Chapter 4

Photocatalytic and Adsorptional Removal of Heavy Metals from Contaminated Water using Nanohybrids

Ankita Guleria, Rohit Sharma, Pooja Shandilya*

School of Advanced Chemical Sciences, Shoolini University, Solan, 173229, Himachal Pradesh, India

*poojashandil03@gmail.com

Abstract

Water contaminated with heavy metals is a major menace for aquatic life and human health consequently its efficient removal remains a crucial challenge for researcher. The utilization of various photocatalytic nanohybrids to synergistically photo-reduce and adsorb heavy metals is a potent strategy to combat water pollution. This book chapter give an overview of the fundamental principle of photocatalysis and various single, binary, ternary and quaternary nanohybrids employed for simultaneous photoreduction and adsorption of heavy metals with its mechanistic insight. Further, conclusion and future prospective as well as limitation of available nanohybrids were addressed. We hope that this book chapter dispenses some noticeable information to heavy metal ions removal from polluted water.

Keywords

Photocatalysis, Nanohybrids, Water Purification, Organic Pollutants, Heavy Metals

Contents

Photocatalytic and Adsorptional Removal of Heavy Metals from Contaminated Water using Nanohybrids.....	113
1. Introduction.....	114
2. Fundamental principle of photocatalysis	117
3. Nanohybrids for photocatalytic removal of heavy metals	120
3.1 Single system	120

3.2	Dual system	123
3.3	Ternary system.....	129
4.	Nanohybrids for adsorptional removal of organic pollutants and heavy metals.....	138
	Conclusions and future prospects	145
	References	146

1. Introduction

Among the wide range of water pollutant, presence of heavy metals (HMs) poses a significant threat to the human society and has become a very prominent environmental issue across the world. HMs pollution can be geo-genic arises due to the natural processes such as weathering of rocks, leaching, wind erosion, glacial erosion and volcanism or it can be anthropogenic. The anthropogenic source is burning of fossil fuels, mining, smelting, automobile exhaust, nuclear power waste, electroplating processes, excessive use of fertilizers, pesticide and herbicide [1,2]. Commonly found heavy metals lead, zinc, cadmium, arsenic, copper, mercury, chromium, tin, and thorium entered directly or indirectly into the water bodies causing several health problems [3]. HMs is responsible for long-term toxic effect due to its non-biodegradable nature and high bio-accumulation rate in food chains [4-6].

The serious toxicological effects caused by HMIs are nausea, vomiting, diarrhoea, asthma, kidney and liver malfunctioning, weight loss, congenital abnormalities and cancer. Copper, above the permissible level damages gastrointestinal tract as well as anorexia and lethargy [7], cobalt induces kidney congestion and decline thyroid movement [8], zinc produces disruption of iron homeostasis along with neurological disorders [9], nickel is responsible for immunotoxicity, damage epithelial cells of respiratory system and also cause lungs or skin cancer [10] similarly, behavioural disorders, acute malfunction of kidneys, anemia were recognized by cause of lead poisoning [11], cadmium damages testicular tissues and bones, along with carcinogenic nature [12], mercury induces neurological disorders, retard intellectual ability, damage of pulmonary and also cause hyperactivity disorder [13]. The excessive concentration of HMs beyond its permissible limits in drinking water recommended by WHO[14] and USEPA[15], may leads to serious health issues efficient as shown in Table 1 [16-21].

Table 1. Permissible limits of HMs in drinking water as recommended by WHO and USEPA.

Heavy metal	Concentration (ppm)		Ill effect	Ref
	WHO	USEPA		
Hg	0.001	0.002	Impairment of pulmonary and kidney function, chest pain and dyspnea, nervous system damage	[16]
Pb	0.05	0.015	Dysfunction in the kidney, reduced neural development, impair liver and reproductive system, hypertension and brain damage	[17]
Cu	1.5	1.3	Vomiting, diarrhea, stomach cramps, and nausea, or even death.	[18]
Cd	0.005	0.05	High blood pressure, kidney damage, and destruction of testicular tissue, carcinogenic	[12]
Cr	0.05	0.1	Lung cancer, chromate ulcer, nasal septum perforation	[19]
As	0.05	0.01	Lung and skin damage, toxicological and carcinogenic effect, bladder cancer	[20]
Mn	0.5	0.05	Inhalation or contact damages to central system	[21]

Earlier, various physical, chemical and biological methods like chemical precipitation [22], ion-exchange [23], membrane separation [24], coagulation [25], adsorption [26], solvent extraction [27] and electrochemical treatment [28] etc. were already explored to detoxify water. These methods bear certain disadvantages such as consumption of costly chemical reagents, ion exchanger, semi-permeable membrane, large amount sludge formation, secondary pollutant generation and less efficient Table 2 [29-38].

Table 2. Advantages and disadvantages of conventional methods for HMs removal.

Conventional method	Advantages	Disadvantages	Ref.
Precipitation	Practicable to most metals, Low cost, Easy operation	Lower removal efficiency, Sludge generation, Secondary pollution, Concentration of heavy metals	[29]
Ions exchanges	Fast kinetics, High treatment capacity, Excellent selectivity of metal ions, Regenerable materials	High cost due to synthetic resins, Small range of action on metal ions.	[30]
Membrane separation	Resource recovery, High separation selectivity, Small space requirement	Requiring amount pretreatment, Low permeate flux, Pore blocking, Poor antibacterial property, Limited pH range,	[31]
Coagulation	Remove the turbidity in addition to heavy metal removal	Extra operational cost for sludge disposal	[32]
Adsorption	Low cost, Having wide pH range High efficiency, Possibility of regenerating adsorbents, Easy operation Effective and economical method	Limited pH range, Difficult to regenerate materials, Low selectivity, Long equilibrium time	[33]
Photocatalysis	Clean and efficient, Simultaneous removing metals and organic pollutant, Low-toxicity by-products.	High raw materials cost, Small range of action on metal ions, Long duration time	[34, [35]
Fenton like oxidation	Fast and efficient, Significant removal of residual organic chelates, Recovery metals	Low water volume treatment capacity, Vast Fe sludge, High cost, Secondary pollution from addition chemicals	[36]
Electrochemical	Metal selective, No consumption of chemicals	High capital and running cost, Initial solution pH, Current density	[37]
Replacements-co-precipitation	Easy operation, Relativity high efficiency, Make full use of iron-based materials	High chemical consumption, Large quantity of sludge and secondary pollution from release of organic chelates	[38]

Thusly, removal of HMs through simultaneous photocatalytic reduction and adsorption is more desirable due to cost effectiveness, easy operation, strong redox ability, green technologies and wide applicability which especially reduce the cost of water treatment. Firstly, TiO₂ photocatalyst a semiconducting material reported by Fujishima and Honda in 1972s utilized for water splitting [39]. Consequently, different semiconductors were originated and exploits for various photocatalytic activity because of eco-friendly nature. Photocatalysis is a promising advanced oxidation process displaying tremendous potential in reducing toxic heavy metal ions into less toxic metal ion and smashing various other pollutants that showed versatile nature of semiconducting material [40]. Generation of strong oxidative species can synergistically degrade organic pollutant and reduce noxious metal ions through photocatalytic reaction. Besides, water purification photocatalysis has been actively employed in water splitting, CO₂ reduction, disinfection process and organic synthesis.

Here, in this book chapter we have summarized the basic principle of photocatalysis with recent emerging direct Z-scheme migration pathway of charge carrier. Different type of single, dual, trinary and quaternary photocatalytic nanohybrids obeying conventional type-II, Z-scheme or dual Z-scheme migratory pathway of electron-hole pair were discussed. Subsequently, various nanocomposites exploited for adsorptional removal with its mechanism were also investigated. We believe that this extensive study on photocatalytic and adsorptional removal of HMs will be beneficial for the researchers and beginners to carry out their research a one step ahead from what reported previously in the literature. Lastly, conclusion and future perspectives were discussed in detail.

2. Fundamental principle of photocatalysis

The basic photocatalytic mechanism occurs in three steps where oxidation and reduction were induced on photocatalyst surface sensitized by solar light. Firstly, generation of charger carrier occurs on exposure to light possessing energy higher or equal to band gap of semiconductor. Secondly, migration of generated electron-hole pair arises on the surface of semiconductor where, electron jumps from valence band to the conduction band of photocatalyst. Thirdly, photogenerated holes oxidizes H₂O molecule to produce hydroxyl radicals ([•]OH) in the valence band and electrons reduces the O₂ molecule to form superoxide radical anion (O₂^{•-}) in the conduction band, respectively as shown below in equation (1-4) [41].

Among the various strategies applied to intensify photocatalytic efficiency, fabrication of heterojunction is a promising alternative magnetizing the interest of researchers across the world. Basically, heterojunction describe as the two semiconductors having different band alignment at the interface. Depending upon the band edge potential of semiconductor, conventional heterojunction was classified into three categories namely: straddling (type-I), staggered (type-II) and broken gap (type-III) as shown in (Fig. 1). In straddling type the CB and VB edges of SCI aligned higher and lower than the corresponding bands of SCII. Consequently, both charge carriers migrate towards SCII surface results in excessive accumulation of electron-hole pair which increases the probability of recombination. Also, both the oxidation and reduction reaction take place on SCII surface bearing lower redox potential will abate the potency of photocatalyst. For staggered heterojunction, CB and VB edges of SCI are higher than the SCII respectively. Thus, electrons will drift from SCI to SCII surface and holes form SCII to SCI due to suitable band alignment resulting in excellent charge separation. The reduction reaction occurs on the SCII with lower CB edge potential and oxidation reaction occur on SCI with lower VB edge potential which is analogous to straddling heterojunction. Therefore, type-II heterojunction also possess lower redox ability. However, in type-III heterojunction band edge potential become so extreme and impaired that the charge migration and separation altogether not possible. In these heterojunction staggered gap is more efficient though certain limitation such as occurrence of redox reaction on semiconductor with lower redox potential and electrostatic repulsion between electron-electron and holes-holes prevent its further migration which bounds its broader utilization.

To maximize the use of higher redox potential and to minimize the electrostatic repulsion in conventional type-II heterojunction, Bard et al. in 1979 come up with the concept of Z-scheme heterojunction where, path of charge migration is similar to letter “Z” [42]. The Z-scheme heterojunction evolves from 1st generation proposed in

1979 to 3rd generation in 2013. The 1st generation Z-scheme also called as conventional Z-scheme or liquid-phase Z-scheme in which two semiconductors are not in direct contact with each other.

Figure 1: Schematic illustration of the (a) typical type-I heterojunction and (b) type-II (conventional heterojunction (c) type-III heterojunction (d) traditional Z-scheme (e) all solid-stat Z-scheme (f) direct Z-Scheme.

The electron migrates from CB of SCII to VB of SCI via acceptor-donor (A/D) pairs where, acceptor is reduced to donor by electron of SCII and donor is oxidized back to acceptor by photogenerated holes of SCI, respectively. Thus, redox reaction is carried out by SCI and SCII with higher reduction and oxidation potential. Such migration limits the rate of

recombination of charge carrier and maintain the redox ability of semiconductor with high potential. However, their fabrication is limited to liquid phase which creates barrier on its wider application. The 2nd generation or all-solid-state Z-scheme was proposed in 2006 by Tada et al., where, the two photosystems are assembled with solid electron mediator such as Pt, Au and Ag [43]. All-solid-state Z-scheme can be applied to solid, liquid and gaseous phase however, high cost of electron mediator limits its usage. The 3rd generation or direct Z-scheme involves the combination of two photocatalyst without mediator was put forward in 2013 by Yu et al. which reduces the fabrication cost [44]. The band alignment in direct Z-scheme is similar to that of type-II heterojunction but differ in charge migration that is physically more favourable due to electrostatic attraction between electrons of SCII and holes of SCI whereas, in conventional heterojunction excessive accumulation of electron in the CB of SCII further cease the electron migration from CB of SCI due to electrostatic repulsion. Moreover, direct Z-scheme also maintain the redox ability of semiconductor with higher reduction and oxidation potential also the band potential can be reform easily according to different photocatalytic reactions. Further, trinary system displaying dual Z-scheme is another route offering immense charge separation with enhanced photo-efficiency and substantial amount of ROS generated on the surface. Since, great achievement in HMs removal have been attained by the various researchers therefore it is more significant to sum up recent achievement and challenges experienced in this filed.

3. Nanohybrids for photocatalytic removal of heavy metals

3.1 Single system

The various conventional metal oxide based photocatalytic material such as TiO₂, ZnO, CuO, CdS, and V₂O₅ etc. were applied to remove inorganic and organic pollutant present in water. Among these TiO₂ and ZnO are largely explored for its photocatalytic activity due to low-cost, non-toxicity and abundance [45, 46]. Arsenate photo-catalytically reduced to arsenite with TiO₂ in the presence of hole scavenger so as to avoid recombination of photogenerated charge carrier [47]. Though, the direct reduction of arsenate with TiO₂ is thermodynamically not favourable because of the reduction potential value of As(V)/As(IV) is -1.2 V more negative than the CB potential -0.3 V of TiO₂. Therefore, indirect reduction using sacrificial electron donor methanol forming hydroxymethyl radical (°CH₂OH) a strong reducing agent possessing 1.4 V reduction potential is now capable of reducing arsenate. Consequently, the reduction process can be elaborated by following equations.

Nearly, complete elimination of Cu (II) were reported under UV light which is just comprise of 5% of solar spectrum. The Cr (II), Ni (II), Ag (I), Cd (II), Mn (II), Cu (II) and Pb (II) ions were eliminated in the presence UV or visible light using ZnO nanoparticle synthesized by solid precipitation method [46]. The removal efficiency in the presence of UV light is more than 85% for Cu (II), Pb (II) and Ag(I) metal ions. The wide band gap of conventional semiconductor restricts their practical implication.

