016/j.cej.2017.02.079>
- [45] J. Ran, L. Wu, Y. He, Z. Yang, Y. Wang, C. Jiang, L. Ge, E. Bakangura, T. Xu, Ion exchange membranes: New developments and applications, *Journal of Membrane Science*, 522 (2017) 267-91. <https://doi.org/10.1016/j.memsci.2016.09.033>
- [46] M. Endo, E. Yoshikawa, N. Muramatsu, N. Takizawa, T. Kawai, H. Unuma, A. Sasaki, A. Masano, Y. Takeyama, T. Kahara, The removal of cesium ion with natural Itaya zeolite and the ion exchange characteristics, *Journal of Chemical Technology & Biotechnology*, 88 (2013) 1597-602. <https://doi.org/10.1002/jctb.4140>
- [47] M. A. Hickner, B. S. Pivovar, The chemical and structural nature of proton exchange membrane fuel cell properties, *Fuel cells*, 5 (2005) 213-29. <https://doi.org/10.1002/fuce.200400064>
- [48] T. Xu, Ion exchange membranes: state of their development and perspective, *Journal of membrane science*, 263(1-2) (2005) 1-29. <https://doi.org/10.1016/j.memsci.2005.05.002>
- [49] G. Zhao, X. Huang, Z. Tang, Q. Huang, F. Niu, X. Wang, Polymer-based nanocomposites for heavy metal ions removal from aqueous solution: a review, *Polymer Chemistry*, 9 (2018) 3562-82. <https://doi.org/10.1039/C8PY00484F>
- [50] W. Jia, B. Tang, P. Wu, Novel composite proton exchange membrane with connected long-range ionic nanochannels constructed via exfoliated nafion–boron nitride nanocomposite, *ACS applied materials & interfaces*, 9 (2017) 14791-800. <https://doi.org/10.1021/acsami.7b00858>
- [51] M. Naushad, G. Sharma, A. Kumar, S. Sharma, A. A. Ghfar, A. Bhatnagar, F. J. Stadler, M. R. Khan, Efficient removal of toxic phosphate anions from aqueous environment using pectin based quaternary amino anion exchanger, *International Journal of Biological Macromolecules*, 106 (2018) 1-0. <https://doi.org/10.1016/j.ijbiomac.2017.07.169>
- [52] Y. Tanaka, S. H. Moon, V. V. Nikonenko, T. Xu, Ion-exchange membranes, *International Journal of Chemical Engineering*, (2012). <https://doi.org/10.1155/2012/528290>

- [53] L. Curkovic, S. Cerjan-Stefanovic, T. Filipan, Metal ion exchange by natural and modified zeolites, *Water research*, 31(6) (1997) 1379-82.
[https://doi.org/10.1016/S0043-1354\(96\)00411-3](https://doi.org/10.1016/S0043-1354(96)00411-3)
- [54] A. Dąbrowski, Z. Hubicki, P. Podkościelny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, *Chemosphere*, 56 (2004) 91-106. <https://doi.org/10.1016/j.chemosphere.2004.03.006>
- [55] Y. F. Yao, J. T. Kummer, Ion exchange properties of and rates of ionic diffusion in beta-alumina, *Journal of Inorganic and Nuclear Chemistry*, 29 (1967) 2453-75.
[https://doi.org/10.1016/0022-1902\(67\)80301-4](https://doi.org/10.1016/0022-1902(67)80301-4)
- [56] A. Nilchi, R. Saberi, M. Moradi, H. Azizpour, R. Zarghami, Adsorption of cesium on copper hexacyanoferrate–PAN composite ion exchanger from aqueous solution, *Chemical Engineering Journal*, 172 (2011) 572-80.
<https://doi.org/10.1016/j.cej.2011.06.011>
- [57] F. Šebesta, V. Štefula, Composite ion exchanger with ammonium molybdophosphate and its properties, *Journal of Radioanalytical and Nuclear Chemistry*, 140 (1990) 15-21. <https://doi.org/10.1007/BF02037360>
- [58] A. Mardan, R. Ajaz, A. Mehmood, S. M. Raza, A. Ghaffar, Preparation of silica potassium cobalt hexacyanoferrate composite ion exchanger and its uptake behavior for cesium, *Separation and purification technology*, 16 (1999) 147-58.
[https://doi.org/10.1016/S1383-5866\(98\)00121-X](https://doi.org/10.1016/S1383-5866(98)00121-X)
- [59] S. A. Nabi, M. Shahadat, R. Bushra, A. H. Shalla, A. Azam, Synthesis and characterization of nano-composite ion-exchanger; its adsorption behaviour, *Colloids and Surfaces B: Biointerfaces*, 87 (2011) 122-8.
