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Metal Detoxification in Nature and Its Translation into Functional Adsorbent Materials

Rega Permana[1,*], **Yudi Nurul Ihsan**[2]

[1]Fisheries Department, Faculty of Fisheries and Marine Science, Padjadjaran University, Jatinangor, Indonesia

[2]Marine Science Department, Faculty of Fisheries and Marine Science, Padjadjaran University, Jatinangor, Indonesia

*E-mail address: rega.permana@unpad.ac.id

ABSTRACT

Nature has a remarkable strategies to overcome the unfavoring environmental condition by producing a unique chemical compounds, including polyphenol. Polyphenol residues in many living organism have been documented to express numerous biological function ranging from antioxidant, mechanical reinforcement as well as metal anchoring substances. This gave us insight of how nature converts toxic metal compound and deposits it into a harmless form. This review will discuss some natural strategies of living organism to metabolize metal in a safe manner so that the metal no longer harmful to them. Example taken from aluminum accumulating plants, vanadium accumulating marine tunicate and iron-reinforced mussel byssus, which all three utilized phenol derivative compound to chelate the metal. Advances made by incorporating cutting edge characterization tools allowed us to understand the exact mechanism of metal chelation at the atomic level. A comprehensive discussion of molecular mechanism governing the complexion between the phenolic compound and metal will be beneficial for further study to fabricate functional materials, for example adsorbent, to remediate contaminated water. Translating these natural strategies into an engineered polyphenol based adsorbent materials will be prospective to be further applied as a remediation agent as it is easily found in nature, cost effective and highly efficient.

***Keywords*:** adsorbent, bioinspired, heavy metal, polyphenol

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1. INTRODUCTION

The effort to remediate numbers of pollutant from environmental niche, particularly water, has been performed for more than decades to promote a healthy and safe living environment. Hundreds of pollutant categorized as priority pollutant according to US EPA, considering their high toxicity. Amongst them, heavy metal resides as the prone pollutant that remains challenging to eradicate due to its non-degradable nature and bioaccumulation behavior. The consequences of heavy metal exposure to environment could be devastating, affecting almost all form of living organism even in a relatively low concentration [1]. Majority of heavy metal transferred to water bodies are coming from several industrial-generated wastewaters such as electroplating, smelting, textile industries, automotive, agriculture, etc. [2]. Furthermore, some naturally high concentration of toxic heavy metal could be found in nature due to natural physical and chemical processes and later threatened the environment [3, 4]. The urgency to remove heavy metal contaminated water with better efficiency as well as minimum environmental damage is certainly still an exploratory research area.

Various methods have been applied to remove heavy metal from wastewater, including electrochemical [5], ion exchange [6], solvent exchange [7], membrane filtration [8], precipitation [9] and adsorption [10]. One of the most frequently used methods is adsorption due to its high efficiency, easy regeneration, and affordable cost while other methods are often costly and generating secondary waste [11]. However, the search for better adsorbent material with higher capacity and sustainable source is still needed for improvement. Nature provides some extraordinary mechanism to detoxify metal either by use it as reinforcement for the physical property or store it in a safe form. The many ways of how nature utilized metal for their own good could be seen in a specific metal-chelating protein expression such as metallothionein [12] and secretion of chelation substance, like polyphenol [13].

Polyphenol is a naturally occurring compound which has long been known to have a superior property as an antioxidant either by free-radical scavenging or sequestering active metals that catalyzed the reaction produces free-radical [14]. Its function and roles in manipulating metal toxicity ranging from tolerance mechanism as well as physical property reinforcement that benefits the organism to survive in a harsh environment. Its abundance in nature, provided in almost every form of plants, making polyphenol stands as a promising candidate to be further utilized as an adsorbent materials. The underlying molecular mechanism and state of the art principle for these natural strategies in metal utilization could be the key for further development of highly efficient and sustainable adsorbent materials that have a similar property to that found in nature. This review paper will discuss about some natural strategies found in nature for metal detoxification and reinforcement. In addition, some proposed mechanism will be gathered to foster our understanding on the local environmental between the ligand and metal in the atomic scale that ruled the complexion which can further help us to mimic their strategy to solve our problem.