Recently, innovative idea of converting toxic heavy metals into a photocatalyst employed for the photodegradation of methylene blue [48]. The steel slag derived calcium silicate hydrate with hierarchical structure and amorphous nature prepared by alkali activation method display outstanding adsorption capacity towards metals. On the surface of calcium silicate hydrate HMs transform into its hydroxide that is responsible for red shift in the absorption edge thus photocatalyst become visible light active. On performing scavenger experiment holes and hydroxyl radical appears to be main active species and the small degradation of organic pollutant were observed when EDTA or IPA is added (Fig 2a). The feasible photocatalytic mechanism of bare and metal coated calcium silicate hydrate is shown in Fig. 2b) indicating holes is responsible for the degradation.

Figure 2. (a) Photocatalytic degradation of MB in the presence of various radical scavengers by CSH-Ni. (b) Possible photocatalytic mechanism of CSH and CSH-M ($M = \text{Cu, Ni, and Zn}$) under visible light. (c,d) Analysis of photocatalytic reduction of (c) Pb^{2+} (d) Cd^{2+} heavy metal impurity using NFO and NFO-Pd nanoparticles. (e, f) Ultraviolet photoemission spectroscopy (UPS) spectra of (e) NFO and (f) Pd nanoparticles. (g) The formation of Schottky barrier in the nanohybrid after contact between NFO semiconductor and Pd metal derived based on the UPS analysis. (h) Magnetic hysteresis plots suggesting superparamagnetic [48,49].

The photocatalytic activity of bare photocatalysts can be enhanced by Fermi level modification. For instance, NiFe₂O₄ narrow band gap semiconductor with superior magnetic property synthesized by solvothermal method employed for Pb²⁺ and Cd²⁺ removal [49]. The rate constant of Pd-NiFe₂O₄ for Pb²⁺ and Cd²⁺ is 1.4 X 10⁻¹ min⁻¹ and 0.86 X 10⁻¹ min⁻¹, respectively (Fig 2c and d). NiFe₂O₄ chemically bonded to Pd by surface modifier 3-aminopropyltriethoxysilane undergo autocatalysis process due to the presence of amino groups. The band structure and alignment of Pd-NiFe₂O₄ were studied by ultraviolet photoemission spectroscopy Fig 2e and f. The work function calculated for NiFe₂O₄ and Pd using following equation is 5.28 eV and 5.92 eV, respectively.

$$W = h\nu - (E_{cut-off} - E_F) \quad (10)$$

From the Fermi edge region in UPS spectrum, the calculated ($E_{cut-off} - E_F$) value for NiFe₂O₄ and Pd is 0.18 and 0.742 eV. The electron affinity of NiFe₂O₄ and Pd is 3.22 and 6.66 eV as calculated using below equation where, 0.187 and 0.742 eV were estimated value of ($E_F - E_{VB}$).

$$X = W + (E_F - E_{VB}) - E_g \quad (11)$$

Accordingly, schottky barrier establish between NiFe₂O₄ and Pd after contact is shown in Fig 2g. Further, magnetic hysteresis loop of Pd-NiFe₂O₄ suggest superparamagnetic nature of photocatalysts responsible for facile magnetic separation from aqueous suspension (Fig 2h). The bare semiconductor has wide band gap, undergo photo corrosion and agglomerate easily. Thus, the immobilization of nanoparticles onto certain stable, low-cost supportive material with large surface area and superior recycling efficiency is highly desirable to construct systematic nanohybrids. Though, photocatalysts can be immobilized over planar surface of glass and ceramics yet poor charge transfer restricts its wider application. Moreover, to enhance the photo-response various strategies of doping with metal, non-metal, noble metal and constructing heterojunction were put together. Among which heterojunction formation is highly in trend to increasing charge carrier separation.

3.2 Dual system

Keeping in view the various limitation of single photocatalytic system, various research groups have constructed dual system to promote photo-efficiency. Li and co-workers investigated TiO₂-graphene hydrogel with three-dimensional (3D) network structure which exhibited outstanding adsorption-photocatalysis activity and removed 100% Cr (VI) from

wastewater within 30 min in the presence of UV light [50]. Nearly, 66.32 and 88.96% of Cd^{2+} and Pb^{2+} ions are removed using TiO_2/GO prepared by hummers, hydrothermal and freeze-drying method (Fig. 3a) [51]. From BET analysis $128.41 \text{ m}^2\text{g}^{-1}$ surface area was calculated for TiO_2/GO as compared to bare TiO_2 which is just $59.51 \text{ m}^2\text{g}^{-1}$. The photocatalytic mechanism of e^-/h^+ pair's generation also reduction and oxidation process of heavy metals on CB and VB of TiO_2/GO surface are shown in (Fig. 3b). In the CB of nanohybrid O_2 is reduced to $^{\circ}\text{O}_2^-$ anion and Cd^{2+} and Pb^{2+} reduced to Cd and Pb, respectively. On the same time holes in the VB produces $^{\circ}\text{OH}$ radical which oxidizes Pb^{2+} to Pb^{4+} and precipitate out it in the form of PbO_2 . Wang et al. prepared magnetically recyclable $g\text{-C}_3\text{N}_4@\text{Fe}^0\text{-rGO}$ composite using vitamin C and KBH_4 as reducing agent (Fig. 3c) [52]. The mechanism of elimination of rhodamine-B dye and hexavalent chromium ion under visible light is shown in (Fig. 3d) and also explained by the equation 12 to 25. The higher surface area of composite provides large adsorption sites to capture e^- for elimination of heavy metal and dye. The quenching experiment reveals the major role of nano Fe^0 and $^{\circ}\text{OH}$ for the removal of rhodamine-B and Cr (VI).

Figure 3. (a) The synthesis route of TiO_2/GO nanocomposites and photocatalytic experiments. (b) Schematic diagram of the charge transfer and separation in the TiO_2/GO nanocomposites under UV light irradiation and the main steps to reduce heavy metal ions. (c) Schematic illustration of synthesis of $g-C_3N_4@Fe^0$ -rGO. (d) Proposed mechanism for the synergistic removal of RhB and Cr(VI) on $g-C_3N_4@Fe^0$ -rGO photocatalyst [51,52].

The most acid stable CdS/TiO₂ heterojunction was reported capable of removing Cr (VI) in strong acidic conditions at pH=2.0–7.0 [53]. The detailed synthesis of CdS/TiO₂ is elaborated in (Fig 4a) where, HPC stands for hydroxypropyl cellulose, CAR-d represents CdS, anatase, rutile complex and d indicate ratio of Cd/Ti.

Figure 4. (a) Scheme of the synthetic process of the raspberry-like CAR-d using the ion-exchange strategy. (b) Mechanism of photocatalytic reduction of metal ions and oxidation of phenol under a strong acid condition. (c) Proposed selective reduction and photocatalytic degradation mechanism of the magnetic ion imprinted heterojunction photocatalyst. Transient photocurrent response (d), Nyquist plots of EIS (e) and PL (f) of CoFe₂O₄ [53,54].

Besides of expedite of charge separation, loading CdS to the bulk TiO₂ also prevents photochemical corrosion or dissolution of CdS nanoparticles (Fig 4b). The magnetically separable polyo-phenylenediamine/CoFe₂O₄ nanohybrids with good stability, active charge separation and recyclability were successfully prepared by microwave-assisted ion imprinted method [54]. The imprinted cavity of Cu²⁺ ion enhance the selective reduction of Cu²⁺ ion over Cd²⁺, Fe²⁺ and Zn²⁺ on magnetic ion imprinted photocatalytic surface as displayed in (Fig 4c). According to the estimated position of band potential, migration pathway of electrons is from CB of CoFe₂O₄ to the CB of polyo-phenylenediamine and

holes transfer from VB of polyo-phenylenediamine to VB of CoFe_2O_4 . The separation of charge carrier further affirmed by better photocurrent response, minimum impedance in electrochemical impedance spectra, and lowest photoluminescence peak intensity for magnetic ion imprinted nanohybrids (Fig 4d, e and f). Gd_2O_3 modified CeO_2 nanoparticle creating p-n type heterojunction synthesized by solid state reaction eliminate Pb^{2+} ions by photoelectron-deposition method [55]. Similarly, 0.7 gL^{-1} CuO/ZnO eliminate 30 gL^{-1} of As (III) in 10 h irradiation of UV light at neutral pH [56].

In another work $\text{ZnO/Fe}_2\text{O}_3$ a type-II heterojunction reported in which photocatalytic mechanism involves the reduction of heavy metals at the CB of Fe_2O_3 (Fig 5a) [57]. The composites photo-reduces 88% of Cr (VI) in 90 min whereas, 100 % reduction were observed in 45 min when tartaric acid is used a sacrificial agent (Fig 5b). Further, after reduction experiment the recovered sample were analyzed using X-ray photoelectron spectroscopy the spectra clearly indicate two peak of Cr (III) at binding energy 576.9 and 586.5 eV assigned to $2p_{3/2}$ and $2p_{1/2}$, respectively (Fig 5c). The various conventional nanohybrids functioning via type-II mechanism of charge migration bears limitation. Newly emerging Z-scheme heterojunction is highly in trend nowadays among scientist and continuously employed in various applications. Recently, $\text{Co}_3\text{O}_4/\text{g-C}_3\text{N}_4$ heterojunction prepared by growing nano-cubes of Co_3O_4 on 2D $\text{g-C}_3\text{N}_4$ nanosheet via hydrothermal method almost reduces 81% of Cr^{+6} into Cr^{+3} [58]. The valence band XPS spectra indicate the position of Fermi level of $\text{g-C}_3\text{N}_4$ and Co_3O_4 at 1.2 eV and 0.6 eV, respectively (Fig 5d and e). Additionally, Fermi level of $\text{g-C}_3\text{N}_4$ and Co_3O_4 is 5.0 and -.4 eV/AVS as explicit by CASTEP code (Fig 5f and g). Based on both the results VB edges of $\text{g-C}_3\text{N}_4$ and Co_3O_4 is -6.2 and -7.0 eV whereas, the calculated band gap is 2.8 and 2.1 eV, respectively. Apparently, the suggest photocatalytic mechanism for $\text{Co}_3\text{O}_4/\text{g-C}_3\text{N}_4$ heterojunction operating via Z-scheme is given in Fig 5h.

Constructing Z-scheme nanohybrids is an ideal way to develop highly efficient photocatalyst to treat water pollution. $\text{Ag}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}/\text{Ag/g-C}_3\text{N}_4$ a 1D//2D Z-scheme nanomaterial prepared by self-assembly method is highly efficient for the reduction of Cr (VI) and photodegradation of methylene orange and tetracycline under visible light [59]. The distinctive band structure, appropriate band gap of 2.7 eV, superior chemical and thermal stability and eco-friendly nature of $\text{g-C}_3\text{N}_4$ make it suitable candidate for constructing Z-scheme heterojunction. Further, Ag loading between the two assemblies direct the electron to recombine from CB of $\text{Ag}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ to VB of $\text{g-C}_3\text{N}_4$ thereby maintains the charge separation process more accurately. Similarly, BiOCl-Ag-AgBr running through Z-scheme mechanism where Ag displayed surface plasmon resonance effect producing negatively charged electrons and positively charged holes on its surface. On photo-excitation electron in the CB of BiOCl migrates to Ag and recombine with

surface plasmon resonance induced holes. On the same time holes from VB of AgBr recombine with surface plasmon resonance induced electron on Ag. Apart from this oxygen vacancy, local surface plasmon resonance and presence of iodine ions are also some off the effective strategy to enhance photo-efficiency [60]. The oxygen vacancy generated by loss of oxygen atom assist in generating more ROS by activating molecular oxygen and also acts as an electron capturing sites. Not only this, but it also creates local surface plasmon resonance that can inject electrons to promote charge transfer.

Figure 5. (a) ZF2 heterojunction showing movement of charge carriers and mechanism for Cr(VI) reduction. (b) The extent of photo-reduction of Cr(VI) under solar light with ZF2 (c) XPS survey scan and Cr 2p spectrum (Inset) of unused ZF2 before final recovery (ZF2 + visible + TA system). VB-XPS spectra of the (d) g-C₃N₄ and (e) Co₃O₄. The Fermi level E_F is located at $E = 0$ eV, as marked by the vertical dotted line. The work function of (f) gC₃N₄, and (g) Co₃O₄. (h) Proposed type-II staggered band alignment of Co₃O₄/g-C₃N₄ and photocatalysis enhancement mechanism of the Z-scheme Co₃O₄/g-C₃N₄ [57,58].

3.3 Ternary system

By combining different photocatalysts with individual inherent advantages and to achieve much higher photo efficient, stability, and larger surface area trinary system were constructed. Hou and co-workers reported photocatalytic reduction of Cr (VI) in the presence of Ag/TiO₂/rGO [61]. Ag loading on TiO₂ reduces the rate of recombination and also assist in the reduction of Cr (VI) to Cr (III) ion. On the same time superoxide radical anion and hydroxyl radical generated at the CB and VB of TiO₂ oxidizes tetracycline into CO₂ and H₂O. The pH of reaction solutions plays a vital role in adsorption and degradation as it not only affects the surface charge on photocatalysts but also affect the ionic state of organic pollutant. The zero-point charge of Ag/TiO₂/rGO is in the range of $pH_{pzc} = 5-6$ therefore when $pH < 5$ photocatalysts surface is positively charged whereas $pH > 6$ surface becomes negatively charges. Moreover, adsorption of Cr (VI) increases with the decrease in pH as positively charged surface of photocatalyst can easily attract negatively charged Cr₂O₇²⁻ ions via electrostatic interaction. Li and co-worker reported Ag@TiON/CoAl-LDH prepared by dark-deposition method exhibit catalytic memory effect with increased performance [62]. The phenomena of retaining catalytic activity for a short period of time even when the light is turned off are called catalytic memory effect. Even certain noble metals such as Ag and Au also demonstrate electron storage properties. Also, broad range absorption, presence of surface hydroxyl group, tunable chemical compositions etc. are some of the advantages associated with 2D layered materials. Further, nitrogen doping in TiO₂ is done to generate oxygen vacancies and to extend visible light absorption. Keeping in view the above advantages Ag@TiON/CoAl-LDH is constructed that reduces 61% of Cr (VI) and degraded 94% methyl orange. To check the catalytic memory effect, photodegradation experiment performed in dark where, excess of electrons entrapped by Ag under light illumination was discharged in dark to various electron acceptors to subsequently generate active free radicals thus maintaining round-the-clock photodegradation. Further, new strategy by combining homogeneous and heterogeneous a multiphase catalytic system was devised to simultaneously remove organic pollutant and heavy metals. In hierarchical 3D Ag/ZnO@carbon foam porous photocatalysts where, Ag used as co-catalysts to smoothen charge separation process indicative of heterogeneous catalysis [63].