<https://doi.org/10.1016/j.colsurfb.2011.05.011>
- [60] A. A. Khan, M. M. Alam, Synthesis, characterization and analytical applications of a new and novel ‘organic–inorganic’ composite material as a cation exchanger and Cd (II) ion-selective membrane electrode: polyaniline Sn (IV) tungstoarsenate, *Reactive and Functional Polymers*, 55 (2003) 277-90. [https://doi.org/10.1016/S1381-5148\(03\)00018-X](https://doi.org/10.1016/S1381-5148(03)00018-X)
- [61] J. K. Moon, K. W. Kim, C. H. Jung, Y. G. Shul, E. H. Lee, Preparation of organic-inorganic composite adsorbent beads for removal of radionuclides and heavy metal ions, *Journal of Radioanalytical and Nuclear Chemistry*, 246 (2000) 299-307.
<https://doi.org/10.1023/A:1006714322455>

- [62] S. A. Nabi, M. Shahadat, R. Bushra, A. H. Shalla, F. Ahmed, Development of composite ion-exchange adsorbent for pollutants removal from environmental wastes, *Chemical Engineering Journal*, 165 (2010) 405-12.
<https://doi.org/10.1016/j.cej.2010.08.068>
- [63] W. W. Ngah, L.C. Teong, M. A. Hanafiah, Adsorption of dyes and heavy metal ions by chitosan composites: A review, *Carbohydrate polymers*, 83 (2011) 1446-56.
<https://doi.org/10.1016/j.carbpol.2010.11.004>
- [64] Z. Shen, G. P. Simon, Y. B. Cheng, Comparison of solution intercalation and melt intercalation of polymer–clay nanocomposites, *Polymer*, 43 (2002) 4251-60.
[https://doi.org/10.1016/S0032-3861\(02\)00230-6](https://doi.org/10.1016/S0032-3861(02)00230-6)
- [65] S. S. Ray, M. Okamoto, Polymer/layered silicate nanocomposites: a review from preparation to processing, *Progress in polymer science*, 28 (2003) 1539-641.
<https://doi.org/10.1016/j.progpolymsci.2003.08.002>
- [66] I. A. Rahman, V. Padavettan, Synthesis of silica nanoparticles by sol-gel: size-dependent properties, surface modification, and applications in silica-polymer nanocomposites-a review, *Journal of Nanomaterials*, (2012) 8.
<https://doi.org/10.1155/2012/132424>
- [67] W. Hou, S. B. Cronin, A review of surface plasmon resonance-enhanced photocatalysis, *Advanced Functional Materials*, 23 (2013) 1612-9.
<https://doi.org/10.1002/adfm.201202148>
- [68] K. Kabra, R. Chaudhary, R. L. Sawhney, Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: a review, *Industrial & engineering chemistry research*, 43 (2004) 7683-96. <https://doi.org/10.1021/ie0498551>
- [69] Y. Wang, Q. Wang, X. Zhan, F. Wang, M. Safdar, J. He, Visible light driven type II heterostructures and their enhanced photocatalysis properties: a review, *Nanoscale*, 5 (2013) 8326-39. <https://doi.org/10.1039/C3NR01577G>
- [70] X. Li, J. Yu, S. Wageh, A. A. Al-Ghamdi, J. Xie, Graphene in photocatalysis: a review, *Small*, 12 (2016) 6640-96. <https://doi.org/10.1002/sml.201600382>
- [71] K. Wenderich, G. Mul, Methods, mechanism, and applications of photodeposition in photocatalysis: a review, *Chemical reviews*, 116 (2016) 14587-619.
<https://doi.org/10.1021/acs.chemrev.6b00327>
- [72] L. K. Putri, W. J. Ong, W. S. Chang, S. P. Chai, Heteroatom doped graphene in photocatalysis: a review, *Applied Surface Science*, 358 (2015) 2-14.
