Pol. J. Environ. Stud. Vol. 27, No. 1 (2018), 175-181
DOI: *10.15244/pjoes/73990* ONLINE PUBLICATION DATE: 2017-12-12

Original Research

Phytoremediation of Copper Pollution by Eight Aquatic Plants

Dongfang Lu, Qitang Huang, Chuanyuan Deng, Yushan Zheng*

College of Landscape Architecture, Fujian Agriculture and Forestry University, Fuzhou 350002, China

Received: 15 March 2017
Accepted: 22 May 2017

Abstract

This study investigated the uptake capacity and bioaccumulation of heavy metal (Cu) in water using eight different aquatic plant species: *Juncus effusus*, *Acorus calamus*, *Eichhornia crassipes, Sagittaria sagittifolia, Arundina graminifolia, Echinodorus major, Nymphaea tetragona* and *Pistia stratiotes*. The results showed that *Eichhornia crassipes* and *Pistia stratiotes* have the best ability for bioaccumulation, while *Arundina graminifolia*, *Nymphaea tetragona,* and *Acorus calamus* also showed good bioaccumulation. However, *Juncus effusus*, *Sagittaria sagittifolia*, and Echinodorus major displayed very weak bioaccumulation. The enrichment capacity for Cu^{2+} in roots and shoots differed among species. Most of the Cu^{2+} was located in the shoot tissues of Juncus effuses, while for *Sagittaria sagittifolia* and *Acorus calamus* it accumulates in their root tissues. However, in the case of *Echinodorus major* the accumulation of copper content in root and shoot tissues is the same. The adsorption rates of heavy metal Cu in different aquatic plants were different. The adsorption rates of *Eichhornia crassipus*, *Pistia stratiotes*, *Echinodorus major*, and *Nymphaea tetragona* were higher than for *Juncus effusus*, *Sagittaria sagittifolia,* and *Acorus calamus*. When different aquatic plants reached the adsorption equilibrium, pH values were different. The Cu enrichment amount in aquatic plants was related to the content of lignin in plants, and the higher the content of lignin, the greater the amount of copper.

Keywords: aquatic plants, phytoremediation, heavy metal, lignin

Introduction

Water pollution caused by the heavy metals released from different industries has received worldwide attention owing to the potentially toxic or carcinogenic properties of heavy metals and the deterioration of the quality of drinking and irrigation water [1-8]. It can also be hazardous to human health when they enter the food chain and water supply system [7-11]. Heavy metals such as copper, zinc, and cobalt are essential for the growth of living organisms. Copper is one of the heavy metals and is usually present at low concentrations in water. It is an essential micronutrient for animal metabolism [12]. However, Cu exceeding its critical level might bring about a serious problem for the environment and water pollution, as well as serious toxicological concerns such as vomiting, cramps, convulsions, or even death [13-14]. Nowadays, with the development of such industries as textiles, metal plating, mining, and fertilizing, copper-containing wastewaters are released into the environment and can cause serious pollution of ground and surface waters [15-16].

*e-mail: fjldf@126.com

Ecologists and environmentalists are therefore facing the task of cost-effective treatment of wastewater containing heavy metals. The conventional methods of heavy metal elimination from wastewater include ion exchange, membrane separation, electro dialysis, etc. However, such methods are not effective, are expensive, need high energy input, and are not eco-friendly [17]. Recently, many approaches have been studied for the safe, cost-effective, and more efficient treatment of heavy metal-loaded wastewater [18-24]. The physical adsorption method has emerged as the best alternative treatment method. It uses an activated carbon, SiO_2, Al_2O_3, fee stone, and diatomite as an adsorbent for water pollutants [25]. It is a remarkably effective method. However, the saturated adsorption agent can become a secondary pollution source and needs to be given a regeneration treatment before it can be available for use. Furthermore, the regeneration process is complex and difficult in operation. The chemical process is an effective and widely used process in industry, employing the reaction of chemical reagents and pollutant components for purification purposes while being simple and inexpensive to operate. But chemicals will often introduce other chemical components of pollution.

Although biological (bacterial) is a method of adopting microbial purification, the microbes are greatly influenced by water quality. Different configurations of microorganisms were used for different water quality levels. In addition, during the process the change in water quality will inhibit the biological treatment effect [26-29]. *In-situ* remediation processes, for example ecological techniques including the use of aquatic plants, has been established for the bioremediation of polluted surface water. This method has many advantages when compared to other techniques, such as low costs, low energy consumption, less adverse impacts on the environment, and no secondary production of pollutants.