Besides, the formation of phenol-chromate (VI) ester intermediates via ligand to metal i.e. benzene ring to Cr (VI) charge transfer process represent homogeneous catalysis as shown in (Fig 6a). DFT calculation were performed to understand the intermolecular interaction between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of ester intermediate formed. As shown in (Fig 6b and c) benzene ring and chromium ion contributes for HOMO and LUMO of phenol-chromate (VI) ester,

respectively where the central Cr (VI) reduced to Cr (III) and phenol oxidizes to innocuous substances. Apart from electrons, superoxide radical also reduces Cr (VI) ion and the generation of $\text{OH}^\bullet$ and $^\bullet\text{O}_2^-$ were further confirmed by ESR technique (Fig 6d and e).

Figure 6. (a) Schematic diagrams for the possible mechanism of simultaneous heterogeneous and homogeneous catalysis for efficient removal of phenol and Cr (VI) over 2.0Ag/ZnO@CF under full arc light irradiation. The charge densities of the (b) HOMO, (c) LUMO of the phenol-chromate (VI) ester. ESR spectra of (d) DMPO-OH and (e) DMPO-O₂⁻ adducts in aqueous and methanol solution [63].

TiO₂/g-C₃N₄/rGO ternary nanohybrids assembled by hydrothermal methods own large surface area, huge photoactive sites, low fluorescence intensity; enhance visible light absorption and photocurrent intensity [64]. The superior photo-catalytic activity of nanocomposites was witnessed reducing 90% of Cr (VI) to Cr (III) in 4h. TiO₂ nanoparticles evenly dispersed over g-C₃N₄ and rGO surface preventing its leaching and agglomeration (Fig 7a). MoS₂/ZnS/ZnO fabricated by hydrothermal method possesses 27 m²g⁻¹ of surface area and ample of active sites exhibit remarkable reduction and adsorption ability for Cr(VI) and rhodamine B [65]. The dual-II heterojunction degraded 98.7% of Cr(VI) in 90 min and scavenging experiment reveals h^+ and $^\bullet\text{O}_2^-$ are the major active species for rhodamine B degradation. The photocatalytic mechanism involves the shifting of electron from CB of MoS₂ and ZnS to the CB of ZnO after irradiation this electron reduces Cr (VI) as well as assist for the generation of $^\bullet\text{O}_2^-$ (Fig 7b). Another ternary BiVO₄/FeVO₄@rGO heterojunction creating nano-channels at interfacial junction was constructed with suitable band alignment for directional charge transfer (Fig 7c) [66]. The

2D rGO provides ample of active sites, large surface area and superb electrical conductivity whereas, BiVO_4 and FeVO_4 visible light driven narrow band gap semiconductor with excellent stability. Ternary heterojunction is employed for the oxidation of tetracycline and reduction of Cr (VI) and ESR measurement clearly depicts h^+ and $^{\circ}\text{O}_2^-$ are the main active species for the photodegradation of tetracycline and electron for the reduction of Cr (VI). Movement of electron-hole pair completely depend upon band alignment, the flat potential of BiVO_4 and FeVO_4 calculated by Mott-Schottky diagram (Fig 7d and e). The CB potential of BiVO_4 and FeVO_4 are -0.57 and -0.64 eV relative to Ag/AgCl which is equivalent to -0.37 and -0.44 eV of NHE at pH 7. Using equation $E_{\text{VB}} = E_{\text{CB}} + E_g$, the VB potential comes out to be 2.09 and 1.53 eV for BiVO_4 and FeVO_4 , respectively.

Figure 7. (a) Mechanism diagram of photocatalytic removal of Cr(VI) in T-CNS-G system. (b) Schematic illustration of photodegradation RhB and Cr (VI) over the MZ2 photocatalyst under Xe lamp irradiation. (c) Possible photocatalytic mechanism scheme of BVO/FVO@rGO under visible-light irradiation. Mott-Schottky plots of (d) BiVO_4 and (e) FeVO_4 [64,65,66].

$\text{HPW}_{12}/\text{CN}@\text{Bi}_2\text{WO}_6$ organic-inorganic nanocomposite synthesized via one-step hydrothermal method exhibit high photocatalytic reduction and oxidation capability towards Cr^{6+} and tetracycline under visible-light irradiation as compared to bare component [67]. The large surface area and pore size of $\text{HPW}_{12}/\text{CN}@\text{Bi}_2\text{WO}_6$ responsible for higher adsorption of Cr^{6+} and tetracycline. Nearly, 98.7% and 97.5% of metal ion and

antibiotic were removed under 90 and 100 min of irradiation (Fig 8a and b). The degradation kinetic for of Cr^{6+} and tetracycline reveals pseudo first-order reactions (Fig. 8c and d). The possible photocatalytic mechanism where the electron-hole pair's generated on Bi_2WO_6 and HPW_{12} surface under visible light shown in (Fig. 8e). Since the CB edges of both Bi_2WO_6 and HPW_{12} is more positive than O_2/O_2^- (-0.33 V) it will not generate O_2^- anion. The conjugated organic CN is an excellent electron capturing materials and immediately transfer electrons from CB of Bi_2WO_6 to VB of HPW_{12} enhancing the charge separation process. On the same time electrons in the CB of HPW_{12} also migrates to CN which is thus participating in reduction process while holes in the VB of Bi_2WO_6 contributes for oxidation.

Figure 8. (a) Photodegradation performance of Cr (VI) (b) Tetracycline under visible light irradiation; (c) Kinetic linear fitting curves of Cr (VI) (d) TC and corresponding apparent rate constants (k) as insets; (e) Possible photocatalytic mechanism scheme of $\text{PW}_{12}/\text{CN}@ \text{Bi}_2\text{WO}_6$ under visible-light irradiation (Reproduced from Ref. 204, with permission from Separation and Purification Technology) [67].

BiOIO₃/C500/MoS₂ all solid-state Z-scheme heterostructure synthesized by sol-gel and hydrothermal method where C500 provide channels for the electron in the CB of BiOIO₃ to recombine with the holes in the VB of MoS₂ [68]. The mechanism of charge migration on the surface of heterojunction is shown in (Fig 9a). The band bending of BiOIO₃ and MoS₂ at the interface is displayed in (Fig 9b). Firstly, electron diffuses from BiOIO₃ surface with larger work function of 5.8 eV towards MoS₂ having smaller work function of 5.2 eV, respectively. The electron diffusion creates surface charge layer generating internal electric field at the interface. The diffusion of electrons continues till the Fermi level equilibrates by shifting upward in BiOIO₃ and downward MoS₂ forming Z-scheme heterojunction after contact. This causes downward bending of CB and VB edges in BiOIO₃ and upward bending of CB and VB edges in MoS₂. (In Fig 9c), the CB of MoS₂ -0.29 eV is more negative as compared to °O₂⁻ potential -0.28 eV whereas, VB potential of BiOIO₃ is 3.51 eV more positive than °OH potential of 2.2 eV, respectively. Both °OH and °O₂⁻ generated in the VB of BiOIO₃ and CB MoS₂ oxidizes 78.32% of Hg⁰ to HgO. The mechanism was further assisted by performing scavenger experiments and ESR techniques. In comparison to conventional type-II heterojunction, Z-scheme based heterojunction is more efficient in terms of accelerating the charge carrier separation and also maintaining the strong redox ability of individual photocatalysts [69].

Figure 9. (a) A schematic diagram of BiOIO₃/MoS₂/C500; (b) The band bending diagram and electron transfer at interface of BiOIO₃ and MoS₂ (c) Photocatalytic mechanism diagram [68].

A multi-component layered double hydroxide based heterostructure $\text{Ag}@\text{Ag}_3\text{PO}_4/\text{g-C}_3\text{N}_4/\text{NiFe}$ were formed by in-situ photoreduction and self-assembly by electrostatic attraction [70]. The quasi-type-II heterojunction photo-catalytically reduced 97% hexavalent chromium in 2 h. The surface plasmon resonance effect of Ag nanoparticles and surface defects on layered material created by oxygen vacancy hastens the charge transfer. Further, the formation of Schottky barrier at the interface of quasi-type-II heterojunction was evident by much spectroscopic technique. Another multicomponent system synthesized by hydrothermal method in which carbon quantum dot is decorated over $\text{CeO}_2/\text{g-C}_3\text{N}_4/\text{V}_2\text{O}_5$ operating through dual Z-scheme mechanism (Fig 10a) [71]. The multicomponent system avails up-conversion phenomena of carbon quantum dots, broad absorption range, large charge separation, operates via two-channel charge transfer. Nearly 99% of Cr (VI) is reduced in 100 min without using sacrificial agent whereas complete reduction is accomplished in 30 min when 10^{-4} mol of tartaric acid as hole scavenger is used as shown in (Fig 10b and c). Tartaric acid retains all the electron free and oxidized itself by scavenging holes. The complete reduction of Cr (VI) into Cr (III) is confirmed by XPS showing the presence of trivalent chromium in the survey scan performed after reduction test (Fig 10 d and e).

On further simplification two peak of Cr (III) at 576.9 and 586.5 eV were obtained assigned to $2p_{3/2}$ and $2p_{1/2}$, respectively. The broad spectrum response of carbon quantum dot decorated $\text{CeO}_2/\text{g-C}_3\text{N}_4/\text{V}_2\text{O}_5$ is due to the red shift accounts for lowering of band gap. Further, two-channel charge transfer mechanism, oxygen vacancies on carbon quantum dots and induced defects of photocatalyst surface by carbon quantum dots arise and their up-conversion phenomena accounts for high photo efficiency. The surface defects entrap the charge carrier and minimizes the process of recombination. Through the bridging material migration of photogenerated electrons from the CB of $\text{g-C}_3\text{N}_4$ to the VB of CeO_2 and V_2O_5 becomes more facile. Such type of electron migration renders the electron with high reduction ability in CB of CeO_2 and V_2O_5 for reduction process (Fig 10f). Different bare, binary, trinary and multicomponent nanohybrids employed for photocatalytic reduction of HMs are summarized in Table 3 (72-85).

Figure 10. (a) Synthesis Scheme. (b) The extent of photo-reduction of Cr(VI) under visible light(c) Effect of reaction parameters onto Cr(VI) photo-reduction with CCGV (f) Initial co-catalysts or sacrificial agents; [catalyst] = 0.3 mg/mL [Cr⁶⁺] = 20 mg L⁻¹, pH=2, temperature = 30 ± 0.5 °C, Visible light intensity 480 mW cm⁻². XPS survey scan (d) Cr²⁺ spectrum (Inset) of unused CCGV before final recovery (CCGV + visible + TA system) (e) Reusability studies for Cr(VI) reduction with CCGV under visible light; (f)Traditional and Z-scheme heterojunction CCGV with possible charge flow [71].

Table 3. Summary of various photocatalytic nanohybrids for the removal of HMs

Nanohybrids	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore Diameter (nm)	Active species	Targeted pollutant	Photodegradation efficiency	Reusability	Ref
Cr-SrTiO ₃	CrSTO=118.8 m ² g ⁻¹ STO=5.0 m ² g ⁻¹	CrSTO = 0.24 m ² g ⁻¹ STO= 0.23 m ² g ⁻¹	CrSTO = 3.0 nm STO= 2.5 nm	-	Cr (VI)	Photoreduction of Cr (VI) (up to ~92%) under visible light	Up to ~6 photocatalytic cycle	[72]
B-Sn ₃ O ₄	Sn ₃ O ₄ =31.35 m ² g ⁻¹ B _{0.3} -Sn ₃ O ₄ =69.14m ² g ⁻¹ ,	Sn ₃ O ₄ =0.126 cm ³ g ⁻¹ B _{0.3} -Sn ₃ O ₄ =0.078cm ³ g ⁻¹	Sn ₃ O ₄ =16.13nm B _{0.3} -Sn ₃ O ₄ =5.77nm	h ⁺ , ·O ₂ ⁻	Cr (VI) Phenol	Photoreduction of Cr (VI) (up to ~80%) under visible light	Up to ~5 photocatalytic cycle	[73]
CdS/TiO ₂	TiO ₂ = 241.32 m ² g ⁻¹ CAR _{0.35} =15.88 m ² g ⁻¹	TiO ₂ = 0.18cm ³ g ⁻¹ CAR _{0.35} = 0.12cm ³ g ⁻¹	TiO ₂ = 2.99nm CAR _{0.35} = 41.07nm	-	Cr (VI) Phenol	73.1 % reduction of Cr(VI) and oxidation of phenol under visible light.	Up to ~5 photocatalytic cycle	[53]
Ag/Ag ₃ PO ₄ /MIL-125-NH ₂	Ag/Ag ₃ PO ₄ = 12.1 m ² /g. AAMN-120= 478.95 m ² /g, MIL-125-NH=1000 m ² /g	-	-	·O ₂ ⁻	Cr (VI)	-	Up to ~5 photocatalytic cycle	[74]
Fe-TNTs	TNTs=272.3 m ² g ⁻¹ Fe-TNT=162.8 m ² g ⁻¹	TNTs=1.26cm ³ g ⁻¹ Fe-TNT = 0.38 cm ³ g ⁻¹	TNTs=18.5nm Fe-TNT = 9.3nm	-	As(III)	Photoreduction of As(III) (up to ~99.6%) under visible light	Up to ~ 5 photocatalytic cycle	[75]
Bi ₂ MoO ₆ /Ti ₃ C ₂	Bi ₂ MoO ₆ /Ti ₃ C ₂ =33.24 m ² g ⁻¹	2 to 45 nm	-	·O ₂ ⁻ h ⁺	Cr(VI) Tetracycline hydrochloride	Photoreduction of Cr(VI) (up to ~100 %) under visible light	Up to ~ 4 photocatalytic cycle	[76]
BiOBr/BiOI ₃	BiOBr=31.83 m ² g ⁻¹ , BiOI ₃ =22.26 m ² g ⁻¹ , BI-10=21.22m ² g ⁻¹	BiOBr = 0.0675cm ³ g ⁻¹ BiOI ₃ =0.1498cm ³ g ⁻¹ BI-10=0.1679cm ³ g ⁻¹	BiOBr = 8.49nm BiOI ₃ = 26.93nm BI-10=31.66 nm	·O ₂ ⁻ h ⁺	Hg ⁰	Photoreduction of Hg ⁰ (up to ~ 90.25%) under visible light	Up to ~ 5 photocatalytic cycle	[77]

