Academic Journal of Environment & Earth Science
ISSN 2616-5872 Vol.5, Issue 3: 13-20, DOI: 10.25236/AJEE.2023.050303

Research on Novel Heavy Metal Wastewater Treatment Methods

Wang Funan*

Department of Resources and Environment, Guangdong Ocean University, Zhanjiang, China
1575961567@qq.com
**Corresponding author*

Abstract: *Heavy metals are frequently present in industrial effluent, and their excess can be detrimental to human health. Therefore, industrial wastewater needs to be treated before it can be discharged. Key solutions for the treatment of heavy metal wastewater are analyzed and evaluated based on existing research, taking into account elements like removal effectiveness, cost, ease of recycling, and number of reuses. This paper introduces two conventional and three novel heavy metal removal technologies are presented. The fundamental ideas, ideal circumstances, benefits, and drawbacks of each technology are summarized, along with a prediction of future technical developments. Although nanosorbents and microbial fuel cells are very efficient, their expenses are expensive. Membrane technology has a wide range of potential applications and is a great choice for the removal of heavy metals when combined with other technologies. Future wastewater treatment for heavy metals has a bright future thanks to all of these technologies.*

Keywords: *heavy metal wastewater, nanosorbent materials, microbial fuel cells, membrane separation technology*

1. Introduction

Heavy metals are very toxic, bioconcentrate quickly, and degrade slowly in the environment.[1] Industrial wastewater frequently contains heavy metals including cadmium (Cd), arsenic (As), chromium (Cr), copper (Cu), zinc (Zn), mercury (Hg), lead (Pb), etc.[2] As a result, the vast majority of industrial effluent must be treated before being discharged. If wastewater containing heavy metals is not treated using appropriate technology, the level of heavy metals will rise over acceptable levels, endangering the health of all species, including humans. Zhou Qiaoqiao et al.[3] found that the concentrations of heavy metals in dissolved cadmium, zinc and arsenic in river and lake waters in China showed an increasing trend between 1980 and 2016; Jian Yantao et al.[4] investigated that the current heavy metal content in lake water bodies showed a sharp increase. Heavy metal wastewater treatment has become a popular topic for research. The most generally used methods for removing heavy metals are chemical precipitation and traditional adsorption because they are both easy to use, adaptable, and affordable. However, traditional adsorption is less efficient and selective, while chemical precipitation results in toxic sludge.[5] Ion exchange and standard electrochemical techniques are among the conventional treatment procedures that have good removal efficiency and the ability to recover heavy metals, but both are expensive and create little sludge. [5-6] A number of researchers have carried out innovations and studies on new heavy metal removal technologies and combined processes, taking into account the influencing factors of the new technologies (e.g. temperature, pH, etc.), heavy metal recoverability, cost, removal efficiency, etc., and carried out experimental designs to produce evaluation results. This paper summarises several key technologies for the treatment of heavy metal wastewater and provides an outlook on their development trends, providing a theoretical basis and new ideas for future technological innovation.

2. Conventional heavy metal treatment technologies

2.1 Chemical precipitation method

Chemical precipitation is currently one of the most commonly used techniques in wastewater treatment applications due to its low cost and simplicity of operation. The basic principle is to remove heavy metals from wastewater by adding a precipitant that converts soluble heavy metal ions into precipitates.[7] Hu Yunjun et al.[8] investigated and compared the removal of Hg(II) by four trapping agents, sodium sulphide, calcium hydroxide, dithiocarbamates (DTCR-2) and 2,4,6-trithiolyl sodium thiotriazine (TMT-18B). The results of this experiment indicate that DTCR-2 was the most effective and the best removal of Hg (II) was achieved at pH 8 with a 10 minutes' reaction. In addition, Cu (II), Pb(II) and Cd(II) in the wastewater inhibited the removal of Hg(II), while Zn(II) promoted the removal of Hg(II). Shao Hongyan et al.[9] improved the sulfide, so the removal of Cd(II) from wastewater with Na_2S-$Al_2(SO_4)_3$-PAM system could reach 99.9%. Wang Junjie et al.[10] synthesized the heavy metal trap MBMIPA with mercaptoethylamine hydrochloride and m-phenylene dicarbonyl chloride. The removal for a single copper-containing wastewater could achieve 99.5%, while the removal for a single mercury-containing wastewater achieved 99.83% .