Experimental

Methods

Juncus effusus, *Acorus calamus*, *Eichhornia crassipes*, *Sagittaria sagittifolia*, *Pistia stratiotes*, *Arundina graminifolia*, *Echinodorus major*, and *Nymphaea tetragona* were collected and fully cleaned to remove dirt. The collected plants were placed in the Hoagland nutrient solution [30] for a 10-day acclimatization period before being exposed to heavy metal contaminants. Then three aquatic plants with similar sizes were respectively put into containers that contained 2 L of 10 mg/L solution containing desired Cu concentrations, and put in dry, ventilative, and sunny conditions. There was one plant in each replicate with three replicates in each treatment. The control sets were similarly maintained in containers containing 2 L of 10 mg/L solution only, without any metal treatments. pH was measured every two days. The volume of water in each tank was kept constant and the change in volume due to evaporation and plant transpiration was compensated for by the addition of deionized water and sampled at a time. The concentration of heavy metals was measured by TAS-990 atomic absorption spectrophotometry (Beijing, China). Then all the results are the mean values from three aquatic plants. After the last sampling, the aquatic plants at 80°C were removed, dried to constant weight, and high-temperature roasting ashing of roots, stems, and leaves was done to digest.

Analyzing Heavy Metal Elements Content

The sample was digested with nitric acid and the high-acid digestion method, and the digestion reaction was carried out in a COOLPEX microwave chemical reactor (Shanghai, China). An amount of 0.200 g ashing samples or 1 ml of the sample solution was first added to the tube digestion, and then we added 5 ml of concentrated nitric acid and the obtained solution was heated for 1 h. The temperature of the stove was adjusted to 150ºC, after 20 min of heating until the surface turned light yellow and was then removed for cooling. Afterward, 1 ml of perchloric acid was added and the temperature was adjusted to 180ºC and heated until dark smoke was produced. After that, we steamed the liquid until the residue turned gray and white and the surface was clean (if there was still some color, then we tried to add more nitric acid with the same amount), and then it was filtered, and the filtrate was transferred to a 50 mL bottle added with pure water. Finally, the content of Cu was analyzed by atomic absorption spectrophotometry.

Results and Discussion

Enrichment Effect of Copper by Aquatic Plants

During the experimental period the plants were grown normally. As can be seen from Fig. 1, there are significant differences in the concentrations of heavy metals in different aquatic plants. These aquatic plants are listed on the basis of their metal accumulation. Accordingly, *Eichhornia crassipes* has received high metal accumulation, which implies: *Eichhornia crassipes* > *Pistia stratiotes* > *Arundina graminifolia* > *Nymphaea tetragona* > *Acorus calamus* > *Echinodorus major* > *Juncus effusus* > *Eichhornia crassipes*. *Acorus Calamus* and *Pistia stratiotes* are more suitable for processing Cu-polluted water due to their significant accumulation on Cu. Fig. 1 also shows that Cu enrichment by aquatic plants occurs mainly in the first six days, then gradually slows down and reaches equilibrium enrichment almost on the 10^{th} day. Different aquatic plants differ in the rates of their Cu enrichment. The adsorption rates of *Eichhornia crassipes*, *Pistia stratiotes*, and *Nymphaea tetragona* were higher than those of *Juncus effusus*, *Acorus calamus*, *Sagittaria sagittifolia*, and *Echinodorus major*. Yanet et al. [31] found that the enrichment rate has a contact area of floating plants and water pollutants. Floating plants

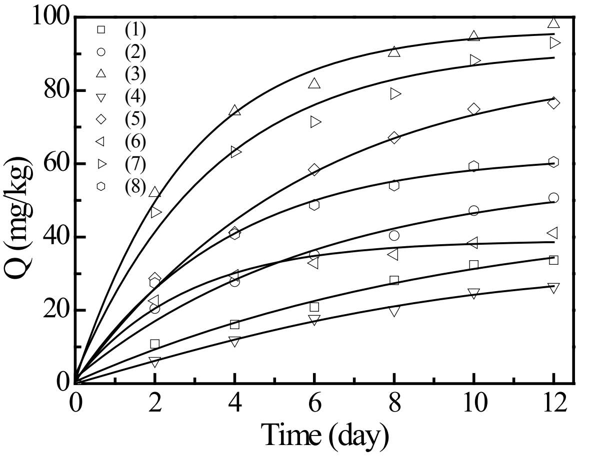

Fig. 1. Effect of aquatic plants on the removal of copper from water: 1) *Juncus effusus*, 2) *Acorus Calamus*, 3) *Eichhornia Crassipes*, 4) *Sagittaria sagittifolia*, 5) *Arundina graminifolia*, 6) *Echinodorus major*, 7) P*istia stratiotes*, and 8) *Nymphaea tetragona*.

and water pollution have more contact area and its leaves and stems are active for absorbing heavy metals, resulting in good enrichment of heavy metals in plants and reaching equilibrium enrichment more quickly.