Cd/Co-based MOFs	-	-	-	$\cdot\text{O}_2^-$	Cr(VI)	Photoreduction of (up to Cr(VI) ~100%) under visible light under UV light	Up to ~5 photocatalytic cycle	[78]
Ag@TiON/Co Al	TiO ₂ = 0.228 (m ² /g), TiON= 0.178(m ² /g), , TiON/LDH= 0.182 (m ² /g), Ag@TiON/Co Al-LDH= 0.132 (m ² /g), ,	TiO ₂ =106.486nm TiON=79.248nm TiON/LDH= 160.554nm Ag@TiON /CoAl-LDH=168.832nm	TiO ₂ = 3.471 (m ³) TiON= 9.293m ³ TiON/LDH= 6.253m ³ Ag@TiON /CoAl-LDH= 5.860m ³	-	Cr(VI) Methyl orange, Methylene blue	Photoreduction of (up to Cr(VI) ~94%) under visible light under UV light	Up to ~5 photocatalytic cycle	[79]
SnIn ₄ S ₈ -CdS	CdS=14.8060 m ² /g SnIn ₄ S ₈ =9.522 6 m ² /g SnIn ₄ S ₈ -CdS=34.6320 m ² /g	0-10 nm	-	$\cdot\text{O}_2^-$ h ⁺	Cr(VI), Methyl orange (MO)	Photoreduction of (up to Cr(VI) ~82% and 100% of MO under visible light	Up to ~5 photocatalytic cycle	[80]
TiO ₂ -2-naphthol	P25 =46.1 m ² g ⁻¹ TiO ₂ = 133 m ² g ⁻¹ TiO ₂ -2-NAP = 130 m ² g ⁻¹	-	TiO ₂ =8.79nm TiO ₂ -2-NAP = 8.77 nm	-	Cr(VI)	Photoreduction of (up to Cr(VI) ~82%)	-	[81]
Bi ₂ S ₃ /β-Bi ₂ O ₃ /ZnIn ₂ S ₄	-	-	15 and 25 nm	$\cdot\text{O}_2^-$	Cr (VI)	96.3% Tetracycline (TCN) degradation and Cr(VI) reduction	-	[82]
Functional amorphous phosphate titanium oxide	-	446 m ² /g	3-7nm	-	Pb (II) Cd (II) Cr (III) Fe (III)	90% degradation of Pb (II), Cd (II), Cr (III) and Fe (III)	Up to 5 photocatalytic cycle	[83]
CoFe-LDH/g-C ₃ N ₄	g-C ₃ N ₄ = 15.16 CoFe-LDH = 67.08 50%-CoFeLDH/g-C ₃ N ₄ = 101.61	g-C ₃ N ₄ = 2.58 nm CoFe-LDH =0.61 50%-CoFeLDH/g-C ₃ N ₄ = 0.36	g-C ₃ N ₄ = 4.12 CoFe-LDH =3.01 50%-CoFeLDH/g-C ₃ N ₄ = 2.58	$\cdot\text{O}_2^-$	Cr (VI)	90% reduction of Cr(VI) under	Up to 5 photocatalytic cycle	[84]

P/SnS ₂	SnS ₂ = 35.38 m ² g ⁻¹ RP= 36.79 m ² g ⁻¹ 50%- RP/SnS ₂ = 40.96 m ² g ⁻¹	SnS ₂ = 3.05 cm ³ g ⁻¹ RP=3.74 cm ³ g ⁻¹ 50%- RP/SnS ₂ =3.76 cm ³ g ⁻¹	SnS ₂ =0.20 nm RP=0.21n m 50%- RP/SnS ₂ = 0.23nm	⁻ O ₂	Cr(VI)	removal Cr(VI) RhB by 50%	of and alytic cycle	Up to 5 photocat	[85]
--------------------	--	--	--	-----------------------------	--------	---------------------------------	------------------------------	---------------------	------

4. Nanohybrids for adsorptional removal of organic pollutants and heavy metals

Adsorption technique is widely used in industrial applications to decontaminate waste water due to its simple operation, high efficiency and low-cost. Physisorption or chemisorption are the two important phenomena through which adsorbent holds a molecule of adsorbate onto it. Adsorption process depends on different parameters such as adsorbent dosage, pH, temperature, contact time, concentration and electrostatic force between the adsorbate and adsorbent. This method is more flexible as adsorption site on the surface of adsorbent can be easily regenerated by reversible adsorption mechanism [86]. Metal, zeolite and carbon based nanosorbent are commonly applied adsorbent for water purification. For the adsorptional removal of HMIs different types of adsorbent like humic acid [87], activated carbons [88], bio-chars, sawdust [89], coal ash [90], resin [91], carbon nanotubes [92], graphene oxide [93], zeolites [94], bio-chars [95], sepiolites [96], palygorskite [97], mesoporous materials [98], and layered double hydroxides (LDHs) [99] were reported for heavy metal ion removal. A broad range of nano-adsorbents based on polyaniline (PANI) and its derivatives also appeared as promising candidate for the removal of heavy metals form polluted water [100].

Apart from bare photocatalytic system, adsorption capacity of simple metal oxide, inorganic bimetallic Mo-Fe-S clusters, graphene and graphene oxide were also reported for heavy metals. The highest adsorption capacity up to 81.2 mg/g at pH 5 for Pb⁺² and lowest about 24.6 mg/g at pH 5 for Cr⁺³ ion was estimated by the iron oxide as adsorbent [101]. Whereas, in another report maximum adsorption of 319.35 mg g⁻¹ for Pb²⁺ were reported by inorganic bimetallic Mo-Fe-S clusters prepared by chemical fixation of tetra thio-molybdate on Fe₃O₄ nanoparticles at room temperature [102]. Further, hierarchical nanoporous material synthesized using trimercaptos--triazine-trisodium salt and trimercaptos-triazine-monosodium salt display efficient adsorption capacity of 735.3 and 3775.9 mgg⁻¹for Hg²⁺ and Pb²⁺ ions, respectively [103]. The outstanding adsorption capacity and mechanical properties of graphene and graphene oxide imparts broader application in water purification [104,105]. About 98.46% and 99.99% is elimination efficiency acquired by graphene and graphene oxide towards Pb²⁺ ion. The various

inorganic NPs were immobilized on certain organic support to avoid agglomeration, enhance surface area, improve recyclability and inhibit leaching of baser nanoparticles [106,107]. Numerous fibrous polymeric materials are also utilized as supportive systems for nanoparticles. The fabrication of polymeric semiconducting materials via polymeric matrices can be achieved by chemical, thermal and photo-induced reaction. The polystyrene based core/shell gel adsorbent display 526.3, 434.8, 555.6 and 476.2 mgg^{-1} , adsorption capacity for Pb^{2+} , Cu^{2+} , Cd^{2+} and Cr^{2+} , respectively [108].

Chitosan is a most abundant alkaline polymer of polysaccharides exhibits excellent hydrophilicity, biocompatibility, biodegradability and renewable capacity. Besides, presence of hydroxyl and amine group serves as adsorption site and make it more beneficial for adsorption of anionic pollutants and heavy metal ions. Guo et al. reported poly-dopamine modified chitosan aerogel and determine their adsorption capacity of 374.4 and 441.2 mg g^{-1} were observed towards Cr (VI) and Pb (II) ions [109]. The optimal pH for Cr (VI) and Pb (II) ions removal is 2.0 and 5.5, respectively and pH_{ZPC} of nanocomposites is 7.5. At lower pH hydroxyl and amine group on nanocomposites get protonated thus possess positively charged surface.

PANI/rGO nanohybrid having surface area of $36.70 \text{ m}^2\text{g}^{-1}$ adsorb nearly 1000 mg/g of Hg^{2+} ions at pH 4.0 obeying second order kinetic model [110]. The surface charge on PANI, rGO, and PANI/rGO is studied by zeta potential analysis (Fig 11a) indicating pH_{ZPC} 5.8, 2.5, and 3.0, respectively. If the pH of reaction solution is below pH_{ZPC} surface become positively charged whereas higher pH makes the surface negatively charged. Therefore, pH of the reaction is extremely important in deciding the optimum pH range for adsorption of pollutant. At low pH adsorption process is greatly reduced due to the electrostatic repulsion between Hg^{2+} ions and positively charged PANI/rGO although higher pH increases adsorption process hence 3-4.0 is the optimal pH range displaying maximum adsorption. Gusain and co-workers reported effective adsorption mechanism for eliminating Pb (II) and Cd (II) by $\text{MoS}_2/\text{SH-MWCNT}$ nanocomposite synthesize by hydrothermal method [111]. Presence of sulphur cite on MoS_2 form metal-sulphur complex on the inner layer of MoS_2 evident by increased interlayer spacing. Nearly, 90.0 and .66.6 mgg^{-1} of Pb (II) and Cd (II) were adsorbed obeying pseudo second order kinetics. The electrostatic interaction, complex formation and ion-exchange process blend together for effective adsorptional removal of metals (Fig 11b).

New emerging class of porous organic materials, metal organic framework such as porphyrins were also exploited for heavy metal ion removal [112,113]. The mesoporous zirconium-based metal-organic framework displayed 277 mgg^{-1} adsorption capacity for Hg^{2+} ions at 7.1 pH where, pyrrolic functional group is an activity for the adsorption of metal ions [114]. In another work sulphonic acid modified metal organic framework

demonstrated 88.7 mgg⁻¹ adsorption capacity of cadmium ions [115] (Fig 11c). Heavy metal removal via adsorption mechanism commonly takes place through electrostatic adsorption, surface bonding, hydrogen bonding, ion exchange etc. The adsorption behaviour can be analyzing using advanced spectroscopic techniques, theoretical calculations and surface complexation models. Another metal organic framework-based nanocomposite possessing high surface area of 268.7 m²g⁻¹ adsorb 200.6 and 152.1 mgg⁻¹ of Cu²⁺ and Cr⁶⁺, respectively [116]. The XPS spectra displaying binding energy peak at 934 eV and 955 eV of 2p_{3/2} and 2p_{1/2} orbital in Cu²⁺ ion whereas, 579.2 and 588.1 eV binding energy represent Cr⁺⁶ (Fig 11d and e).

Thiosalicylhydrazide-modified magnetic nano-adsorbent employed for Pb²⁺, Cd²⁺, Cu²⁺, Zn²⁺, and Co²⁺, ions removal from industrial wastes with adsorption capacity 188.7, 107.5, 7.9, 51.3, and 27.7 mgg⁻¹, respectively [117]. Fe₂O₃ nanoparticle surface is modified with thiosalicylhydrazide ligating agent so as to minimize the involvement of alkaline earth metal on adsorption process. Moreover, immobilization of Fe₂O₃ nanoparticle onto poly-acrylic acid polymer shell reduces its aggregation and maintains dispersion. The schematic preparation of magnetic nano-adsorbent with possible adsorption mechanism of metal ion shown in (Fig 11f).

Cellulose-based amphoteric adsorbent owning amino and carboxyl functional group on the surface beneficial for the removal of Cr²⁺, Cd²⁺, Cu²⁺, Zn²⁺ and Pb²⁺ ions [118]. The percentage removal and adsorption ability are decided by density of functional group which should be at least 10.0 mmolg⁻¹ that prove absolute removal of metal ions and can be calculated using below mention equations.

$$\text{Amino group contents} = \frac{m \times W_t}{m \times M} \times 1000 \quad (26)$$

$$\text{Carboxyl group contents} = \frac{m \times W_t}{m \times M} \times 1000 \times W'_t \quad (27)$$

Where, m, M, W_t and W'_t represents sample weight used in EA (g), relative atomic mass (molg⁻¹), element proportion (wt%), and percentage of carboxyl group measured by XPS, respectively. Owing to the high density of amino group having great affinity for anionic Cr (VI) responsible for its complete removal as compared to cationic Cd²⁺, Cu²⁺, Zn²⁺ and Pb²⁺ ions. The electrostatic interactions, chelating reactions, and oxidation–reduction reactions explained the adsorption mechanism elaborated in (Fig 11g). Further, 3D hydrogel having great potential to undergo structure deformation arises due to swelling property by simply absorbing water that facilitate penetration of ions. EDTA cross-linked

chitosan and polyacrylamide based hydrogel employed for Cd^{2+} , Cu^{2+} and Pb^{2+} ions with sorption capacity of 86.0, 99.4 and 138.4 mg g^{-1} , respectively [119].