2. NATURAL METAL DETOXIFICATION

Diverse organism in nature either solitary or associated with other form of life [15] Some organisms are well-adapt in a harsh environment like metal-contaminated area by metabolizing the metal in a safe manner. A detail assessment of this unique strategy can provide us the key to a new inspiration for synthesizing a novel material, such as in water treatment technology. Several studies have unveiled some natural mechanism performed by various organisms. This section will talk more about three organism that handle metal quiet safe and mild, particularly vanadium accumulating marine tunicate, iron-reinforced mussel byssus and aluminum accumulating plants

2. 1. Vanadium-accumulating Marine Tunicate

Tunicate is an ancient invertebrate which belongs to chordate and live their life as a sessile organism attaching to a hard substrate in the ocean floor. The name came from their hard extracellular armor composed by cellulose nanofiber called tunic which have an outstanding self-healing property [16]. This filter feeder organism effectively filtered thousands of gallons water every day to physiologically eat and survive. Some genera known to be effectively accumulate a superior amount of vanadium from seawater. Vanadium is a minor element in seawater and exists as a positively charged form in the column water with relatively very low concentration [17]. Elevated concentration might be observed near shore where industrial waste is coming. Typically, vanadium concentration in seawater ranging from 0.5 to 3 μg/kg [17]. In comparison, some tunicate can effectively accumulate vanadium up to 3000 mg/l or thousand times than that contented in seawater [18].

This superior strategy of tunicate to sequester vanadium in a high concentration attracts many scientists to unveil the mechanism behind. It has been proposed that the pyrogallol-containing peptide called tunichrome, playing a critical role for the sequestration [16]. Tunichrome is a small peptide isolated from the blood cells of tunicate, giving the blood a bright green and yellow color. The pyrogallol moieties or 3,4,5-trihydroxyphenylalanine (TOPA) is a phenolic compound that has a high affinity to metal ion [19]. The chelating phenomena can be described as noncovalent bonding between the metal and the hydroxyl group of the TOPA moieties in the peptide. The vanadium concentrated in the blood cells are in the form of trivalent state which is very sensitive to oxidation [16]. The role of vanadium for tunicate physiological function remains unclear with some studies said it exhibits a defensive role towards biofouling, predation and bacterial infection [18].

Few studies have reported the use of tunicate as a bioremediation agent for metal pollutant such as cadmium, lead, mercury as well as vanadium [20]. This approach can be further developed as a monitoring tool for ocean pollution indexing as it shows a promiscuous application as biosensor. However, considering it application in real waste water treatment service, using tunicate as agent is a risky choice since it has many limitations like uptake capacity, life cycle and sustainability issues. Furthermore, in some area, especially eastern Asia, tunicate are popular seafood commodity and served as a major economic income for coastal area.

2. 2. Iron-reinforced Mussels Byssus

Several genera of bivalve or mussels, a class of marine invertebrate, have a unique strategy to survive in a harsh marine environment. Some of them are even considered as a threat in aquatic ecosystem [21] For example, the blue mussels or *Mytilus edulis*, are known to attach themselves in a hard substrate so strong that it can survive the encountering ocean wave. They secreted 4 to 5 cm long, fine hundreds of thread formed a bundle which called as byssus, plural from byssal thread [22]. This byssus is coated by a delicate layer of protein that protects them from the stresses coming from its surrounding. In addition, this attachment is not disturbed even though they are physically submerged in the fluidic ocean water, where we know that most adhesive attachment failed under the water. This extraordinary natural strategy has attracted interest of scientist and researcher for years. The key underwater adhesive point is apparently the most appealing part for many researchers across fields like biomedical [23], environmental [24] and material science [25].