Upon the adaptation of aquatic plants to Cu pollution, the concentration of Cu in the model was changed. It was also found that when the concentration of Cu^{2+} was 14 mg/L, the old *Pistia stratiotes* leaves appear to yellow and wither after four days while the roots drop off after six days. However, the remaining aquatic plants grew normally. Therefore, when the Cu ion concentration reaches 18 mg/L, the old leaves of *Eichhornia crassipes* appear to yellow and wither after being cultured for two days on the plant root, plus root shedding after four days. On the sixth day *Sagittaria sagittifolia* and *Echinodorus major* appear yellow, on the 10th day the leaves next to the root of *Arundina graminifolia* turn yellow and the tail of *Acorus calamus* leaves also began to turn yellow, but *Juncus effusus* and *Nymphaea tetragona* did not change significantly.

Accumulation of Copper in the Root and Shoot Tissues of Aquatic Plants

The distribution of Cu^{2+} in plants varies within the different plant species. Plants uptake heavy metals through their roots and transfer to the stems and leaves. Then these heavy metals get complexation with functional groups of amine in the plant body, which results in enriching the heavy metals. In addition, they can also bond with functional groups of cellulose, lignin, and hemicellulose. Furthermore, free lignin plays the role of flocculation on heavy metals.

As observed in Table 1, aquatic plants showed good copper enrichment amounts in their roots and shoot tissues. It can be seen that the concentration of heavy metal Cu by the plant before and after the experiment is basically the same as the concentration of Cu measured by the plant (Fig. 1). Accumulation of Cu was different in various parts of aquatic plants, with the ratio of Cu concentration in the shoot to that in the root of the plant calculated as the translocation factor (TF), and TF is different. In addition, the translocation factor can show that there were also differences in the concentrations of heavy metals in the same parts of different aquatic plants. The accumulation of Cu in stems and leaves of the *Juncus effusus*, *Sagittaria sagittifolia*, and *Pistia stratiotes* were significantly higher than those in the roots, while the accumulation of copper in the root of *Arundina Graminifolia*, *Eichhornia Crassipes*, *Nymphaea tetragona*, and *Acorus Calamus* was significantly higher than that of the stems, and while Cu accumulation in the root of *Echinodorus major* is basically the same as that in stems. The enrichment experiment is carried out in a period of 20 and 30 days, respectively. It was found that TF did not change significantly, indicating that within the experimental period, the transfer of heavy metals in plants reached the equilibrium.

Table 1. Content of Cu in root and shoot tissues of aquatic plants (mg/kg).

Aquatic plants	Section adsorption		k Root/shoot ratio	q (mg/kg)	Q (mg/kg)	Equilibrium pH
	Roots	Stems/leaves				
Juncus effusus	13.8	19.1	0.72	33.7	32.9	7.25
Acorus calamus	30.2	21.8	1.39	50.7	52.0	7.20
Eichhornia crassipes	63.1	34.3	1.84	98.1	97.4	6.07
Sagittaria sagittifolia	11.0	15.9	0.69	26.4	26.8	6.11
Arundina graminifolia	51.6	25.8	2.00	76.6	77.4	6.76
Echinodorus major	21.4	20.3	1.05	41.1	41.7	6.17
Pistia stratiotes	39.8	52.3	0.76	93.0	92.1	6.74
Nymphaea tetragona	39.8	21.0	1.90	60.5	60.8	6.68

k: Plant root/(stem+leaf) enrichment ratio, q: accumulation by plant test (mg/kg), Q: enrichment measured by the change of solution concentration (mg/kg)

Table 2. Change of pH value of adsorption process solution.

Aquatic plants	pH						
	0d	2d	4d	6d	8d	10d	12d
Juncus effusus	6.68	6.88	6.97	7.12	7.20	7.22	7.25
Acorus calamus	6.67	6.83	6.92	7.05	7.18	7.19	7.20
Eichhornia crassipes	6.67	6.42	6.33	6.27	6.20	6.15	6.07
Sagittaria sagittifolia	6.69	6.46	6.37	6.26	6.17	6.13	6.11
Arundina graminifolia	6.68	6.75	6.77	6.73	6.75	6.78	6.76
Pistia stratiotes	6.68	6.52	6.40	6.35	6.26	6.20	6.17
Echinodorus major	6.67	6.71	6.75	6.72	6.73	6.74	6.74
Nymphaea tetragona	6.68	6.69	6.65	6.67	6.66	6.67	6.68

Changes of pH in the Solution of the Enrichment Process of Aquatic Plants

The purification of heavy metals by aquatic plants has many forms, such as physical adsorption, chemical adsorption, complexation, etc. The root-specific surface area of aquatic plants (*Juncus effusus*, *Acorus calamus, Eichhornia crassipes*, *Sagittaria sagittifolia*, *Arundina graminifolia*, *Echinodorus major*, *Nymphaea tetragona*, and *Pistia stratiotes*) is relatively small. Combined with the experiment of the concentration of the roots and leaves of the aquatic plant, it can shed some light on the enrichment of heavy metals by aquatic plants. The adsorption capacity of the physical adsorption is not dominant.