Figure 11(a) Zeta potential of PANI, RGO and PANI/RGO composites in a 0.02M NaNO_3 solution [110]; (b) Diagrammatic illustration of $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$ adsorption mechanism on $\text{MoS}_2/\text{SH-MWCNTs}$ [112]; (c) Proposed mechanism for $\text{Cd}(\text{II})$ adsorption in $\text{Cu}_3(\text{BTC})_2\text{-SO}_3\text{H}$ [115]; XPS spectra of (d) Cu^{2+} signal region (e) Cr^{2+} signal region [116]; (f) Scheme for the preparation of $\text{Fe}_3\text{O}_4@\text{PAA}@\text{TSH}$ MNPs and a possible mechanism for adsorption of metal ions on them [117] (g) Specialization and cooperation mechanism of MCC/DTPA-PEIA for heavy metal ions [119].

$\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ oxidizes 65% of Hg^0 to Hg^{+2} at 250-350 °C in CO_2 enriched atmosphere [120]. Several parallel mechanisms occur for the oxidation of Hg^0 elaborated in successive

equations. Different multicomponent nanohybrids employed for adsorptional removal of HMs are summarized in Table 4 (121-140).

(1) Oxidation by V_2O_5

(2) Oxidation by chemisorbed oxygen

(3) Oxidation by CO_2

Table 4. Summary of different nanohybrids with distinct adsorption capacity

Adsorbent	Targeted pollutant	Concentration	Dosages	pH	Surface area (m^2/g^{-1})	Pore size (nm)	Adsorption capacity (mg/g)	Ref.
EDTA/Nanoporous starch-based nanomaterial (EDTA/3D-PSN)	Cd (II) Hg (II) Pb (II) Cu (II)	2.00 mg/L	0.25g	2.4	83.75 m^2/g^{-1} .	-	Cd (II)= 532.28 mg/g Hg (II)= 381.47 mg/g Cu (II)=354.15 mg/g Pb (II)=238.39 mg/g	[121]
Sodium alginate grafted polyacrylamide / graphene oxide hydrogel (SA-PAM/GO)	Cu (II) Pb (II)	25 mg/L 50 mg/L	-	5	SA-PAM/GO= 190.89 dm^2/g	SA-PAM/GO=6.794 nm to 19.8052 nm 9.451 dm^3/g	68.76 mg/g 240.69 mg/g,	[122]
N-[4-morpholinecarboximidamido]carboximidamidomethylatedpolyphenylenesulfide (MCMPPS)	Pb (II) Cr (III) Cu (II) Cd (II) Ni (II)	-	-	4.5 4.5 4.5 4.0 4.5	4.49 m^2/g^{-1} .	-	Pb (II)= 186.92 mg/g Cd (II)= 189.75 mg/g Cr (III)= 120.04 mg/g Cu (II)= 119.33 mg/g Ni (II)= 134.05 mg/g	[123]
$\text{Fe}_2\text{O}_3@\text{CaCO}_3$	As (V) Cr (VI) Pb (II)	1.0-30 ppm	0.5 mg/mL	2-12	53.4 m^2/g^{-1}	13.2 nm	As (V)=184.1 mg/g Cr (VI)= 251.6, mg/g Pb (II)= 1041.9 mg/g	[124]
Inorganic polymer microspheres	Pb (II) Cu (II) Cd (II)	200 mg/L		5	87.74 m^2/g	8.9 nm	Pb =310.84 mg/g Cu =47.71 mg/g Cd = 36.26 mg/g	[125]

Gum ghatti – <i>graft</i> – poly(4-acryloylmorpholine) hydrogel (Ggh-g-PAcM hydrogel polymer)	Cu (II) Hg (II)	20-1000 mgL ⁻¹		1.2	0.11 to 0.21 m ² g ⁻¹	90.6, 103.6, 224.8, 213.8 mgg-1	Cu(II) =249.9 mg/g, Hg(II) =235.1 mg/g,	[126]
PANI/JF (jute fiber) composite	Cd (II) Cr (VI)	50 mg·L ⁻¹	0.05 to 1.0 g	7	1.0 m ² g ⁻¹	140 and 50mg.g ⁻¹	8.43 mg·g ⁻¹	[127]
Ganguemicrosphere/geopolymer (GM/KGP)	Cu (II) Cd (II) Zn (II) Pb (VI)	100 mg/L	6 g/L	5	KGP=1 7.59m ² / g GM=6.0 3m ² /g	KGP =45.18n m GM= 28.39nm	~30 mg/g.	[128]
Polysulfide/MgAl LDH	Hg (II) Pb (II) Ag (II) Zn (II)	10 mM	0.02 g	3-5	-	-	Hg (II) =686 Pb (II) =483, Ag (II) =383, Zn (II)=145m g/g	[129]
Amino functionalized silica (Ni (II), Cd (II) and Pb (II))	Ni (II), Cd (II) Pb (II)	50 mg/L	5 g/L	5	966 m ² /g	4.85 nm	Ni (II)= 12.36 Cd (II)=18.25 Pb (II)= 57.74 mg/g 122 mg/g	[130]
Nano-hydroxyapatite/chitosan composite	Cd (II)	100-500 mg/L	5 g/L	5.6	-	-	122 mg/g	[131]
Fe ₃ O ₄ /PANI/MnO ₂ Core-Shell Hybrids	Cd (II) Zn (II) Pb (II) Cu (II)	20 mg/L	1 g/L	6.2 - 6.4	63.96 m ² /g	4.12 nm	158 (428) mg/g	[132]
Fe ₃ O ₄ / MnO ₂	Cd (II)	10 mg/L	1 g/L (0.02 g)	6.2 - 6.4	118 m ² /g	3.3 nm	53.2 mg/g	[133]
Fe ₃ O ₄ @Mesoporous Silica-Graphene Oxide	Pb (II) Cu (II)	20 mg/L	100 mg/L	7.1	-	-	Pb (II)= 333 mg/g Cu (II)= 167 mg/g 400 mg/g	[134]
Fe ₃ O ₄ magnetic polypyrrole-graphene oxide Hg (II)	Hg (II)	20-100 mg/L	0.01- 0.09 g/L	7	1737.6 m ² /g	4.2 nm		[135]

Polyaniline/maghemite (PANI/ γ -Fe ₂ O ₃)	Cr (VI) Cu (II)	100 mg/L	2 mg	Cr (VI)) =2. 0 Cu (II) =5. 5	60 m ² /g	5.1 nm	Cr (VI)=195. 7 mg/g Cu (II)= 106.8 mg/g	[136]
Fe ₃ O ₄ /xanthate GO	Hg (II)	20 mg/L	2-14 mg	7	30.13 m ² /g	-	118.55 mg/g	[137]
MnO ₂ /carbon nanotubes	Hg (II)	1-50 mg/L	0.02 g	6	110.38 m ² /g	2.70 nm	58.8 mg/g	[138]
Multiwalled carbon nanotubes	Hg (II)	0.1-10 mg/L	0.5 g	7	270 m ² /g	-	25.64 mg/g	[139]
Magnetic graphene oxide	Hg (II)	100 mg/L	0.5g/L	6	58.6 m ² /g	-	71.3 mg/g	[140]

Conclusions and future prospects

Water pollution is the major challenge faced by the humans of 21st century and the speedy growth in industrialization and population poses considerable threat on water resources. Due to the toxicity, recalcitrance persistence and large scale discharge of heavy metals into the environment, photocatalysis is a coherent approach. Though various adsorbent were also reported for their removal yet construction of multitasking nanohybrids that only reduces HMs but also work upon other toxic pollutant present in aqueous solution. The incomplete removal of HMs by implementing bare adsorption process is their major limitation due to which the treated water could left out with certain amount of toxic metal ion. Optimizing reaction condition to design adsorbing material retaining high density of functional group that accomplishes complete removal.

The use of photocatalytic system is cost effective technique providing large specific surface area, enhance photostability, less toxicity, less energy consumption and broad solar absorption range. Many heterojunction formations of semiconductors have been explored operating through conventional type-II charge migration however, recently Z-scheme type of migration of charge carrier is broadly explored by scientist. Z-scheme based photocatalyst is a potential candidate for different photocatalytic reactions as it retains the strong redox ability of individual semiconductor and reforming their band potential is also more facile. Fast rate of recombination of charge carrier, narrow absorption range and small surface area are some of the major limitation of photocatalysts that should be addressed while constructing a next generation photocatalysts. Thus, band gap engineering of

semiconductors will remain open and challenging field for researchers to work upon in the future.

Rather than using individual photocatalytic reduction and adsorption method for HMs removal, constructing and implementing such nanohybrids that can simultaneously photocatalytically reduce metal ion into less toxic ions followed by their complete adsorptional removal is most recommendable. Therefore, nanohybrid should be such that assure complete removal of HMs so that its concentration should met the standard of safe drinking level as per US-EPA protocols. And if somehow there is the chance of incomplete removal from the water system then at least the metal ion is photo-catalytically reduced to innocuous metal ion. Thusly, considering the economic benefit such photocatalytic system needs to come-up with simultaneous and efficient elimination of coexisting hazardous organic contaminants and heavy metals from the polluted water. The aim of integrating different photocatalysts is to synergistically avail the independent property of semiconductors and to construct ideal systems with enhanced photo-efficiency by regenerating the active sites.

References

- [1] A. Azimi, A. Azari, M. Rezakazemi, M. Ansarpour, Removal of heavy metals from industrial wastewaters: a review, *Chemical and Biochemical Engineering Review*, 4 (2017) 37–59. <https://doi.org/10.1002/cben.201600010>
- [2] S. Xu, Y. Lv, X. Zeng, D. Cao, ZIF-derived nitrogen-doped porous carbons as highly efficient adsorbents for removal of organic compounds from wastewater, *Chemical Engineering Journal*, 323 (2017) 502–511. <https://doi.org/10.1016/j.cej.2017.04.093>
- [3] I. Díaz, Environmental uses of zeolites in Ethiopia, *Catalysis Today*, 285 (2017) 29–38. <https://doi.org/10.1016/j.cattod.2017.01.045>
- [4] Y. Wang, G. Ye, H. Chen, X. Hu, Z. Niu, S. Ma, Functionalized Metal–Organic Framework as a New Platform for Efficient and Selective Removal of Cadmium (II) from Aqueous Solution, *Journal of Materials Chemistry A*, 3 (2015) 15292–15298. <https://doi.org/10.1039/C5TA03201F>
- [5] X. Li, C. Bian, X. Meng, F.S. Xiao Design and Synthesis of an Efficient Nanoporous Adsorbent for Hg^{2+} and Pb^{2+} Ions in Water. *Journal of Materials Chemistry A*, 4 (2016) 5999–6005. <https://doi.org/10.1039/C6TA00987E>
- [6] H. C. J. Godfray, J. R. Beddington, I. R. Crute, L. Haddad, D. Lawrence, J. F. Muir, Food Security: The Challenge of Feeding 9 Billion People, *Science*, 327 (2010) 812–818. <https://doi.org/10.1126/science.1185383>

- [7] T. Theophanides, J. Anastassopoulou, Copper and carcinogenesis. Critical reviews in oncology/hematology, 42 (2002) 57–64. [https://doi.org/10.1016/S1040-8428\(02\)00007-0](https://doi.org/10.1016/S1040-8428(02)00007-0)
- [8] S. Strachan, Trace Elements, Current Anaesthesia & Critical Care, 21 (2010) 44–48. <https://doi.org/10.1016/j.cacc.2009.08.004>
- [9] J. Lemire, R. Mailloux, V.D. Appanna, Zinc Toxicity Alters Mitochondrial Metabolism and Leads to Decreased ATP Production in Hepatocytes, Journal of Applied Toxicology: An International Journal, 28 (2008) 175–182. <https://doi.org/10.1002/jat.1263>
- [10] G.D. Leikauf, S.A. McDowell, S.C. Wesselkamper, W.D. Hardie, J.E. Leikauf, T.R. Korfhagen, D.R. Prows. Acute Lung Injury: Functional Genomics and Genetic Susceptibility, Chest, 121 (2002) 70S– 75S. https://doi.org/10.1378/chest.121.3_suppl.70S
- [11] M.R. Awual, M.M. Hasan, Novel conjugate adsorbent for visual detection and removal of toxic lead (II) ions from water, Microporous and mesoporous materials, 196 (2014) 261-269. <https://doi.org/10.1016/j.micromeso.2014.05.021>
- [12] M. Dinari, M. Hatami, Novel N-riched crystalline covalent organic framework as a highly porous adsorbent for effective cadmium removal, Journal of Environmental Chemical Engineering, 7 (2019) 102-907. <https://doi.org/10.1016/j.jece.2019.102907>
- [13] B. Weiss, P.J. Landrigan, The Developing Brain and the Environment: An Introduction, Environmental health perspectives, 108 (2000) 373– 374. <https://doi.org/10.1289/ehp.00108s3373>
- [14] W.H. Organization, Guidelines for drinking-water quality: recommendations, World Health Organization, 2004
- [15] C. Griffiths, H. Klemick, M. Massey, C. Moore, S. Newbold and D. Simpson, et al., US Environmental Protection Agency valuation of surface water quality improvements, Review of Environmental Economics and Policy, 6 (2012) 130-146. <https://doi.org/10.1093/reep/rer025>
- [16] J.P.F. D’Mello Food Safety: Contaminants and Toxins, Scottish Agricultural College, UK (2003) 206. <https://doi.org/10.1079/9780851996073.0000>
- [17] M.R. Awual, M.M. Hasan, Novel conjugate adsorbent for visual detection and removal of toxic lead (II) ions from water, Microporous and mesoporous materials, 196 (2014) 261-269. <https://doi.org/10.1016/j.micromeso.2014.05.021>
- [18] R.A.K. Rao, S. Ikram, Sorption studies of Cu (II) on gooseberry fruit (*emblica officinalis*) and its removal from electroplating wastewater. Desalination, 277 (2011) 390–398. <https://doi.org/10.1016/j.desal.2011.04.065>