To date, the most prominent research in the protective coated layer of the byssus is the protein which called mussels foot protein (MFP). In Mytilus edulis, the protein consists of roughly 85 decapeptides with a special residue of post-translational form of tyrosine, cathecolic compound 3,4-dihydroxyphenilalanine or DOPA [26]. The approximate molecular weight of this protein is around 110 kDA with 10 to 15% of DOPA is present [22]. These moieties of DOPA served as active sites for iron complexation, creating an unusual mechanical property with high stiffness yet excellent elongation [27]. It is reported that Fe (III) form an exceptional stabile complex with DOPA in bis and tris manner, accustomed to the environment condition, e.g. pH.

The byssus secreted by foot, however, has an extraordinary mechanical properties spanning in axial orientation along the threads. The end of the byssus, or plaque, has typically higher mechanical property than the other part. This in agreement with the MFP content which showed highest concentration in the plaque [28]. Simultaneously, moving upward to the distal and proximal part, the mechanical property decreases as well as the MFP content [22]. This gradient of molecular constituent and mechanical property exhibit fascinating natural strategies of how mussels control their biophysical function.

Metals other than iron have been studied to have interaction with byssus, although the most studied one is iron. Iron can exist in seawater as dissolved ion in Fe(II) or Fe(III) state and the concentration relatively low [29]. However, the MFP cannot directly attract iron from the seawater instead of utilized the available iron already reside in the mussel body from the filter-feeding activity performed by most bivalve. This iron that taken through the water, distributed evenly to many body parts of mussel by the amoebocytes including the foot, which where the byssus made [30].

The incorporation of iron in MFP although still debated, draws a substantial key to understand how organisms deal with foreign compound like metal. Using the exact similar strategies utilizing the metal affinity towards a strong natural ligand can extend the effectiveness of remediation practice in waste water treatment. The limitation experienced by these natural strategies can be overcome by incorporating a synthetic or engineered additional compound to tackle the problems that might surface later such as sensitivity to oxidation.

2. 3. Alumunium-accumulating plants

Alumunium trivalent (+3) species is known as toxic substance to many plants, which distinctly manage to reside in acidic environment. Although alumunium in low concentration may promote some beneficial effect on plants such as the uptake and transport of several essential nutrient including Ca, Mg, P and Fe [31], in higher concentration it can disturb cellular function of the cell thus creating a detrimental effect [32]. Under acidic soils, the presence of alumunium interrupted the root development and growth giving a most distinguished cellular damage compare to other part, e.g. leaves [32]. This toxicity towards some plants species can be seen as a challenge as it is reported that almost 40% arable land in world turned acidic.

This can happen due to natural phenomena but mostly human activity like mining causes the environmental change.

Plants that suffer from this toxicity are forced to survive by several mechanisms like exclusion and tolerance. The exclusion mechanism involved in secretion of chelating substance by the plants so that alumunium fixed by the chelating agent outside the cell [33]. While the tolerance mechanism fix the metal in the cell wall or other organelle in an unreactive form thus decreasing their toxicity.

Some genera of plants can afford the detrimental consequences of alumunium toxicity by secreting polyphenol substances that able to chelate the metal efficiently. Polyphenol compound, both high and low molecular weight, is known to perform alumunium detoxification in plants. For instance, a high molecular weight tannin, flavan-3-ol, found in camphor tree or *Lotus pedunculatus*, have been identified as alumunium detoxifying agent[33]. Typical organic acids such as malate, citrate and oxalate are a good example of compounds secreted by plants for the exclusion mechanism. The anionic acids were released from the roots of the plants and strongly bind with Alumunium at the root-soil interface [34]. *Tritticum aestivum* or wheat, corn and snapbean are one of many plants reported to secret these acids [35].

The production and secretion of the organic acid are continuously performed as the root of the plants growing through the acidic soils, but the detoxification only necessary around the apical root cells where the alumunium sensitivity is highest [34]. Both polyphenol and organic acid exhibit a critical role in tolerating alumunium toxicity in plants. This mechanism gives another set of example of how nature cooperates with metal, easily and safe. It is not possible to mimic the same mechanism for other metals having relatively similar property with alumunium.