2.2 Traditional adsorption methods

The key to adsorption is the adsorbent. There are two main forms of adsorption: physical and chemical. The basic idea is that adsorbents with large specific surface area or unique functional groups absorb heavy metal ions in water.[11] Some studies have shown that peanut shells can adsorb Cu (II), Pb (II), Cd (II), Ni(II) and Cr(III) in wastewater. By comparison, the peanut shells were found to adsorb the largest amount of Pb (II) at 32.25 mg/g[12] . Pingxiao Wu et al.[13] did a study which was conducted on modified iron montmorillonite. The results of this study showed that the adsorption of Cd (II) was enhanced by the modified iron montmorillonite compared to the original montmorillonite, and the adsorption of Cd (II) by iron montmorillonite increased with the increase of pH. Zhou Limin et al.[14] found that fly ash also had adsorption capacity for Cd(II) and Ni(II), and the adsorption efficiency of fly ash for heavy metal ions increased with increasing pH. The factors influencing the adsorption of adsorbents have been summarised in studies, mainly pH, adsorption time, initial heavy metal ion concentration and temperature[15-16] .

3. New heavy metal treatment technologies

3.1 Novel nanosorbent materials

Nanomaterials (NMs) are defined as a kind of materials with geometrical dimensions up to the nanoscale and with special properties.[17] Nanomaterials have a wide range of applications as new adsorbents in the treatment of heavy metal wastewater.[18] Nanomaterials are used in a variety of applications in heavy metal wastewater treatment. There are three types of nanomaterials used in heavy metal wastewater treatment: carbon-based nanomaterials, metal nanomaterials, and nanocomposites. [19] Nanomaterials are highly efficient and selective in removing pollutants from the environment, but they also have the disadvantages of poor stability, aggregation and repeatability.[5] By improving and innovating nanomaterials, we can improve their disadvantages and obtain better adsorbent materials to improve the removal efficiency of heavy metals.[20] The improvement and innovation of nanomaterials can lead to better adsorption materials and more efficient removal of heavy metals.

3.1.1 Carbon-based nanomaterials

Carbon based nanomaterials are available in various forms such as fullerenes, graphene (GR), carbon nanotubes (CNTs), carbon nanofibres, carbon black, etc. [19] Carbon nanotubes and graphene are commonly used in water treatment applications. Carbon nanotubes (CNTs) have a unique structure, high specific surface area and adsorption of some pollutants, and their use as adsorbents can remove heavy metal ions. However, it also has the disadvantages of poor dispersion, difficult reuse and limited adsorption capacity.[21] Therefore, researchers have modified carbon nanotubes to improve the adsorption effect of carbon nanotubes.[20] Zhang Zhikun introduced two kinds of metal oxides on the surface of carbon nanotubes, and calcined Mg-Al-CNTs and Mg-Fe-CNTs at high temperature. [22] The study concluded that the carbon nanotubes modified by the bimetallic oxides could be reused seven times, which greatly improved the reusability and the adsorption capacity of Cr(VI) compared to CNTs. Shitong Yang et al.[23] investigated the adsorption of oxidised multi-walled carbon nanotubes (MWCNTs) on Ni(II) at (20±2)°C, pH=6.4±0.1 and an initial Ni(II) concentration of 1.02×10^{-4} mol/L for 0.8 g/L, 1.0 g/L and 1.2 g/L of MWCNTs, respectively. This study found that as the mass of the multi-walled carbon nanotubes increased, the adsorption became better, but all reached adsorption equilibrium at 2 hour. The adsorption of oxidised carbon nanotubes was not only influenced by the mass of the carbon nanotubes but also by the pH value. Among them, the adsorption of Ni(II) by oxidized carbon nanotubes reached 90% at pH=8.6.[23] Xu Di et al.[24] found that the adsorption of Pb(II) by oxidised multi-walled CNTs was influenced by the pH value, with the pH value between 7 and 10 being the optimum condition and the maximum adsorption efficiency reaching 90%. Wang Zhongbing et al.[25] studied the multi-walled magnetic CNTs' selective adsorption of heavy metals in wastewater and found that they adsorbed Cd(II), Pb(II) and Cu(II). The material showed the best adsorption for Pb(II) with a maximum capacity of 215.05 mg/g. The adsorption of all three was most efficient at pH 6, and this modified adsorbent has magnetic properties that facilitate the subsequent recovery of heavy metals.