- [19] X. He, P. Li Surface water pollution in the middle Chinese Loess Plateau with special focus on hexavalent chromium (Cr^{6+}): occurrence, sources and health risks, *Exposure and Health*, (2020) 1-7. <https://doi.org/10.1007/s12403-020-00344-x>
- [20] T. Joseph, B. Dubey, E.A. Mc Bean, Human health risk assessment from arsenic exposures in Bangladesh, *Science of the Total Environment*, 527 (2015) 552-560. <https://doi.org/10.1016/j.scitotenv.2015.05.053>
- [21] A.Galadima, Z.N. Garba, L. Leke, M.N.Almustapha, I.K. Adam, Domestic water pollution among local communities in Nigeria-causes and consequences, *European Journal of Scientific Research*, 52(4) (2011) 592-603. <https://doi.org/10.5539/jsd.v4n4p22>
- [22] M. Kobya, E. Demirbas, E. Senturk, M. Ince, Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone, *Bioresource technology*, 96 (2005) 1518-1521. <https://doi.org/10.1016/j.biortech.2004.12.005>
- [23] A. Oehmen, R. Viegas, S. Velizarov, M.A.M. Reis, J.G. Crespo. Removal of heavy metals from drinking water supplies through the ion exchange membrane bioreactor, *Desalination*, 199 (2006) 405-407. <https://doi.org/10.1016/j.desal.2006.03.091>
- [24] E. Salazar, M.I. Ortiz, A.M. Urtiaga, Irabien JA. Kinetics of the separation–concentration of chromium (VI) with emulsion liquid membranes, *Industrial & engineering chemistry research*, 31 (1992)1523. <https://doi.org/10.1021/ie00006a015>
- [25] F.M. Pang, P. Kumar, T.T. Teng, A. K. M Omar, K.L. Wasewar Removal of lead, zinc and iron by coagulation–flocculation. *Journal of the Taiwan Institute of Chemical Engineers*, 42 (2011) 809–815. <https://doi.org/10.1016/j.jtice.2011.01.009>
- [26] W. Maatar, S. Boufi, Poly (methacrylic acid-co-maleic acid) grafted nanofibrillated cellulose as a reusable novel heavy metal ions adsorbent, *Carbohydrate Polymers*, 126 (2015) 199–207. <https://doi.org/10.1016/j.carbpol.2015.03.015>
- [27] S.K. Sahu, V.K. Verma, Bagchi D., V. Kumar, B.D. Pandey, Recovery of chromium (VI) from electroplating effluent by solvent extraction with tri-n-butyl phosphate. *Indian J Chem Technol* 126 (2008) 397.
- [28] N. Meunier., P. Drogui, C. Montane, R. Hausler, G. Mercier, J.F. Blais, Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate, *Journal of hazardous materials*, 137 (2006) 581-590. <https://doi.org/10.1016/j.jhazmat.2006.02.050>
- [29] T.A. Kurniawan, G.Y. Chan, W.H. Lo, S. Babel Physico–chemical treatment techniques for wastewater laden with heavy metals, *Chemical engineering journal*, 118 (2006) 83-98. <https://doi.org/10.1016/j.cej.2006.01.015>

- [30] A. Dabrowski, Z. Hubicki, P. Podkoscielny, E. Roben, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, *Chemosphere* 56, 91 (2004) 106. <https://doi.org/10.1016/j.chemosphere.2004.03.006>
- [31] J. Gao, S.P. Sun, W.P. Zhu, T.S. Chung, Chelating polymer modified P84 nanofiltration (NF) hollow fiber membranes for highly efficient heavy metal removal, *Water Research*, 63 (2014) 252-261. <https://doi.org/10.1016/j.watres.2014.06.006>
- [32] D. Kong, B. Liang, H. Yun, H. Cheng, J. Ma, et al. Cathodic degradation of antibiotics: characterization and pathway analysis, *Water Research*, 72 (2015) 281–292. <https://doi.org/10.1016/j.watres.2015.01.025>
- [33] M. Dakiky, M. Khamis, A. Manassra, M. Mereb. Selective adsorption of chromium (VI) in industrial wastewater using low-cost abundantly available adsorbents, *Advances in environmental research*, 6 (2002) 533–540. [https://doi.org/10.1016/S1093-0191\(01\)00079-X](https://doi.org/10.1016/S1093-0191(01)00079-X)
- [34] M. Brienza, I.A. Katsoyiannis. Sulfate radical technologies as tertiary treatment for the removal of emerging contaminants from wastewater, *Sustainability*, 9(9) (2017) 1604. <https://doi.org/10.3390/su9091604>
- [35] K. Villa, X. Domènech, U.M. García-Pérez, J. Peral Photocatalytic Hydrogen Production Under Visible Light by Using a CdS/WO₃ Composite, *Catalysis Letters*, 146 (2016) 100–108. <https://doi.org/10.1007/s10562-015-1612-6>
- [36] L. Soler, V. Magdanz, V.M. Fomin, S. Sanchez, O.G. Schmidt. Self-Propelled Micromotors for Cleaning Polluted Water, *ACS Nano*, 7 (2013) 9611–9620. <https://doi.org/10.1021/nn405075d>
- [37] Liu C, Wu T, Hsu PC, Xie J, Zhao J, Liu K, et al. Direct/Alternating Current Electrochemical Method for Removing and Recovering Heavy Metal from Water Using Graphene Oxide Electrode, *ACS nano*, 2019. <https://doi.org/10.1021/acsnano.8b09301>
- [38] He HP, Wu DL, Zhao LH. Luo C. Sequestration of chelated copper by structural Fe (II): reductive decomplexation and transformation of Cu (II)-EDTA, *Journal of hazardous materials*, 309 (2016) 116–125. <https://doi.org/10.1016/j.jhazmat.2016.02.009>
- [39] A. Fujishima, K. Honda, Electrochemical Photolysis of Water at a Semiconductor Electrode, *Nature*, 238 (1972) 37-38. <https://doi.org/10.1038/238037a0>
- [40] J. Efome, D. Rana, T. Matsuura, C. Lan, Metal organic frameworks supported on nanofibers to remove heavy metals, *Journal of Materials Chemistry A*, 22(2018) 24577-24583.

- [41] J. Low, C. Jiang, B. Cheng, S. Wageh, A.A. Al-Ghamdi, J. Yu, A review of direct Z-scheme photocatalysts, *Small Methods*, 5 (2017) 1700080.
<https://doi.org/10.1002/smtd.201700080>
- [42] A.J. Bard, Photoelectrochemistry and heterogeneous photo-catalysis at semiconductors, *Journal of Photochemistry*, 10(1) (1979) 59-75.
[https://doi.org/10.1016/0047-2670\(79\)80037-4](https://doi.org/10.1016/0047-2670(79)80037-4)
- [43] H. Tada, T. Mitsui, T. Kiyonaga, T. Akita, K. Tanaka, All-solid-state Z-scheme in CdS–Au–TiO₂ three-component nanojunction system, *Nature materials*, 5(10) (2006) 782-6. <https://doi.org/10.1038/nmat1734>
- [44] J. Yu, S. Wang, J. Low, W. Xiao, Enhanced photocatalytic performance of direct Z-scheme gC₃N₄–TiO₂ photocatalysts for the decomposition of formaldehyde in air, *Physical Chemistry Chemical Physics*, 15(39) (2013) 16883-90.
<https://doi.org/10.1039/c3cp53131g>
- [45] M.A. Barakat, Y.T. Chen, C.P. Huang, Removal of toxic cyanide and Cu (II) Ions from water by illuminated TiO₂ catalyst, *Applied Catalysis B: Environmental*, 53 (2004) 13-20. <https://doi.org/10.1016/j.apcatb.2004.05.003>
- [46] A.T. Le, S.Y. Pung, S. Sreekantan, A. Matsuda, Mechanisms of removal of heavy metal ions by ZnO particles. *Heliyon*, 5 (2019) 01440.
<https://doi.org/10.1016/j.heliyon.2019.e01440>
- [47] A. Samad, S. Ahsan, I. Tateishi, M. Furukawa, H. Katsumata, T. Suzuki, S. Kaneco, Indirect photocatalytic reduction of arsenate to arsenite in aqueous solution with TiO₂ in the presence of hole scavengers, *Chinese Journal of Chemical Engineering*, 26(3) (2018) 529-33. <https://doi.org/10.1016/j.cjche.2017.05.019>
- [48] N. Shao, S. Li, F. Yan, Y. Su, F. Liu, Z. Zhang, An all-in-one strategy for the adsorption of heavy metal ions and photodegradation of organic pollutants using steel slag-derived calcium silicate hydrate. *Journal of hazardous materials*, 382 (2020) 121120. <https://doi.org/10.1016/j.jhazmat.2019.121120>
- [49] B. Thomas, L.K. Alexander Removal of Pb²⁺ and Cd²⁺ toxic heavy metal ions driven by Fermi level modification in NiFe₂O₄–Pd nano hybrids, *Journal of Solid-State Chemistry*, (2020) 121417. <https://doi.org/10.1016/j.jssc.2020.121417>
- [50] Y. Li, W. Cui, L. Liu, R. Zong, W. Yao, Removal of Cr (VI) by 3D TiO₂-graphene hydrogel via adsorption enriched with photocatalytic reduction, *Applied Catalysis B: Environmental*, 199 (2016) 412-423. <https://doi.org/10.1016/j.apcatb.2016.06.053>
- [51] H. Zhang, X. Wang, N. Li, J. Xia, Q. Meng, Synthesis and characterization of TiO₂/graphene oxide nanocomposites for photoreduction of heavy metal ions in

reverse osmosis concentrate, RSC advances, 8 (2018) 34241-34251.

<https://doi.org/10.1039/C8RA06681G>

- [52] X. Wang, M. Lu, J. Ma, P. Ning, Preparation of air-stable magnetic g-C₃N₄@ Fe⁰-graphene composite by new reduction method for simultaneous and synergistic conversion of organic dyes and heavy metal ions in aqueous solution, Separation and Purification Technology, 1 (2019) 586-96.
<https://doi.org/10.1016/j.seppur.2018.11.052>
- [53] Y. Deng, Y. Xiao, Y. Zhou, T. Zeng, M. Xing, J. Zhang, A structural engineering-inspired CdS based composite for photocatalytic remediation of organic pollutant and hexavalent chromium, Catalysis Today, 335 (2019) 101-109.
<https://doi.org/10.1016/j.cattod.2018.09.012>
- [54] F. He, Z. Lu, M. Song, X. Liu, H. Tang, P. Huo, W. Fan, H. Dong, X. Wu, S. Han, Selective reduction of Cu²⁺ with simultaneous degradation of tetracycline by the dual channels ion imprinted POPD-CoFe₂O₄ heterojunction photocatalyst, Chemical Engineering Journal, 369 (2019) 750-61. <https://doi.org/10.1016/j.cej.2018.12.034>
- [55] J. Ayawanna, W. Teoh, S. Niratisairak, K. Sato, Gadolinia-modified ceria photocatalyst for removal of lead (II) ions from aqueous solutions, Materials Science in Semiconductor Processing, 40 (2015) 136-9.
<https://doi.org/10.1016/j.mssp.2015.06.058>
- [56] A. Samad, M. Furukawa, H. Katsumata, T. Suzuki, S. Kaneco, Photocatalytic oxidation and simultaneous removal of arsenite with CuO/ZnO photocatalyst, Journal of Photochemistry and Photobiology A: Chemistry, 325 (2016) 97-103.
<https://doi.org/10.1016/j.jphotochem.2016.03.035>
- [57] P. Dhiman, S. Sharma, A. Kumar, M. Shekh, G. Sharma, M. Naushad, Rapid visible and solar photocatalytic Cr (VI) reduction and electrochemical sensing of dopamine using solution combustion synthesized ZnO-Fe₂O₃ nano heterojunctions: mechanism Elucidation, Ceramics International, 2020.
<https://doi.org/10.1016/j.ceramint.2020.01.275>
- [58] W. Zhao, J. Li, T. She, S. Ma, Z. Cheng, G. Wang, P. Zhao, W. Wei, D. Xia, D.Y. Leung, Study on the Photocatalysis Mechanism of the Z-Scheme Cobalt Oxide Nanocubes/Carbon Nitride Nanosheets Heterojunction Photocatalyst with High Photocatalytic Performances, Journal of Hazardous Materials, 402 (2020) 123839.
<https://doi.org/10.1016/j.jhazmat.2020.123839>
- [59] X. Zhao, Y. Zhang, Y. Zhao, H. Tan, Z. Zhao, H. Shi, E. Wang, Y. Li, Ag_x H_{3-x} PMo₁₂ O₄₀/Ag nanorods/gC₃N₄ 1D/2D Z-scheme heterojunction for highly efficient