<https://doi.org/10.1016/j.apsusc.2015.08.177>

- [73] Y. Boyjoo, H. Sun, J. Liu, V. K. Pareek, S. Wang, A review on photocatalysis for air treatment: from catalyst development to reactor design, *Chemical Engineering Journal*, 310 (2017) 537-59. <https://doi.org/10.1016/j.cej.2016.06.090>
- [74] J. Byrne, P. Dunlop, J. Hamilton, P. Fernández-Ibáñez, I. Polo-López, P. Sharma, A. Vennard, A review of heterogeneous photocatalysis for water and surface disinfection, *Molecules*, 20 (2015) 5574-615. <https://doi.org/10.3390/molecules20045574>
- [75] M. N. Chong, B. Jin, C. W. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: a review, *Water research*, 44 (2010) 2997-3027. <https://doi.org/10.1016/j.watres.2010.02.039>
- [76] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, *Chemical reviews*, 93(1) (1993) 341-57. <https://doi.org/10.1021/cr00017a016>
- [77] A. Ibhadon, P. Fitzpatrick, Heterogeneous photocatalysis: recent advances and applications. *Catalysts*, 3 (2013) 189-218. <https://doi.org/10.3390/catal3010189>
- [78] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chemical reviews*, 95 (1995) 69-96. <https://doi.org/10.1021/cr00033a004>
- [79] R. K. Nath, M. F. Zain, A. A. Kadhum, Photocatalysis—a novel approach for solving various environmental and disinfection problems: a brief review, *Journal of Applied Sciences Research*, 8 (2012) 4147-55.
- [80] T. Ramesh, B. Nayak, A. Amirbahman, C. P. Tripp, S. Mukhopadhyay, Application of ultraviolet light assisted titanium dioxide photocatalysis for food safety: A review, *Innovative food science & emerging technologies*, 38 (2016) 105-15. <https://doi.org/10.1016/j.ifset.2016.09.015>
- [81] D. Pathania, G. Sharma, A. Kumar, M. Naushad, S. Kalia, A. Sharma, Z. A. ALOthman, Combined sorptional–photocatalytic remediation of dyes by polyaniline Zr (IV) selenotungstophosphate nanocomposite, *Toxicological & Environmental Chemistry*, 97 (2015) 526-37. <https://doi.org/10.1080/02772248.2015.1050024>
- [82] G. Sharma, A. Kumar, M. Naushad, D. Pathania, M. Sillanpää, Polyacrylamide@Zr (IV) vanadophosphate nanocomposite: ion exchange properties, antibacterial activity, and photocatalytic behavior, *Journal of Industrial and Engineering Chemistry*, 33 (2016) 201-8. <https://doi.org/10.1016/j.jiec.2015.10.011>
- [83] D. Pathania, G. Sharma, R. Thakur, Pectin@ zirconium (IV) silicophosphate nanocomposite ion exchanger: photo catalysis, heavy metal separation and

- antibacterial activity, *Chemical Engineering Journal*, 267 (2015) 235-44.
<https://doi.org/10.1016/j.cej.2015.01.004>
- [84] V. K. Gupta, D. Pathania, N. C. Kothiyal, G. Sharma, Polyaniline zirconium (IV) silicophosphate nanocomposite for remediation of methylene blue dye from waste water, *Journal of Molecular Liquids*, 190 (2014) 139-45.
<https://doi.org/10.1016/j.molliq.2013.10.027>
- [85] V. K. Gupta, S. Agarwal, D. Pathania, N. C. Kothiyal, G. Sharma, Use of pectin–thorium (IV) tungstomolybdate nanocomposite for photocatalytic degradation of methylene blue, *Carbohydrate polymers*, 96 (2013) 277-83.
<https://doi.org/10.1016/j.carbpol.2013.03.073>
- [86] D. Pathania, G. Sharma, A. Kumar, N. C. Kothiyal, Fabrication of nanocomposite polyaniline zirconium (IV) silicophosphate for photocatalytic and antimicrobial activity, *Journal of Alloys and Compounds*, 588 (2014) 668-75.
<https://doi.org/10.1016/j.jallcom.2013.11.133>
- [87] V. K. Gupta, Sharma G, D. Pathania, N. C. Kothiyal, Nanocomposite pectin Zr (IV) selenotungsto phosphate for adsorptional/photocatalytic remediation of methylene blue and malachite green dyes from aqueous system, *Journal of Industrial and Engineering Chemistry*, 21 (2015) 957-64. <https://doi.org/10.1016/j.jiec.2014.05.001>
- [88] D. Pathania, G. Sharma, M. Naushad, A. Kumar, Synthesis and characterization of a new nanocomposite cation exchanger polyacrylamide Ce (IV) silico phosphate: photocatalytic and antimicrobial applications, *Journal of Industrial and Engineering Chemistry*, 20 (2014) 3596-603. <https://doi.org/10.1016/j.jiec.2013.12.054>
- [89] V. K. Gupta, D. Pathania, P. Singh, B. S. Rathore, P. Chauhan, Cellulose acetate–zirconium (IV) phosphate nano-composite with enhanced photo-catalytic activity, *Carbohydrate polymers*, 95 (2013) 434-40.