Graphene (GR) is a layered structure[26] with a large specific surface area.[27] It has good adsorption capacity, but is poorly dispersed as it contains fewer functional groups.[28] Graphene oxide (GO), a derivative of graphene, has an oxygen-containing functional group, which increases the hydrophilicity of GO and improves its dispersibility.[28] Guo Lijuan[29]found that the maximum adsorption capacity of modified graphene oxide material (TC-GO) reached 156.5 mg/g and 151.1 mg/g for Cu(II) and Cd(II), respectively, and the adsorption equilibrium was basically reached within two hours. The optimum pH value for GO's adsorption was about 7, while it was not greatly affected by temperature. Qiyu Lian et al.[30] studied the adsorption capacity of GOCS on Pb(II), and enhanced the adsorption capacity of GO on Pb(II) by modifying GO with carbon disulfide. The results of this experiment showed that when the concentration exceeded 800 mg/L, the maximum adsorption capacity of GOCS was 383.4 mg/g, which was 31% more than that of GO.

3.1.2 Metal nanomaterials and nanocomposites

The main metal nanomaterials used in water treatment are magnetic nanoparticles such as iron, cobalt, manganese, triiron tetroxide and ferrite.[31] Duan Zhengyang et al.[32] studied the application of magnetic Fe_3O_4 in heavy metal wastewater. Fe_3O_4 nanoparticles has great potential for application in removing heavy metals from wastewater due to the simplicity of preparation, high specific surface area and magnetic properties. It also has the advantage of using magnets for recycling in water. By preparing ferrite nanoparticles and conducting experimental investigations, Jing Hu et al.[33] found that the adsorption of $MnFe_2O_4$ reached adsorption equilibrium for Cr(VI) in 5 minutes at an optimum pH of 2, and the adsorption efficiency was as high as 99.5%. Compared with the adsorption efficiency of Fe_3O_4 nanoparticles on Cr(VI), the adsorption efficiency of $MnFe_2O_4$ was higher[33] .

Current developments in sorbent innovation support the combination of Fe_3O_4 nanoparticles or other kinds of materials to create new nanocomposites.[34] Yuzhe Shi et al.[35] investigated the application of heavy metal removal technology and found that catechin-functionalised Fe_3O_4 nanoparticles possess good adsorption capacity for Cu(II), Cd(II) and Pb(II). The study showed that the maximum adsorption efficiencies were 88.2%, 62.9% and 86.5% at an optimum pH of 8. Alaa E Alia et al.[20] synthesised a straw-cobalt ferrite nanocomposite (RS-CoFe2O4) which was a highly efficient new nanocomposite. The removal rates of Fe and Mn were 84.25% and 92.45%, respectively, while the removal rates of Cu, Cd, Pb, Ni and Zn were 100%. Yongxue Li et al.[36] synthesized a novel magnetic chitosan nanocomposite (MCS/GO-PEI) modified with graphene oxide and polyethyleneimine. The adsorbent displayed some repeatability and stability in use, with the best adsorption effects on arsenic and mercury ions at pH=7 and pH=9, respectively. The maximum adsorption levels were 220.26 mg/g and 124.84 mg/g, respectively.

3.2 Biotechnology

A microbial fuel cell (MFC) is a device that uses microorganisms as catalysts to oxidise inorganic and organic substances in the absence of oxygen and convert chemical energy into electrical energy.[37-40] Logan Bruce E et al.[41] noted that microbial fuel cell devices must periodically replenish the substrate of anodic oxidation in order to avoid being mistaken for a biological cell. Microbial fuel cells, in the opinion of Minghua Zhou et al.[42] , have a lot of potential for treating wastewater. MFC is classified into two types based on whether or not a proton exchange membrane exists: single-chamber MFC and double-chamber MFC.[43] A proton exchange membrane (PEM) is typically a membrane chosen to permit one proton (such as H^+) to pass through.[44] Double-chamber MFC is extensively utilized in heavy metal wastewater treatment. MFCs can be divided into three main categories based on their structure: plant microbial fuel cells (P-MFC)[45] the sediment microbial fuel cell (S-MFC)[46-47] and artificial wetland microbial fuel cells (CW-MFC).[48]