- visible-light photocatalysis, Dalton Transactions, 48(19) (2019) 6484-91.
<https://doi.org/10.1039/C9DT00744J>
- [60] T. Jia, J. Wu, J. Song, Q. Liu, J. Wang, Y. Qi, P. He, X. Qi, L. Yang, P. Zhao, In situ self-growing 3D hierarchical BiOBr/BiOIO₃ Z-scheme heterojunction with rich oxygen vacancies and iodine ions as carriers transfer dual-channels for enhanced photocatalytic activity, Chemical Engineering Journal, (2020) 125258.
<https://doi.org/10.1016/j.cej.2020.125258>
- [61] Y. Hou, S. Pu, Q. Shi, S. Mandal, H. Ma, S. Xue, G. Cai, Y. Bai, Ultrasonic impregnation assisted in-situ photoreduction deposition synthesis of Ag/TiO₂/rGO ternary composites with synergistic enhanced photocatalytic activity, Journal of the Taiwan Institute of Chemical Engineers, 104 (2019) 139-150.
<https://doi.org/10.1016/j.jtice.2019.08.023>
- [62] C. Li, G. Zhao, T. Zhang, T. Yan, C. Zhang, A novel Ag@ TiON/CoAl-layered double hydroxide photocatalyst with enhanced catalytic memory activity for removal of organic pollutants and Cr (VI), Applied Surface Science, 504 (2020) 144352.
<https://doi.org/10.1016/j.apsusc.2019.144352>
- [63] H. Liang, T. Li, J. Zhang, D. Zhou, C. Hu, X. An, R. Liu, Liu H., 3-D hierarchical Ag/ZnO@ CF for synergistically removing phenol and Cr (VI): Heterogeneous vs. homogeneous photocatalysis, Journal of colloid and interface science, 558 (2020) 85-94. <https://doi.org/10.1016/j.jcis.2019.09.105>
- [64] G. Li, Y. Wu, M. Zhang, B. Chu, W. Huang, Enhanced Removal of Toxic Cr (VI) in Wastewater by Synthetic TiO₂/g-C₃N₄ Microspheres/rGO Photocatalyst under Irradiation of Visible Light, Industrial & Engineering Chemistry Research, 58 (2019) 8979-8989. <https://doi.org/10.1021/acs.iecr.8b05990>
- [65] D. Zhao, T. Wu, Y. Zhou, Dual II heterojunctions metallic phase MoS₂/ZnS/ZnO ternary composite with superior photocatalytic performance for removing contaminants, Chemistry—A European Journal, 41 (2019) 9710-20.
<https://doi.org/10.1002/chem.201901715>
- [66] R. Yang, Z. Zhu, C. Hu, S. Zhong, L. Zhang, B. Liu, W. Wang, One-step preparation (3D/2D/2D) BiVO₄/FeVO₄@rGO heterojunction composite photocatalyst for the removal of tetracycline and hexavalent chromium ions in water, Chemical Engineering Journal, 390 (2020) 124522. <https://doi.org/10.1016/j.cej.2020.124522>
- [67] R. Yang, S. Zhong, L. Zhang, Liu B., PW₁₂/CN@ Bi₂WO₆ composite photocatalyst prepared based on organic-inorganic hybrid system for removing pollutants in water, Separation and Purification Technology, 235 (2020) 116270.
<https://doi.org/10.1016/j.seppur.2019.116270>

- [68] T. Jia, K. Xu, J. Wu, Q. Liu, Y. Lin, M. Gu, F. Tian, W. Pan, J. Wu, Y. Xiao, Constructing 2D BiOIO₃/MoS₂ Z-scheme heterojunction wrapped by C500 as charge carriers transfer channel: enhanced photocatalytic activity on gas-phase heavy metal oxidation, *Journal of Colloid and Interface Science* (2019). <https://doi.org/10.1016/j.jcis.2019.11.100>
- [69] F. Chen, C. Yu, L. Wei, Q. Fan, F. Ma, J. Zeng, J. Yi, K. Yang, H. Ji, Fabrication and characterization of ZnTiO₃/Zn₂Ti₃O₈/ZnO ternary photocatalyst for synergetic removal of aqueous organic pollutants and Cr (VI) ions, *Science of The Total Environment*, 706 (2020) 136026. <https://doi.org/10.1016/j.scitotenv.2019.136026>
- [70] S. Nayak, K.M. Parida, Dynamics of charge-transfer behavior in a plasmon-induced quasi-type-II p–n/n–n dual heterojunction in Ag@Ag₃PO₄/g-C₃N₄/NiFe LDH nanocomposites for photocatalytic Cr (VI) reduction and phenol oxidation, *ACS omega*, 3 (2018) 7324-7343. <https://doi.org/10.1021/acsomega.8b00847>
- [71] A. Kumar, S.K. Sharma, G. Sharma, M. Naushad, F.J. Stadler, CeO₂/g-C₃N₄/V₂O₅ ternary nano hetero-structures decorated with CQDs for enhanced photo-reduction capabilities under different light sources: Dual Z-scheme mechanism, *Journal of Alloys and Compounds*, 2020 155692. <https://doi.org/10.1016/j.jallcom.2020.155692>
- [72] D. Yang, X. Zhao, X. Zou, Z. Z. Zhou, Jiang. Removing Cr (VI) in water via visible-light photocatalytic reduction over Cr-doped SrTiO₃ nanoplates. *Chemosphere* 215 (2019) 586-595. <https://doi.org/10.1016/j.chemosphere.2018.10.068>
- [73] C. Yu, D. Zeng, O. Fan, K. Yang, J. Zeng, L. Wei, J. Yi, H. Ji, The distinct role of boron doping in Sn₃ O₄ microspheres for synergistic removal of phenols and Cr (vi) in simulated wastewater. *Environmental Science: Nano*, 1 (2020) 286-303. <https://doi.org/10.1039/C9EN00899C>
- [74] Y.C. Zhou, P. Wang, H. Fu, C. Zhao, C.C. Wang., Ternary Ag/Ag₃PO₄/MIL-125-NH₂ Z-scheme heterojunction for boosted photocatalytic Cr (VI) cleanup under visible light. *Chinese Chemical Letters*. (2020)25. <https://doi.org/10.1016/j.cclet.2020.02.048>
- [75] Liu W, Zhao X, Borthwick AG, Wang Y, Ni J. Dual-enhanced photocatalytic activity of Fe-deposited titanate nanotubes used for simultaneous removal of As (III) and As (V). *ACS Appl. Mater Interfaces* 2015; 7: 19726-19735. <https://doi.org/10.1021/acsami.5b05263>
- [76] Zhao, D. and Cai, C., 2020. Preparation of Bi₂MoO₆/Ti₃C₂ MXene Heterojunction Photocatalyst for Fast Tetracycline Degradation and Cr (VI) Reduction. *Inorganic Chemistry Frontiers*. <https://doi.org/10.1039/D0QI00540A>
- [77] Jia, T., Wu, J., Song, J., Liu, Q., Wang, J., Qi, Y., He, P., Qi, X., Yang, L. and Zhao, P., 2020. In situ self-growing 3D hierarchical BiOBr/BiOIO₃ Z-scheme heterojunction

- with rich oxygen vacancies and iodine ions as carriers transfer dual-channels for enhanced photocatalytic activity. *Chemical Engineering Journal*, p.125258.
<https://doi.org/10.1016/j.cej.2020.125258>
- [78] Yi XH, Wang FX, Du XD, Fu H, Wang CC. Highly efficient photocatalytic Cr (VI) reduction and organic pollutants degradation of two new bifunctional 2D Cd/Co-based MOFs. *Polyhedron* 2018; 152: 216-24. <https://doi.org/10.1016/j.poly.2018.06.041>
- [79] Li C, Zhao G, Zhang T, Yan T, Zhang C et al. A novel Ag@TiON/CoAl-layered double hydroxide photocatalyst with enhanced catalytic memory activity for removal of organic pollutants and Cr (VI). *Appl Surf Sci* 2020; 504: 144352.
<https://doi.org/10.1016/j.apsusc.2019.144352>
- [80] Zhang, B. Zhang, Y. Jiang, Y. Xiao, W. Zhang, H. Xu, X. Yang, Z. Liu, Zhang J. In-situ constructing of one-dimensional SnIn₄S₈-CdS core-shell heterostructure as a direct Z-scheme photocatalyst with enhanced photocatalytic oxidation and reduction capabilities, *Appl Surf Sci* 2021; 148618. <https://doi.org/10.1016/j.apsusc.2020.148618>
- [81] P. Karthik, R. Vinoth, S.G. Babu, M. Wen, T. Kamegawa, H. Yamashita, B. Neppolian, Synthesis of highly visible light active TiO₂-2-naphthol surface complex and its application in photocatalytic chromium (vi) reduction, *RSC Advances*, 50 (2015)39752-9. <https://doi.org/10.1039/C5RA03831F>
- [82] D. Majhi, K. Das, R. Bariki, S. Padhan, A. Mishra, R. Dhiman, P. Dash, B. Nayak, B.G. Mishra, A facile reflux method for in situ fabrication of a non-cytotoxic Bi₂S₃/β-Bi₂O₃/ZnIn₂S₄ ternary photocatalyst: a novel dual Z-scheme system with enhanced multifunctional photocatalytic activity, *Journal of Materials Chemistry A*, 41 (2020) 21729-43. <https://doi.org/10.1039/D0TA06129H>
- [83] P. Wang, D. Sun, M. Deng, S. Zhang, Q. Bi, W. Zhao, F. Huang, Amorphous phosphated titanium oxide with amino and hydroxyl bifunctional groups for highly efficient heavy metal removal, *Environmental Science: Nano*, 4 (2020)1266-74.
<https://doi.org/10.1039/C9EN01466G>
- [84] B. Ou, J. Wang, Y. Wu, S. Zhao, Z., Wang Efficient removal of Cr (VI) by magnetic and recyclable calcined CoFe-LDH/g-C₃N₄ via the synergy of adsorption and photocatalysis under visible light. *Chemical Engineering Journal*, 380 (2020) 122600.
<https://doi.org/10.1016/j.cej.2019.122600>
- [85] X. Bai, Y. Du, W. Xue, X. Hu, J. Fan, J. Li, E. Liu, Enhancement of the photocatalytic synchronous removal of Cr (vi) and RhB over RP-modified flower-like SnS₂. *Nanoscale Advances*, 9 (2020) 4220-8. <https://doi.org/10.1039/D0NA00489H>
- [86] X. Liu, M. Liu, L. Zhang, Co-adsorption and sequential adsorption of the co-existence four heavy metal ions and three fluoroquinolones on the functionalized

- ferromagnetic 3D NiFe_2O_4 porous hollow microsphere, *Journal of colloid and interface science*, 511 (2018)135-44. <https://doi.org/10.1016/j.jcis.2017.09.105>
- [87] D.P. Sounthararajah, P. Loganathan, J. Kandasamy, S. Vigneswaran, Effects of humic acid and suspended solids on the removal of heavy metals from water by adsorption onto granular activated carbon, *International Journal of Environmental Research and Public Health*, (2015) 10475-89. <https://doi.org/10.3390/ijerph120910475>
- [88] M.M. Rahman, M. Adil, A.M. Yusof, Y.B..Kamaruzzaman, R.H. Ansary, Removal of heavy metal ions with acid activated carbons derived from oil palm and coconut shells, *Materials*, 7(5) 2014 3634-50. <https://doi.org/10.3390/ma7053634>
- [89] M.N. Sahmoune, A.R. Yeddou, Potential of sawdust materials for the removal of dyes and heavy metals: examination of isotherms and kinetics, *Desalination and Water Treatment*, 57(50) (2016) 24019-34. <https://doi.org/10.1080/19443994.2015.1135824>
- [90] J. Hizal, E. Tutem, K. Guclu, M. Hugul, S. Ayhan, R. Apak, F.Kilincakale, Heavy metal removal from water by red mud and coal fly ash: an integrated adsorption–solidification/stabilization process, *Desalination and water treatment*, 51(37-39) (2013) 7181-93. <https://doi.org/10.1080/19443994.2013.771289>
- [91] Z. Yang, X. Huang, X. Yao, H. Ji, Thiourea modified hyper-crosslinked polystyrene resin for heavy metal ions removal from aqueous solutions, *Journal of Applied Polymer Science*, 135(1) (2018) 45568. <https://doi.org/10.1002/app.45568>
- [92] C. Zhang, J. Sui, J. Li, Y. Tang, W. Cai, Efficient removal of heavy metal ions by thiol-functionalized superparamagnetic carbon nanotubes, *Chemical Engineering Journal*, 210 (2012) 45-52. <https://doi.org/10.1016/j.cej.2012.08.062>
- [93] Zhang Y., Zhang S., Chung T.S. Nanometric graphene oxide framework membranes with enhanced heavy metal removal via nanofiltration, *Environmental science & technology*, 49(16) (2015) 10235-42. <https://doi.org/10.1021/acs.est.5b02086>
- [94] S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, *Chemical engineering journal*, 156(1) (2010) 11-24. <https://doi.org/10.1016/j.cej.2009.10.029>
- [95] E.B. Son, K.M. Poo, J.S. Chang, K.J. Chae, Heavy metal removal from aqueous solutions using engineered magnetic biochars derived from waste marine macro-algal biomass, *Science of the Total Environment*, 615 (2018) 161-168. <https://doi.org/10.1016/j.scitotenv.2017.09.171>
- [96] M.F. Brigatti, C. Lugli, L. Poppi, Kinetics of heavy-metal removal and recovery in sepiolite, *Applied Clay Science*, 16 (2000) 45-57. [https://doi.org/10.1016/S0169-1317\(99\)00046-0](https://doi.org/10.1016/S0169-1317(99)00046-0)