3. SYNTHETIC METAL ADSORBENT INSPIRED BY NATURE

The extent of natural strategies in metal detoxification or utilization emerged its application in real-life problem solving particularly those related to metal pollution. However, direct use of biological organism as a remediation agent have some efficiency and most prominently, sustainable issues. For example, to utilize tunicate or mussel as bioremediation agent, practically hundreds or even thousands organism needed to sufficiently keep up with the industrial waste daily load. Extracting the key compound, such as tunichrome, will not give any significance neither. The extraction of tunichrome as well as other key compound will need a sophisticated technique that requires advance and expensive tools. In addition, the result will not be sufficient enough for further scale up.

Alternative approach is by synthetically fabricating analogue materials having similar property to that expressed in nature. For example, TOPA or pyrogallol moieties in tunichrome is also found in nature like tea, fruits or wood barks in the form of gallic acid [36]. Similarly, cathecolic compound are also found in green tea and already commercially produce [37].

The latter stage of translating this natural mechanism can be achieved by surface modification or functionalization to suitable backbone such as carbon or biopolymer, which will follow by the enhancement of their uptake capacity, thus creating a superior efficiency compare to the unmodified one.

A few research reported the beneficial impact of using bioinspired approach in synthetizing a highly efficient adsorbent, not limited to heavy metal but also performed well for other pollutant like synthetic dye [38] or even oil [39]. Some gathered publication regarding to this is given in Table 1.

Table 1. List of Synthetic Bioinspired Adsorbent.

No.	Materials	Inspiration	Metals or Ions	References
1	Gallic acid conjugated chitin nanofiber	Tunicate	Chromium, Gold	[40] , [41]
2	Graphene oxide coated polydopamine	Mussels	Lead, Copper, Cadmium, Mercury	[42]
3	Carbide-derived carbon	Diatom	Mercury	[43]
4	Metal oxides	Eggshell membrane	Nanoparticle	[44]
5	Cellulose Nanofiber-Humic Acid	Soil	Copper	[45]
6	2D-Carbon Flakes and Fe_3O_4 Nanoparticle Composites	Onion	Arsenic	[46]
7	Polydopamine Coated Natural Zeolite	Mussels	Copper	[47]
8	Polyvynilgallol	Polyphenol	Gold, Nickel, Alumunium	[48]
9	Amine Functionalized Carbon Nanotube	Mussels	Copper	[49]
12	Polydopamine coated Cellulose Nanofibrils aerogel	Mussels	Copper	[50]
13	MXenes-based polymeric composites (Ti_3C_2TX-PDOPA)	Mussels	Copper	[51]
14	Carrageenan/laponite multilayers	Layer by layer structure of organisms	Lithium, Magnesium	[52]
15	Hybrid nanofiber of *Spirulina* sp. And polystyrene	Microorganism	Copper, Manganese	[53]
16	Superheated steam-activated biochar (SABC)	Root system	Chromium Hexavalent	[54]

17	Catechol-Containing Acrylic Poly(ionic liquid) Hydrogels	Mussels	Arsenic, Chromium	[55]
18	Zeolite-based materials	Paddy soil	Ammonium ion	[56]
19	Nanoparticle-Assembled Hybrid Microsphere Structure	Paddy soil	Arsenic and Chromium	[57]
20	Trimethoxysilyl group terminated poly(1-vinylimidazole)-modified-chitosan	Shell crabs	Chromium	[58]
21	Poly-dopamine/reduced graphene oxide composite membranes	Mussels	Copper	[59]
22	Nanoporous polymer thin films	Peptide glutathione	Cadmium, Lead	[60]
23	Amyloid lysozyme fibrils conjugated with polyethyleneimine (PEI)	Egg lysozyme	Lead	[61]
24	RGO/Fe_3O_4 magnetic nanoparticles	*Murrayakoenigii* (Mk) leaves extract	Lead	[62]
25	NZVI immobilized on dopamine and l-DOPA functionalized polyacrylonitrile	Mussels	Chromium	[63]

4. CONCLUSIONS

In general, the natural mechanism of metal utilization for subsequent detoxification is an interesting alternative for generating sustainable, efficient adsorbent materials to be used in waste water treatment facility. Here we unveiled the mechanism governing the detoxification of metal in marine tunicate, mussel and plants with phenolic compound or moieties playing a major role in their mechanism. The translations of this natural mechanism have been performed by several studies but more research addressing practical application is still needed. Furthermore, there are still many mechanisms in nature that poorly understood thus opening a future opportunity for investigation and finding more new, higher capacity and efficient mechanism.