Mi-ax[43] simulates the treatment of Cu(II)-containing wastewater with dual-chamber MFC, and found that MFC treated Cu(II) wastewater in the micro-oxygen state (6-7 μmol/L dissolved oxygen) had better removal effect than in the anaerobic state. With the increase of the initial concentration of Cu(II), the removal effect of Cu(II) was better. However, this system showed competition between the two ions when treating mixed Cu(II) and Cr(VI) wastewater, which had an inhibitory effect on the heavy metal removal effect. The experiment also investigated the removal effect of heavy metals with different cathode materials, and the results showed that the removal effect of stainless steel sheet, titanium sheet and graphite plate increased in order. Wei Zhao et al.[49] Sun Caiyu et al.[51] simulated soybean product wastewater and traditional Chinese medicine wastewater as the anode substrate and cadmium-containing wastewater as the cathode solution respectively. The results showed that the Cd(II) removal rate was 84.6% and 74.0% respectively, i.e. the Cd(II) removal rate of the soybean product wastewater group was higher than that of the traditional Chinese medicine wastewater group. Wang Yian et al.[52] constructed the CW-MFC with a removal rate of up to 99% for Cr(VI) wastewater. Ding Guoqing et al.[53] concluded that the removal efficiency of CW-MFC for heavy metals was related to the material and particle size of the substrate, pH value, type and concentration of heavy metals, electrode material and redox potential gradient.

3.3 Membrane separation technology

The basic principle is to use membranes with selective permeability to prevent the passage of heavy metal ions under the action of external forces.[54-55] According to pore size and separation mechanism, membranes can be classified into: Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO) membranes.[56] Membrane separation technology has the advantages of simple operation, low cost, energy efficiency, environmental friendliness and no secondary pollution.[54] Ultrafiltration membranes are commonly used in this area. Studies have shown that membrane technology has achieved excellent results in the removal of heavy metals from wastewater. Generally heavy metal ions can only be captured in combination with water-soluble macromolecular polymers or other large complex metals, as shown in Figure 1.[57]

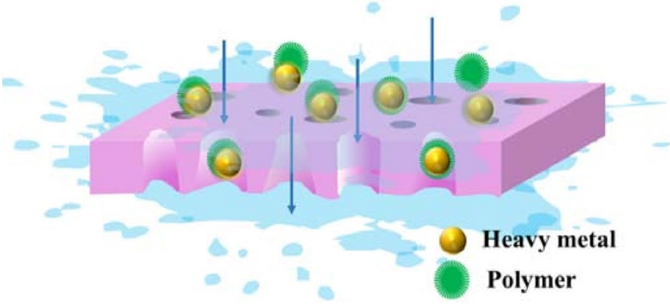

Figure 1: Schematic diagram of the principle of membrane separation

Zhou Rongzhong et al.[56] selected PVDF hollow fiber membrane to treat heavy metal wastewater. The experimental results show that the rate of membrane contamination decreases with increasing pumping stoppage time. Considering the the water production performance of the system, the optimum pumping stoppage ratio was 7 min:2 min. The experiment also concluded that an optimum aeration rate was $70m^3/(m^2 \cdot h)$, a maximum suspension concentration was 20 g/L and an optimum membrane flux was $0.5m^3/(m^2 \cdot d)$. Under the above optimum conditions, the removal rates of Cu(II) and Zn(II) by PVDF membrane reached 99.80% and 99.07% respectively. According to research by R. Molinari et al. [58], the removal efficiency of arsenic from wastewater by paired photocatalysis and complicated ultrafiltration might reach 100% at pH=7.56. A double-layer polybenzimidazole/polyethersulfone (PBI/PES) hollow fiber nanofiltration membrane was created by Wen-Ping Zhu et al.[59] to remove Cd(II) and Pb(II). According to the findings, under the ideal experimental circumstances, the clearance rates of Cd(II) and Pb(II) were over 95% and 93%, respectively. Jing Gao et al[60] recovered nickel from wastewater using complexation ultrafiltration with sodium polyacrylate (PAAS) as the complexing agent, with a final nickel recovery rate of 98.26%. When PAAS and polyethyleneimine are used as complexing agents, the effectiveness of extracting nickel from wastewater by complexing ultrafiltration is 99.5% and 93%, respectively [61] . The removal of Mn(II), Ni(II), Zn(II), and Cu(II) from wastewater can be increased to over 98.8% when PMA-100 is used in conjunction with a hollow fiber ultrafiltration membrane.[62] It is proved that the removal rate of Pb(II), Cd(II), Ni(II), Zn(II), and Cu(II) from wastewater by micellar enhanced ultrafiltration was over 99.0% . Rhamnolipid has a particularly high affinity for the heavy metals Cu(II), Pb(II), and Cd(II). The study showed the most optimal operating conditions are: transmembrane pressure of (69±2) kPa, molar ratio of biosurfactant to metal of approximately 2:1 (depending on metal type), temperature of (25±1) °C and pH of 6.9±0.1; the best removal of heavy metals could be achieved under optimal conditions[63].