- [97] X. Zhang, Y. Qin, G. Zhang, Y. Zhao, C. Lv, X. Liu, L. Chen, Preparation of PVDF/hyperbranched-nano-palygorskite composite membrane for efficient removal of heavy metal ions, *Polymers*, 11 (2019) 156. <https://doi.org/10.3390/polym11010156>
- [98] Y. Kim, J. Yi, Advances in environmental technologies via the application of mesoporous materials, *Journal of Industrial and Engineering Chemistry*, 10 (2004) 41-51.
- [99] J. Wang, P. Wang, H. Wang, J. Dong, W. Chen, Preparation of molybdenum disulfide coated Mg/Al layered double hydroxide composites for efficient removal of chromium (VI), *ACS Sustainable Chemistry & Engineering*, 5 (2017) 7165-7174. <https://doi.org/10.1021/acssuschemeng.7b01347>
- [100] J. Chen, N. Wang, Y. Liu, J. Zhu, J. Feng, W. Yan, Synergetic effect in a self-doping polyaniline/TiO₂ composite for selective adsorption of heavy metal ions, *Synthetic Metals*, 245 (2018) 32-41. <https://doi.org/10.1016/j.synthmet.2018.08.006>
- [101] M. Maiti, M. Sarkar, M.A. Malik, S. Xu, Q. Li, S. Mandal, Iron oxide NPs facilitated a smart building composite for heavy-metal removal and dye degradation, *ACS Omega*, 3 (2018) 1081-1089. <https://doi.org/10.1021/acsomega.7b01545>
- [102] W. Zhang, S. Shi, W. Zhu, C. Yang, S. Li, In-situ fixation of all-inorganic Mo-Fe-S clusters for the highly selective removal of lead (II), *ACS Applied Materials & Interfaces* 9 (2017) 32720-32726. <https://doi.org/10.1021/acsami.7b08967>
- [103] X. Li, C. Bian, X. Meng, F.S. Xiao, Design and synthesis of an efficient nanoporous adsorbent for Hg²⁺ and Pb²⁺ ions in water, *Journal of Materials Chemistry A*, 4(16) (2016) 5999-6005. <https://doi.org/10.1039/C6TA00987E>
- [104] M. Musielak, A. Gagor, B. Zawisza, E. Talik, R. Sitko, Graphene Oxide/Carbon Nanotube Membranes for Highly Efficient Removal of Metal Ions from Water, *ACS Applied Materials & Interfaces*, 11.31 (2019) 28582-28590. <https://doi.org/10.1021/acsami.9b11214>
- [105] J. Hao, L. Ji, C. Li, C. Hu, K. Wu, Rapid, efficient and economic removal of organic dyes and heavy metals from wastewater by zinc-induced in-situ reduction and precipitation of graphene oxide, *Journal of the Taiwan Institute of Chemical Engineers*, 88 (2018) 137-145. <https://doi.org/10.1016/j.jtice.2018.03.045>
- [106] G. Ognibene, D.A. Cristaldi, R. Fiorenza, I. Blanco, G. Cicala, Photoactivity of hierarchically nanostructured ZnO-PES fibre mats for water treatments, *RSC advances*, 6 (2016) 42778-42785. <https://doi.org/10.1039/C6RA06854E>
- [107] D. Mauc̆ec, A. Šuligoj, A. Ristic, G. Dražic, A. Pintar, N.N. Tušar, Titania versus zinc oxide nanoparticles on mesoporous silica supports as photocatalysts for removal

- of dyes from wastewater at neutral pH, *Catalysis Today*, 310 (2018) 32–41.
<https://doi.org/10.1016/j.cattod.2017.05.061>
- [108] K. Naseem, R. Begum, W. Wu, M. Usman, A. Irfan, Adsorptive removal of heavy metal ions using polystyrene-poly (N-isopropylmethacrylamide-acrylic acid) core/shell gel particles: adsorption isotherms and kinetic study. *Journal of Molecular Liquids*, 277 (2019) 522-531. <https://doi.org/10.1016/j.molliq.2018.12.054>
- [109] D.M. Guo, Q.D. An, Z.Y. Xiao, S.R. Zhai, D.J. Yang, Efficient removal of Pb (II), Cr (VI) and organic dyes by polydopamine modified chitosan aerogels, *Carbohydrate polymers*, 202 (2018) 306–314. <https://doi.org/10.1016/j.carbpol.2018.08.140>
- [110] R. Li, L. Liu, F. Yang, Preparation of polyaniline/reduced graphene oxide nanocomposite and its application in adsorption of aqueous Hg (II), *Chemical Engineering Journal*, 229 (2013) 460-468. <https://doi.org/10.1016/j.cej.2013.05.089>
- [111] R. Gusain, N. Kumar, E. Fosso-Kankeu, S.S. Ray. Efficient removal of Pb (II) and Cd (II) from industrial mine water by a hierarchical MoS₂/SH-MWCNT nanocomposite. *ACS omega* 4 (9) (2019) 13922-13935.
<https://doi.org/10.1021/acsomega.9b01603>
- [112] A. Fateeva, P.A. Chater, C.P. Ireland, A.A. Tahir, Y.Z. Khimyak, A Water-Stable Porphyrin-Based Metal–Organic Framework Active for Visible-Light Photocatalysis, *Angewandte Chemie International Edition*, 124 (2012) 7558-7562.
<https://doi.org/10.1002/ange.201202471>
- [113] X. Wang, C. Yang, S. Zhu, M. Yan, S. Ge, J. Yu, 3D origami electrochemical device for sensitive Pb²⁺ testing based on DNA functionalized iron-porphyrinic metal-organic framework, *Biosensors and Bioelectronics*, 87 (2017) 108-115.
<https://doi.org/10.1016/j.bios.2016.08.016>
- [114] Z.S. Hasankola, R. Rahimi, H. Shayegan, E. Moradi, V., Safarifard, Removal of Hg²⁺ heavy metal ion using a highly stable mesoporous porphyrinic zirconium metal-organic framework, *Inorganica Chimica Acta* 501, (2020) 1192649.
<https://doi.org/10.1016/j.ica.2019.119264>
- [115] Y. Wang, G. Ye, H. Chen, X. Hu, Z. Niu, S. Ma, Functionalized metal–organic framework as a new platform for efficient and selective removal of cadmium (II) from aqueous solution, *Journal of Materials Chemistry A*, 3 (2015) 15292-8.
<https://doi.org/10.1039/C5TA03201F>
- [116] D. Li, X. Tian, Z. Wang, Z. Guan, X. Li, H. Qiao, H. Ke, L. Luo, Q. Wei, Multifunctional adsorbent based on metal-organic framework modified bacterial cellulose/chitosan composite aerogel for high efficient removal of heavy metal ion and

- organic pollutant, *Chemical Engineering Journal*, 383 (2020) 123127.
<https://doi.org/10.1016/j.cej.2019.123127>
- [117] K. Zargoosh, H. Abedini, A. Abdolmaleki, M.R. Molavian, Effective removal of heavy metal ions from industrial wastes using thiosalicylhydrazide-modified magnetic nanoparticles, *Industrial & Engineering Chemistry Research* 52, (2013) 14944-14954.
<https://doi.org/10.1021/ie401971w>
- [118] H. Zhou, H. Zhu, F. Xue, H. He, Wang S., Cellulose-based amphoteric adsorbent for the complete removal of low-level heavy metal ions via a specialization and cooperation mechanism, *Chemical Engineering Journal*, (2019) 123879.
<https://doi.org/10.1016/j.cej.2019.123879>
- [119] J. Ma, G. Zhou, L. Chu, Y. Liu, C. Liu, S. Luo, Y. Wei, Efficient removal of heavy metal ions with an EDTA functionalized chitosan/polyacrylamide double network hydrogel, *ACS Sustainable Chemistry & Engineering*, 5 (2016) 843-851.
<https://doi.org/10.1021/acssuschemeng.6b02181>
- [120] F. Wang, G. Li, B. Shen, Y. Wang C. He, Mercury removal over the vanadia–titania catalyst in CO₂-enriched conditions, *Chemical Engineering Journal*, 263 (2015) 356-63. <https://doi.org/10.1016/j.cej.2014.10.091>
- [121] Y. Fang, X. Lv, X. Xu, J. Zhu, P. Liu, L. Guo, C. Yuan, B. Cui., Three-dimensional nanoporous starch-based material for fast and highly efficient removal of heavy metal ions from wastewater, *International Journal of Biological Macromolecules*, 164 (2020) 415-26. <https://doi.org/10.1016/j.ijbiomac.2020.07.017>
- [122] H. Jiang, Y. Yang, Z. Lin, B. Zhao, J. Wang, J. Xie, A. Zhang., Preparation of a novel bio-adsorbent of sodium alginate grafted polyacrylamide/graphene oxide hydrogel for the adsorption of heavy metal ion, *Science of The Total Environment*, 744 (2020) 140653. <https://doi.org/10.1016/j.scitotenv.2020.140653>
- [123] C Z. Zhang, H. Sheng, Y X. Su, J Q. Xu., An efficient and health-friendly adsorbent N-[4-morpholinecarboximidamidoyl] carboximidamidoylmethylated polyphenylene sulfide for removing heavy metal ions from water, *Journal of Molecular Liquids*, 296 (2019) 111860. <https://doi.org/10.1016/j.molliq.2019.111860>
- [124] MS. Islam, W. San Choi, B. Nam, C. Yoon, H J. Lee., Needle-like iron oxide@CaCO₃ adsorbents for ultrafast removal of anionic and cationic heavy metal ions, *Chemical Engineering Journal*, 307 (2017) 208-19.
<https://doi.org/10.1016/j.cej.2016.08.079>
- [125] Q. Tang, K. Wang, J. Su, Y. Shen, S. Yang, Y. Ge, X. Cui., Facile fabrication of inorganic polymer microspheres as adsorbents for removing heavy metal ions,

Materials Research Bulletin, 113 (2019) 202-8.

<https://doi.org/10.1016/j.materresbull.2019.02.009>

- [126] P. Kulal, V. Badalamoole. Efficient removal of dyes and heavy metal ions from waste water using Gum ghatti-graft-poly (4-acryloylmorpholine) hydrogel incorporated with magnetite nanoparticles, Journal of Environmental Chemical Engineering, 8 (2020) 104207. <https://doi.org/10.1016/j.jece.2020.104207>
- [127] Q. Huang, D. Hu, M. Chen, C. Bao, X. Jin., Sequential removal of aniline and heavy metal ions by jute fiber biosorbents: A practical design of modifying adsorbent with reactive adsorbate, Journal of Molecular Liquids, 285 (2019) 288-98. <https://doi.org/10.1016/j.molliq.2019.04.115>
- [128] S. Yan, F. Zhang, Wang. L, Y. Rong, P. He, D. Jia, J. Yang., A green and low-cost hollow gangue microsphere/geopolymer adsorbent for the effective removal of heavy metals from wastewaters. Journal of environmental management, 246 (2019) 174-83. <https://doi.org/10.1016/j.jenvman.2019.05.120>
- [129] S. Ma, Q. Chen, H. Li, P. Wang, S.M. Islam, Q. Gu, X. Yang., M.G Kanatzidis. Highly selective and efficient heavy metal capture with polysulfide intercalated layered double hydroxides, Journal of Materials Chemistry A, 2(2014) 10280-9. <https://doi.org/10.1039/C4TA01203H>
- [130] A. Heidari, H. Younesi, Z. Mehraban., Removal of Ni (II), Cd (II), and Pb (II) from a ternary aqueous solution by amino functionalized mesoporous and nano mesoporous silica, Chemical Engineering Journal, 153 (2009) 70-9. <https://doi.org/10.1016/j.ccej.2009.06.016>
- [131] T.A. Salah, A.M. Mohammad, M.A. Hassan, B.E. E.l-Anadouli, Development of nano-hydroxyapatite/chitosan composite for cadmium ions removal in wastewater treatment, Journal of the Taiwan Institute of Chemical Engineers, 4 (2014) 1571-7. <https://doi.org/10.1016/j.jtice.2013.10.008>
- [132] J. Zhang, J. Han, M. Wang, R. Guo., Fe₃O₄/PANI/MnO₂ core-shell hybrids as advanced adsorbents for heavy metal ions, Journal of Materials Chemistry A, 5(8) (2017) 4058-66. <https://doi.org/10.1039/C6TA10499A>
- [133] EJ. Kim, CS. Lee, YY. Chang, YS. Chang., Hierarchically structured manganese oxide-coated magnetic nanocomposites for the efficient removal of heavy metal ions from aqueous systems, ACS applied materials & interfaces, 5(19) (2013) 9628-34. <https://doi.org/10.1021/am402615m>
- [134] Y. Wang, S. Liang, B. Chen, F. Guo, S. Yu, Y. Tang., Synergistic removal of Pb (II), Cd (II) and humic acid by Fe₃O₄@ mesoporous silica-graphene oxide composites, PloS one, 8(6) (2013) 65634. <https://doi.org/10.1371/journal.pone.0065634>

- [135] C. Zhou, H. Zhu, Q. Wang, J. Wang, J. Cheng, Y. Guo, X. Zhou, R. Bai., Adsorption of mercury (II) with an Fe₃O₄ magnetic polypyrrole–graphene oxide nanocomposite, *RSC advances*, 7(30) (2017) 18466-79. <https://doi.org/10.1039/C7RA01147D>
- [136] A.E. Chávez-Guajardo, J.C. Medina-Llamas, L. Maqueira, C.A. Andrade, K.G. Alves, C.P. de Melo., Efficient removal of Cr (VI) and Cu (II) ions from aqueous media by use of polypyrrole/maghemite and polyaniline/maghemite magnetic nanocomposites, *Chemical Engineering Journal*, 281 (2015) 826-36. <https://doi.org/10.1016/j.cej.2015.07.008>
- [137] L. Cui, X. Guo, Q. Wei, Y. Wang, L. Gao, L. Yan, T. Yan, B. Du., Removal of mercury and methylene blue from aqueous solution by xanthate functionalized magnetic graphene oxide: sorption kinetic and uptake mechanism, *Journal of colloid and interface science*, 439 (2015) 112-20. <https://doi.org/10.1016/j.jcis.2014.10.019>
- [138] HK. Moghaddam, M. Pakizeh., Experimental study on mercury ions removal from aqueous solution by MnO₂/CNTs nanocomposite adsorbent, *Journal of Industrial and Engineering Chemistry*, 21 (2015) 221-9. <https://doi.org/10.1016/j.jiec.2014.02.028>
- [139] K. Yaghmaeian, RK. Mashizi, S. Nasser, AH. Mahvi, M. Alimohammadi, S. Nazmara., Removal of inorganic mercury from aquatic environments by multi-walled carbon nanotubes, *Journal of Environmental Health Science and Engineering*, 13(1) (2015) 55. <https://doi.org/10.1186/s40201-015-0209-8>
- [140] Y. Guo, J. Deng, J. Zhu, X. Zhou, R. Bai., Removal of mercury (II) and methylene blue from a wastewater environment with magnetic graphene oxide: adsorption kinetics, isotherms and mechanism. *RSC Advances*, 6 (2016) 82523-36. <https://doi.org/10.1039/C6RA14651A>