References

[1] Zahir F, Rizwi SJ, Haq SK and Khan RH, Low dose mercury toxicity and human health. *Environ. Toxicol. Pharmacol.* 20(2) (2005) 351-60

[2] Fu F and Wang Q, Removal of heavy metal ions from wastewaters: a review. *J. Environ. Manage.* 92(3) (2011) 407-18

[3] Gonzalez AR, Ndung'u K and Flegal AR, Natural Occurrence of Hexavalent Chromium in the Aromas Red Sands Aquifer, California. *Environ. Sci. Technol.* 39(15) (2005) 5505-11

[4] Jamal, A., and Sarim, M, Heavy metals distribution in different soil series of district Swabi, Khyber Pakhunkhawa, Pakistan. *World Scientific News*, 105, (2018). 1-13.

[5] Basha CA, Bhadrinarayana NS, Anantharaman N and Begum KM, Heavy Metal Removal from Copper Smelting Effluent using Electrochemical Cylindrical Flow Reactor. *J. Hazard. Mater.* 152(1) (2008) 71-8

[6] Dąbrowski A, Hubicki Z, Podkościelny P and Robens E, Selective Removal of The Heavy Metal Ions from Waters and Industrial Wastewaters by Ion-Exchange Method. *Chemosphere*. 56(2) (2004) 91-106

[7] Yun CH, Prasad R, Guha AK and Sirkar KK, Hollow fiber solvent extraction removal of toxic heavy metals from aqueous waste streams. *Ind. Eng. Chem. Res.* 32(6) (1993) 1186-95

[8] Blöcher C, Dorda J, Mavrov V, Chmiel H, Lazaridis NK and Matis KA, Hybrid flotation - membrane filtration process for the removal of heavy metal ions from wastewater. *Water. Res.* 37(16) (2003) 4018-26

[9] Salt DE, Blaylock M, Kumar NP, Dushenkov V, Ensley BD, Chet I and Raskin I, Phytoremediation: A Novel Strategy for the Removal of Toxic Metals from the Environment Using Plants. *Nat. Biotechnol*. 13(5) (1995) 468

[10] Kobya M, Demirbas E, Senturk E and Ince M, Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. *Bioresour. Technol.* 96(13) (2005) 1518-21

[11] Ali I and Gupta VK, Advances in water treatment by adsorption technology. *Nat. Protoc.* 1(6) (2006) 2661

[12] Hogstrand C and Haux C, Binding and detoxification of heavy metals in lower vertebrates with reference to metallothionein. *Comp. Biochem. Physiol. C. Comp. Pharmacol.* 100(1-2) (1991) 137-41

[13] Morita A, Yanagisawa O, Maeda S, Takatsu S and Ikka T, Tea plant (Camellia sinensis L.) roots secrete oxalic acid and caffeine into medium containing aluminum. *Soil Sci. Plant Nutr.* 57(6) (2011) 796-802

[14] Elhabiri M, Carrër C, Marmolle F and Traboulsi H, Complexation of iron (III) by catecholate-type polyphenols. *Inorganica Chim. Acta* 360(1) (2007) 353-9

[15] Rizal, A., Akbarsyah, N., Kdyp, P., Permana, R., & Andhikawati, A, Molecular diversity of the bacterial community associated with Acropora digitifera (Dana, 1846) corals on Rancabuaya coastline, Garut District, Indonesia. *World Scientific News* 144, (2020) 384-396

[16] Taylor SW, Kammerer B and Bayer E, New perspectives in the chemistry and biochemistry of the tunichromes and related compounds. *Chem. Rev.* 97(1) (1997) 333-46