4. Technology comparison

(1) Compared to previous technologies, microbial fuel cells are not only more effective in removing heavy metals, but they also produce power and make it easier to recover heavy metals. (2) Membrane separation technology is a method with high heavy metal removal efficiency and heavy metal recovery rate. (3) New adsorbents can be modified or compounded using magnetic nanoparticles (e.g. Fe_3O_4 particles) to make the adsorbent magnetic, which can also achieve the effect of easy recovery of heavy metals.

Because of this, coupling technologies, such as CW-MFC technology[53] or micelle enhanced ultrafiltration treatment technology[64] etc.,are often used in practical applications to improve the removal of heavy metals from wastewater.

5. Summary and prospect

This paper summarizes existing research on heavy metal treatment using chemical precipitation, conventional adsorption, nanosorbent materials, microbial fuel cells, and membrane separation. Nano-sorbent materials and microbial fuel cells are two novel technologies that are more efficient at removing heavy metals, but their high cost limits their widespread application. Membrane separation technologies are frequently combined with other technologies to achieve good heavy metal removal and are an excellent choice for heavy metal wastewater treatment.

References

[1] Dou Hongbin, Guo Wei. Heavy metal pollution and its harmful effects on soil and water[J]. Ecological Economy, 2022, 38(11):5-8.
[2] Chen Cheng, Chen Ming. The hazards and remediation of environmental heavy metal pollution[J]. Environmental Protection, 2010, No. 437(03):55-57.
[3] ZHOU Qiaoqiao, REN Bo, LI Youzhi, NIU Yandong, DING Xiaohui, YAO Xin, BIAN Hualin. Analysis of heavy metal pollution trends and sources in Chinese river and lake water bodies[J]. Environmental Chemistry, 2020, 39(08):2044-2054.
[4] Jian Yantao, Geng Hui, Shi Huiwen. Current status of heavy metal pollution in hydrogeological water bodies and measures to control it[J]. World Nonferrous Metals, 2020(17):194-195.
[5] Cao Wengeng, Wang Yan Yan, Zhang Dong, Sun Xiaoyue, Wen Aixin, Na Jing. Research status and progress of heavy metal removal technology for industrial wastewater[J/OL]. China Geology, 2023: 1-28.
[6] Liu Y. Research on the status and development trend of heavy metal wastewater treatment technology[J]. Leather Making and Environmental Protection Technology, 2020, 1(16):66-71.
[7] YANG X, LI Xinyu, ZHOU Juanping, JIANG Nanzhe. Research progress of wastewater treatment technology containing heavy metal ions[J/OL]. Materials Guide, 2023(09):1-19.
[8] HU Yunjun, SHENG Tiantian, XUE Xiaoqin, TAN Lisa, XU Xinhua. Study on the treatment of trace Hg (II) in water by heavy metal traps[J]. Environmental Science, 2013, 34(09):3486-3492.
[9] SHAO Hongyan, YU Haining, XIONG Xiaolong et al. Improvement of sulfide precipitation method for the treatment of cadmium plating wastewater with ammonia carboxylate ligands[J]. Electroplating and Environmental Protection, 2018, 38(01):61-63.
[10] WANG Junjie, WANG Fenghe, LEI Wu, XIA Mingzhu, WANG Fengyun. Novel heavy metal trap NBMIPA for the treatment of copper and mercury containing wastewater [J]. Journal of Environmental Engineering, 2012, 6(11):3933-3936.
[11] Deng Jingheng, Yu Kanping, Xiao Guoguang, Xie Jianguo. Research progress of heavy metal wastewater treatment by adsorption method [J]. Industrial Water Treatment, 2014, 34(11):4-7.
[12] ZHANG Zaili, LIANG Qun, JIA Xiaoshan. Kinetic and thermodynamic studies on the adsorption of Pb~(2+), Cu~(2+), Cr~(3+), Cd~(2+) and Ni~(2+) by peanut shells[J]. Journal of Ecology and Environment, 2010, 19(12):2973-2977.
[13] Pingxiao Wu, Weimin Wu, Shuzhen Li, Ning Xing, Nengwu Zhu, Ping Li, Jinghua Wu, Chen Yang, Zhi Dang. Removal of Cd 2+ from aqueous solution by adsorption using Fe-montmorillonite[J]. Journal of Hazardous Materials, 2009, 169(1).