<https://doi.org/10.1016/j.carbpol.2013.02.045>
- [90] M. Thakur, G. Sharma, T. Ahamad, A. A. Ghfar, D. Pathania, M. Naushad, Efficient photocatalytic degradation of toxic dyes from aqueous environment using gelatin-Zr (IV) phosphate nanocomposite and its antimicrobial activity, *Colloids and Surfaces B: Biointerfaces*, 157 (2017) 456-63.
<https://doi.org/10.1016/j.colsurfb.2017.06.018>
- [91] V. K. Gupta, T. A. Saleh, D. Pathania, B. S. Rathore, G. Sharma, A cellulose acetate based nanocomposite for photocatalytic degradation of methylene blue dye under solar light, *Ionics*, 21 (2015) 1787-93. <https://doi.org/10.1007/s11581-014-1323-9>

- [92] G. Sharma, M. Naushad, D. Pathania, A. Kumar, A multifunctional nanocomposite pectin thorium (IV) tungstomolybdate for heavy metal separation and photo remediation of malachite green, *Desalination and Water Treatment*, 57 (2016) 19443-55. <https://doi.org/10.1080/19443994.2015.1096834>
- [93] B. S. Rathore, D. Pathania, Styrene–tin (IV) phosphate nanocomposite for photocatalytic degradation of organic dye in presence of visible light, *Journal of Alloys and Compounds*, 606 (2014) 105-11. <https://doi.org/10.1016/j.jallcom.2014.03.160>
- [94] D. Pathania, M. Thakur, A. K. Mishra, Alginate-Zr (IV) phosphate nanocomposite ion exchanger: Binary separation of heavy metals, photocatalysis and antimicrobial activity, *Journal of Alloys and Compounds*, 701 (2017) 153-62. <https://doi.org/10.1016/j.jallcom.2017.01.112>
- [95] D. Pathania, M. Thakur, A. Sharma, S. Agarwal, V. K. Gupta, Synthesis of lactic acid–Zr (IV) phosphate nanocomposite ion exchanger for green remediation, *Ionics*, 23 (2017) 699-706. <https://doi.org/10.1007/s11581-016-1858-z>
- [96] D. Pathania, M. Thakur, G. Sharma, A. K. Mishra, Tin (IV) phosphate/poly (gelatin-cl-alginate) nanocomposite: Photocatalysis and fabrication of potentiometric sensor for Pb (II), *Materials Today Communications*, 14 (2018) 282-93. <https://doi.org/10.1016/j.mtcomm.2018.01.005>
- [97] D. Pathania, M. Thakur, V. Puri, S. Jasrotia, Fabrication of electrically conductive membrane electrode of gelatin-tin (IV) phosphate nanocomposite for the detection of cobalt (II) ions, *Advanced Powder Technology*, 29 (2018) 915-24. <https://doi.org/10.1016/j.appt.2018.01.009>
- [98] M. Thakur, D. Pathania, Sol–gel synthesis of gelatin–zirconium (IV) tungstophosphatenano composite ion exchanger and application for the estimation of Cd (II) ions, *Journal of Sol-Gel Science and Technology*, (2019) 1-3. <https://doi.org/10.1007/s10971-019-04919-2>
- [99] D. Pathania, S. Agarwal, V. K. Gupta, M. Thakur, N. S. Alharbi, Zirconium (IV) phosphate/poly (gelatin-cl-alginate) nanocomposite as ion exchanger and Al^{3+} potentiometric sensor, *International Journal of Electrochemical Science*, 13 (2018) 994-1012. <https://doi.org/10.20964/2018.01.80>
- [100] D. Pathania, M. Thakur, S. Jasrotia, S. Agarwal, V. K. Gupta, Gelatin-zirconium dioxide nanocomposite as a Ni (II) selective potentiometric sensor: Heavy Metal Separation and Photocatalysis, *International Journal of Electrochemical Science*, 12 (2017) 8477-94. <https://doi.org/10.20964/2017.09.49>

- [101] S. Kaushal, R. Badru, P. Singh, S. Kumar, S. K. Mittal, Nanocomposite zirconium phosphoborate ion-exchanger incorporating carbon nanotubes with photocatalytic activity, *Separation Science and Technology*, 51 (2016) 2896-902.
<https://doi.org/10.1080/01496395.2016.1234487>