[17] Dupont V, Auger Y, Jeandel C and Wartel M, Determination of vanadium in seawater by inductively coupled plasma atomic emission spectrometry using chelating resin column preconcentration. *Anal. Chem*. 63(5) (1991) 520-2

[18] Odate S and Pawlik JR, The Role of Vanadium in the Chemical Defense of the Solitary Tunicate, Phallusia nigra. *J. Chem. Ecol*. 33(3) (2007) 643-54

[19] Scalbert A, Mila I, Expert D, Marmolle F, Albrecht AM, Hurrell R, Huneau JF and Tomé D 1999 *Polyphenols, metal ion complexation and biological consequences*. (Boston: MA Springer) (pp. 545-554).

[20] Tamilselvi M, Akram AS, Arshan MK and Sivakumar V, Comparative study on bioremediation of heavy metals by solitary ascidian, Phallusia nigra, between Thoothukudi and Vizhinjam ports of India. *Ecotoxicol. Environ. Saf*. 121 (2015) 93-9

[21] Aksu, S., Yıldız, D., and Güngör, A. P, How Zebra mussels threaten to water supply security and effects of preventive measures in Turkey. *World Scientific News* 64 (2017) 99-126

[22] Sun C and Waite JH, Mapping chemical gradients within and along a fibrous structural tissue, mussel byssal threads. *J Biol. Chem.* 280(47) (2005) 39332-6

[23] Nurunnabi M, Khatun Z, Nafiujjaman M, Lee DG and Lee YK, Surface coating of graphene quantum dots using mussel-inspired polydopamine for biomedical optical imaging. *ACS Appl. Mater. Interfaces* 5(16) (2013) 8246-53

[24] Ryou MH, Lee YM, Park JK and Choi JW, Mussel-inspired polydopamine-treated polyethylene separators for high-power Li-ion batteries. *Adv. Mater*. 23(27) (2011) 3066-70

[25] Lee H, Dellatore SM, Miller WM and Messersmith PB, Mussel-inspired surface chemistry for multifunctional coatings. *Science* 318(5849) (2007) 426-30

[26] Waite JH, Evidence for a repeating 3, 4-dihydroxyphenylalanine-and hydroxyproline-containing decapeptide in the adhesive protein of the mussel, Mytilus edulis L. *J. Biol. Chem*. 258(5) (1983) 2911-5

[27] Holten-Andersen N, Fantner GE, Hohlbauch S, Waite JH and Zok FW, Protective coatings on extensible biofibres. *Nat. Mater.* 6(9) (2007) 669

[28] Suresh S, Graded materials for resistance to contact deformation and damage. *Science* 292(5526) (2001) 2447-51

[29] Liu X and Millero FJ, The solubility of iron in seawater. *Mar. Chem.* 77(1) (2002) 43-54

[30] George SG, Pirie BJ and Coombs TL, The kinetics of accumulation and excretion of ferric hydroxide in Mytilus edulis (I.) and its distribution in the tissues. *J. Exp. Mar. Bio. Ecol.* 23(1) (1976) 71-84

[31] Foy CD 1992 *Soil chemical factors limiting plant root growth in Limitations to plant root growth* (New York: NY Springer) (pp. 97-149).

[32] Rout G, Samantaray S and Das P, Aluminium toxicity in plants: a review. *Agronomie* 21(1) (2001) 3-21

[33] Zhang L, Liu R, Gung BW, Tindall S, Gonzalez JM, Halvorson JJ and Hagerman AE, Polyphenol–Aluminum Complex Formation: Implications for Aluminum Tolerance in Plants. *J. Agric. Food Chem.* 64(15) (2016) 3025-33

[34] Ma JF, Ryan PR and Delhaize E, Aluminium tolerance in plants and the complexing role of organic acids. *Trends Plant Sci.* 6(6) (2001) 273-8

[35] Kochian LV, Hoekenga OA and Pineros MA, *Annu. Rev. Plant Biol.* 55 (2004) 459-93