[14] Zhou Limin, Jin Jieyun, Wang Yiping, Huang Qunwu. Adsorption characteristics of Cd~(2+) and Ni~(2+) on fly ash[J]. Journal of Fuel Chemistry, 2008(05):557-562.

[15] Xie Zimin, Chen Zhen, Liu Tanggui, Dai Youzhi. Study on the influencing factors and regeneration of iron-modified seafoam for antimony removal [J]. Industrial Water Treatment, 2009, 29(11): 35-38+79.

[16] LI Shuangshuang, DAI Youzhi, YU Lei, HU Kewei. Study on the influencing factors of iron-modified seafoam for antimony removal [J]. Journal of Environmental Engineering, 2009, 3(03): 485-488.

[17] Luo Yingdi, Liu Yi. Advances in the study of toxicity of nanomaterials[J]. Henan Chemical Industry, 2022, 39(07):11-14.

[18] Kashiwa Sansan, Bao Yanwei, Sun Xiujun, Guo Xiang. Research progress of nanosorbent materials for removal of pollutants in aqueous environment[J]. Industrial Water Treatment, 2016, 36(12): 1-5+21.

[19] Abid Namra, Khan Aqib Muhammad, Shujait Sara, Chaudhary Kainat, Ikram Muhammad, Imran Muhammad, Haider Junaid, Khan Maaz, Khan Qasim, Maqbool Muhammad . Synthesis of nanomaterials using various top-down and bottom-up approaches, influencing factors, advantages, and disadvantages: A review[J]. Advances in Colloid and Interface Science, 2022, 300.

[20] Alaa E Alia, Whadad M Salema, Sara M Younes and Amal Z Elabdeen. Ferrite Nanocomposite (Rice Straw-CoFe2O4) as New Chemical Modified of for Treatment of Heavy Metal from Waste Water[J]. Hydrology: Current Research, 2019, 10(1).

[21] Xuemei Ren, Changlun Chen, Masaaki Nagatsu, Xiangke Wang. Carbon nanotubes as adsorbents in environmental pollution management: A review[J]. Chemical Engineering Journal, 2010, 170(2).

[22] Zhang Zhikun. Preparation and adsorption performance of metal hydroxide modified multi-walled carbon nanotubes[D]. Lanzhou University of Technology, 2021.

[23] Shitong Yang, Jiaxing Li, Dadong Shao, Jun Hu, Xiangke Wang. Adsorption of Ni(II) on oxidized multi-walled carbon nanotubes: Effect of contact time, pH, foreign ions and PAA[J]. Journal of Hazardous Materials, 2008, 166(1).

[24] Xu Di, Tan Xiaoli, Chen Changlun, Wang Xiangke. Removal of Pb(II) from aqueous solution by oxidized multiwalled carbon nanotubes.[J]. Journal of hazardous materials, 2008, 154(1-3).

[25] Wang Zhongbing, Xu Wenbin, Jie Fanghui, Zhao Zongwen, Zhou Kai, Liu Hui. The selective adsorption performance and mechanism of multiwall magnetic carbon nanotubes for heavy metals in wastewater [J]. Scientific Reports, 2021, 11(1).

[26] SONG Jian, LI Tianle, LI Pei, SUN Xinli, BI Shaodan. Adsorption of heavy metals by graphene oxide composites[J]. Liaoning Chemical Industry, 2022, 51(11):1606-1608.

[27] Songdi Zhang, Huihui Wang, Jianping Liu, Chenlu Bao. Measuring the specific surface area of monolayer graphene oxide in water[J]. Materials Letters, 2020, 261(C).

[28] ZHANG Wenbo, LI Sicun, MA Jianzhong. Application of graphene oxide/natural polymer composite adsorbent materials in water treatment[J]. Fine Chemicals, 2021, 38(04):683-693.

[29] Guo Lijuan. Study on the adsorption performance of modified graphene oxide materials for Cu~(2+) and Cd~(2+)[D]. Hunan University, 2016.

[30] Qiyu Lian, Zaki Uddin Ahmad, Daniel Dianchen Gang, Mark E. Zappi, Dhan Lord B. Fortela, Rafael Hernandez. The effects of carbon disulfide driven functionalization on graphene oxide for enhanced Pb(II) adsorption: Investigation of adsorption mechanism[J]. Chemosphere, 2020, 248(C).

[31] Anupama Asthana, Renu Verma, Ajaya Kumar Singh, Md. Abu Bin Hasan Susan. Glycine functionalized magnetic nanoparticle entrapped calcium alginate beads: a promising adsorbent for removal of Cu(II) ions[J]. Journal of Environmental Chemical Engineering, 2016, 4(2).

[32] Duan Zhengyang, Liu Shuli, Xu Xiaojun, Xie Daolei, He Changhua, Wang Yao. Preparation, functionalization and application of magnetic Fe_3O_4 *nanoparticles in heavy metal wastewater[J]. Chemical Progress, 2017, 36(05):1791-1801.*

[33] Jing Hu, Irene M.C. Lo, Guohua Chen. Comparative study of various magnetic nanoparticles for Cr(VI) removal[J]. Separation and Purification Technology, 2007, 56(3).

[34] Chen ZAN, Li YINHUI. Preparation of magnetic ferric tetroxide and purification of heavy metal ions from wastewater[J]. Inorganic Salt Industry, 2015, 47(06):20-22.

[35] Shi Yuzhe, Sun Congcong, Li Jingchao, Deng Shixian, Zhao Baihan, Liu Zhiguo. Synthesis of catechin-functionalized Fe_3O_4 *magnetic nanoparticles and its study on heavy metal ion removal[J]. New Chemical Materials, 2021, 49(06):271-275.*

[36] Li Yongxue, Dong Xinyi, Zhao Longshan. Application of magnetic chitosan nanocomposites modified by graphene oxide and polyethyleneimine for removal of toxic heavy metals and dyes from water[J]. International Journal of Biological Macromolecules, 2021, 192.

[37] Berk R. S.; Canfield J. H. Bioelectrochemical energy conversion. Appl. Microbiol. 1964, 12,

10-12.

[38] Rao J. R.; Richter G. J.; Von Sturm F.; Weidlich E. The performance of glucose electrodes and the characteristics of different biofuel cell constructions. Bioelectrochem. Bioenerg. 1976, 3, 139-150.

[39] Davis J. B.; Yarbrough H. F. Preliminary experiments on a microbial fuel cell. Science 1962, 137, 615-616.

[40] Cohen B. The bacterial culture as an electrical half-cell. J. Bacteriol. 1931, 21, 18-19.

[41] Logan Bruce E, Hamelers Bert, Rozendal René, Schröder Uwe, Keller Jürg, Freguia Stefano, Aelterman Peter, Verstraete Willy, Rabaey Korneel. Microbial fuel cells: methodology and technology. [J]. Environmental science & technology, 2006, 40(17).

[42] Minghua Zhou, Meiling Chi, Jianmei Luo, Huanhuan He, Tao Jin. An overview of electrode materials in microbial fuel cells[J]. Journal of Power Sources, 2011, 196(10).

[43] Mi Yue. Research on the treatment of heavy metal wastewater with copper and chromium by microbial fuel cells[D]. Xi'an University of Technology, 2021.

[44] Kyu Jung Chae, Mijin Choi, Folusho F. Ajayi, Wooshin Park, In Seop Chang, In S. Kim. Mass Transport through a Proton Exchange Membrane (Nafion) in Microbial Fuel Cells[J]. Energy & Fuels, 2008, 22(1).

[45] M.A. Moqsud, J. Yoshitake, Q.S. Bushra, M. Hyodo, K. Omine, David Strik. Compost in plant microbial fuel cell for bioelectricity generation[J]. Waste Management, 2015, 36.

[46] Jiaying Xu, Han Xu, Xiaoli Yang, Rajendra Prasad Singh, Tao Li, Yan Wu, Hai-Liang Song. Simultaneous bioelectricity generation and pollutants removal of sediment microbial fuel cell combined with submerged macrophyte[J]. International Journal of Hydrogen Energy, 2020(prepublish).

[47] Xinshan Song, Wenting Wang, Xin Cao, Yuhui Wang, Lixiong Zou, Xiaoyan Ge, Yufeng Zhao, Zhihao Si, Yifei Wang. Chlorella vulgaris on the cathode promoted the performance of sediment microbial fuel cells for electrogenesis and pollutant removal[J]. Science of the Total Environment, 2020, 728 (prepublish).