[36] Yilmaz Y and Toledo RT, How do crop plants tolerate acid soils? Mechanisms of aluminum tolerance and phosphorous efficiency. *J. Agric. Food Chem.* 52(2) (2004) 255-60

[37] Colon M and Nerin C, Role of catechins in the antioxidant capacity of an active film containing green tea, green coffee, and grapefruit extracts. *J. Agric. Food Chem.* 60(39) (2012) 9842-9

[38] Fu J, Chen Z, Wang M, Liu S, Zhang J, Zhang J, Han R and Xu Q, Adsorption of methylene blue by a high-efficiency adsorbent (polydopamine microspheres): kinetics, isotherm, thermodynamics and mechanism analysis. *Chem. Eng. J.* 259 (2015) 53-61

[39] Zhu Q and Pan Q, Mussel-inspired direct immobilization of nanoparticles and application for oil–water separation. *ACS Nano* 8(2) (2014) 1402-9

[40] Dwivedi AD, Permana R, Singh JP, Yoon H, Chae KH, Chang YS and Hwang DS, Tunichrome mimetic matrix, its perspective in abatement for carcinogenic hexavalent chromium and specific coordination behavior. *Chem. Eng. J.* 328 (2017) 629-38

[41] Dwivedi AD, Permana R, Singh JP, Yoon H, Chae KH, Chang YS and Hwang DS, Tunichrome-inspired gold-enrichment dispersion matrix and its application in water treatment: a proof-of-concept investigation. *ACS Appl. Mater. Interfaces*, 9(23) (2017) 19815-24

[42] Dong Z, Wang D, Liu X, Pei X, Chen L and Jin J, Bio-inspired surface-functionalization of graphene oxide for the adsorption of organic dyes and heavy metal ions with a superhigh capacity. *J Mater. Chem. A* 2(14) (2014) 5034-40

[43] Fischer C, Oschatz M, Nickel W, Leistenschneider D, Kaskel S and Brunner E, Bioinspired carbide-derived carbons with hierarchical pore structure for the adsorptive removal of mercury from aqueous solution. *Chem. Comm.* 53(35) (2017) 4845-8

[44] Mallampati R and Valiyaveettil S, Biomimetic metal oxides for the extraction of nanoparticles from water. *Nanoscale* 5(8) (2013) 3395-9

[45] Sehaqui H, de Larraya UP, Tingaut P and Zimmermann T, Humic acid adsorption onto cationic cellulose nanofibers for bioinspired removal of copper (II) and a positively charged dye. *Soft Matter*. 11(26) (2015) 5294-300

[46] Venkateswarlu S, Lee D and Yoon M, Bioinspired 2D-Carbon Flakes and Fe3O4 Nanoparticles Composite for Arsenite Removal. *ACS Appl. Mater. Interfaces,* 8(36) (2016) 23876-85

[47] Yu Y, Shapter JG, Popelka-Filcoff R, Bennett JW and Ellis AV, Copper removal using bio-inspired polydopamine coated natural zeolites. *J. Hazard. Mater.* 273 (2014) 174-82

[48] Zhan K, Ejima H and Yoshie N, Antioxidant and adsorption properties of bioinspired phenolic polymers: A comparative study of catechol and gallol. *ACS Sustain. Chem. Eng.* 4(7) (2016) 3857-63

[49] Zhang X, Huang Q, Liu M, Tian J, Zeng G, Li Z, Wang K, Zhang Q, Wan Q, Deng F and Wei Y, Preparation of amine functionalized carbon nanotubes via a bioinspired strategy and their application in Cu2+ removal. *Appl. Surf. Sci.* 343 (2015) 19-27

[50] Tang, J., Song, Y., Zhao, F., Spinney, S., da Silva Bernardes, J., & Tam, K. C, Compressible cellulose nanofibril (CNF) based aerogels produced via a bio-inspired strategy for heavy metal ion and dye removal. *Carbohydrate Polymers*, 208 (2019) 404-412