[48] NANDY, LIU Lifen, ZHANG Yalei, HAN Jianqing. Research on water purification by artificial wetlands coupled with microbial fuel cells[J]. Environmental Pollution and Prevention, 2020, 42(09): 1137-1141.

[49] ZHAO Wei, MAO Haoran, ZHOU Cunyin, YANG Yang, YANG Lei, SUN Caiyu. Study on the performance of bi-directional treatment of coking-heavy metal wastewater by microbial fuel cells[J]. Environmental Science and Technology, 2022, 35(02):23-26+31.

[50] ZHANG Yongjuan, LI Yongfeng, LIU Chunyan et al. Electricity generation characteristics of simulated wastewater treatment using a dual-chamber microbial fuel cell[J]. Environmental Science, 2012, 33(07):2427-2431.

[51] Sun Caiyu, Li Lixin, Wang Jing et al. Study on the performance of dual-chamber microbial fuel cells for treating organic and heavy metal wastewater[J]. Water Treatment Technology, 2019, 45(08): 99-102.

[52] Wang Yian, Zhang Xuehong, Xiao Ling, Lin Hua. The in-depth revelation of the mechanism by which a downflow Leersia hexandra Swartz constructed wetland- microbial fuel cell synchronously removes Cr(VI) and p-chlorophenol and generates electricity[J]. Environmental Research, 2023, 216(P1).

[53] DING Guoqing, WANG Xiao, WU Xie, NAN Jing, SONG Hailiang, YANG Yuli. Research progress of artificial wetlands coupled with microbial fuel cells for the treatment of heavy metal wastewater[J/OL]. Energy Environmental Protection, 2023:1-11.

[54] Huang Fengxiang, Man Ruilin, Liu Xiaoqin et al. Research progress on the treatment of heavy metal wastewater by coupling technology[J]. Non-ferrous metals (Smelting part), 2014(01):66-70.

[55] WANG Hua, LIU Yanfei, PENG Dongming, WANG Fudong, LU Manxia. Research progress and application prospect of membrane separation technology [J]. Applied Chemistry, 2013, 42(03):532-534.

[56] ZHOU Rongzhong, XIE Jinwen, LI Panrong, DAI Zhenpeng, WANG Jiaqi, YI Jialu, LI Wen. Research on membrane separation technology for heavy metal wastewater from organosilicon production industry [J]. China Water Supply and Drainage, 2022, 38(13):90-96.

[57] Ying Zhu, Wenhong Fan, Tingting Zhou, Xiaomin Li. Removal of chelated heavy metals from aqueous solution: A review of current methods and mechanisms [J]. Science of the Total Environment, 2019, 678.

[58] R. Molinari, P. Argurio. Arsenic removal from water by coupling photocatalysis and complexation -ultrafiltration processes: a preliminary study[J]. Water Research, 2017, 109.

[59] Wenping Zhu, Shipeng Sun, Jie Gao, Fengjiang Fu, Taishung Chung. Dual-layer polybenzimidazole/polyethersulfone (PBI/PES) nanofiltration (NF) hollow fiber membranes for heavy metals removal from wastewater [J]. Journal of Membrane Science, 2014, 456.

[60] Jing Gao, Yunren Qiu, Ben Hou, Qiang Zhang, Xiaodong Zhang. Treatment of wastewater containing nickel by complexation- ultrafiltration using sodium polyacrylate and the stability of PAA-Ni complex in the shear field [J]. Chemical Engineering Journal, 2018, 334.
[61] Jiahui Shao, Shu Qin, Joshua Davidson, Wenxi Li, Yiliang He, H. Susan Zhou. Recovery of nickel from aqueous solutions by complexation-ultrafiltration process with sodium polyacrylate and polyethylenimine [J]. Journal of Hazardous Materials, 2013, 244-245(Jan.15).
[62] Qiu Yunren, Mao Lianjun. Removal of heavy metal ions from aqueous solution by ultrafiltration assisted with copolymer of maleic acid and acrylic acid [J]. Desalination, 2013, 329.
[63] M.A. Monem El Zeftawy, Catherine N. Mulligan. Use of rhamnolipid to remove heavy metals from wastewater by micellar-enhanced ultrafiltration (MEUF) [J]. Separation and Purification Technology, 2010, 77(1).
[64] Huang Fengxiang, Man Ruilin, Liu Xiaoqin et al. Research progress on the treatment of heavy metal wastewater by coupling technology[J]. Non-ferrous metals(Smelting part), 2014(01):66-70.