[51] Gan, D., Huang, Q., Dou, J., Huang, H., Chen, J., Liu, M., ... & Wei, Y, Bioinspired functionalization of MXenes (Ti3C2TX) with amino acids for efficient removal of heavy metal ions. *Applied Surface Science*, 504 (2020) 144603

[52] Prasannan, A., Udomsin, J., Tsai, H. C., Wang, C. F., & Lai, J. Y, Robust underwater superoleophobic membranes with bio-inspired carrageenan/laponite multilayers for the effective removal of emulsions, metal ions, and organic dyes from wastewater. *Chemical Engineering Journal*, (2019) 123585

[53] Shammas, M., Zinicovscaia, I., Humelnicu, D., Cepoi, L., Nirwan, V., Demčák, Š., & Fahmi, A, Bioinspired elelctrospun hybrid nanofibers based on biomass templated within polymeric matrix for metal removal from wastewater. *Polymer Bulletin*, (2019) 1-16

[54] Banerjee, S., Barman, S., & Halder, G, Elucidation of preferential elimination of Cr (VI) via bioinspired adsorbents: a comparative assessment. *Environmental earth sciences*, 78(4) (2019) 121

[55] Gallastegui, A., Porcarelli, L., Palacios, R. E., Gómez, M. L., & Mecerreyes, D. Catechol-Containing Acrylic Poly (ionic liquid) Hydrogels as Bioinspired Filters for Water Decontamination. *ACS Applied Polymer Materials*, 1(7) (2019) 1887-1895

[56] Li, Y., Jin, F., Pan, L., Cheng, M., Zhang, W., & Jing, Z. Bioinspired paddy-soil-like superior purification materials for sewage treatment. *Materials Letters*, 254 (2019) 226-229

[57] Manna, J., Shilpa, N., Bandarapu, A. K., & Rana, R. K, Oxyanion-Binding in a Bioinspired Nanoparticle-Assembled Hybrid Microsphere Structure: Effective Removal of Arsenate/Chromate From Water. *ACS Applied Nano Materials*, 2(3) (2019)1525-1532

[58] Islam, M. N., Khan, M. N., Mallik, A. K., & Rahman, M. M. Preparation of bio-inspired trimethoxysilyl group terminated poly (1-vinylimidazole)-modified-chitosan composite

for adsorption of chromium (VI) ions. *Journal of Hazardous Materials*, 379 (2019) 120792

[59] Ma, J., He, Y., Zeng, G., Li, F., Li, Y., Xiao, J., & Yang, S. Bio-inspired method to fabricate poly-dopamine/reduced graphene oxide composite membranes for dyes and heavy metal ion removal. *Polymers for Advanced Technologies*, 29(2) (2018) 941-950

[60] Weidman, J. L., Mulvenna, R. A., Boudouris, B. W., & Phillip, W. A. Nanoporous block polymer thin films functionalized with bio-inspired ligands for the efficient capture of heavy metal ions from water. *ACS Applied Materials & Interfaces*, 9(22) (2017) 19152-19160

[61] Liu, M., Jia, L., Zhao, Z., Han, Y., Li, Y., Peng, Q., & Zhang, Q. Fast and Robust Lead (II) Removal from Water by Bioinspired Amyloid Lysozyme Fibrils Conjugated with Polyethyleneimine (PEI). *Chemical Engineering Journal*, (2020) 124667

[62] Prasad, C., Murthy, P. K., Krishna, R. H., Rao, R. S., Suneetha, V., & Venkateswarlu, P. Bio-inspired green synthesis of RGO/Fe3O4 magnetic nanoparticles using Murrayakoenigii leaves extract and its application for removal of Pb (II) from aqueous solution. *Journal of Environmental Chemical Engineering*, 5(5) (2017) 4374-4380

[63] Liu, P., Wang, X., Ma, J., Liu, H., & Ning, P. Highly efficient immobilization of NZVI onto bio-inspired reagents functionalized polyacrylonitrile membrane for Cr (VI) reduction. *Chemosphere* 220 (2019) 1003-1013