As shown in Table 2, the change of pH value in the heavy metal enrichment process by aquatic plants can be divided into three types. In the experiment of *Acorus calamus* and *Juncus effusus* pH increases because the root of aquatic plants contains amino groups with the amino functional groups, which can form complexes with the heavy metal ions of Cu, resulting in an increase of pH of the solution. In the experiment of *Eichhornia crassipes*, *Sagittaria sagittifolia*, and *Pistia stratiotes*, pH drops because aquatic plants are mainly made of wood, cellulose, and hemicellulose, which are rich in oxygen-functional groups (C=O (ketones, lactones, and carbonyl group). When C-O (alcoholic hydroxyl and ether) and C (=O)-O (esters, carboxylic acid, and carboxylate) are combined, these oxygen-containing functional groups can form complexes with metal ions and release H^+, resulting in a decrease of pH value. In adition, heavy metal ions in the presence of ions during the immersion process have an exchange reaction with a hydrogen ion, decreasing the sample solution pH. The pH in the experiment of the *Arundina graminifolia*, *Echinodorus major*, and *Nymphaea tetragona* enrichment process remains unchanged.

Effect of Initial pH on the Concentration of Heavy Metals in Aquatic Plants

The pH value of the water body not only affects the growth of aquatic plants, but also affects the ability of the aquatic plants to enrich the heavy metals. The initial pH value of the solution was adjusted using 0.1 mol/L of HCl and NaOH solution, and a number of heavy metals accumulated by aquatic plants are presented in Table 3 after

Table 3. Concentration of heavy metals in aquatic plants under different pH.

Aquatic plants	pH					
	4	5	6	6.68	8	9
Juncus effusus	10.2	28.4	39.3	32.9	21.7	9.8
Acorus calamus	17.6	39.8	54.5	52.0	40.5	12.8
Eichhornia crassipes	—	58.5	90.6	97.4	73.0	—
Sagittaria sagittifolia	—	15.1	22.4	26.8	18.9	—
Arundina graminifolia	39.5	60.0	81.1	77.4	57.7	17.2
Echinodorus major	—	11.0	33.8	41.7	29.4	—
Pistia stratiotes	—	50.7	90.5	92.1	79.6	—
Nymphaea tetragona	—	35.1	62.6	60.8	51.1	28.1

Note: the accumulation of Q was measured by the plant (mg/kg)

12 days of growth. In the process of the experiment, it was found that when the pH values were 4 and 9, *Eichhornia crassipes*, *Pistia stratiotes*, *Sagittaria sagittifolia*, and *Echinodorus major* did not shoot new roots. In contrast, the original root slowly started disintegrating and leaves slowly turned yellow and withered; *Nymphaea tetragona* and *Arundina graminifolia* did not have obvious loss and decay on their roots, but the leaves gradually yellowed; *Juncus effusus* and *Acorus calamus* had no obvious yellow and withered leaves, and the root did not appear to be shed or decay. From the table it can be seen that, with pH value increased, Cu extraction by total plants increased at first, but progressively declined at subsequent higher doses. Better pH rush by *Acorus calamus* accumulation of heavy metals was 5-6, it was weak acid; *Sagittaria sagittifolia* accumulated heavy metals better in the pH 6.5-7 range. *Echinodorus major* stayed in the weak acid and neutral regions to maintain a stable amount of adsorption. The appropriate *Pistia stratiotes*, *Eichhornia crassipes*, *Echinodorus major*, and *Sagittaria sagittifolia* at pH 4 began to have rot roots after 4-6 days. In addition, under different acid and alkali conditions, heavy metal ions must be combined with H^+, which is not the same as heavy metal ions combined with OH^-. For instance, pH in Cu^{2+} and Pb^{2+} form suspended matters in the larger pH conditions, which greatly affect the aquatic plant's absorption capacity on Cu^{2+} and Pb^{2+}. Better pH for most aquatic plants for the enrichment of heavy metals is neutral and weak acid.

Effect of Plant Age on Heavy Metal Accumulation

In order to study the effect of plant age on the accumulation of heavy metals, *Eichhornia crassipes* of different plant ages (native strains – first generation, native strains branch plants – second generation, and proton plant branching out plants – third generation) and *Nymphaea tetragona* cultured for different times (to seed culture for 4, 6, 8, 10, and 12 weeks) were used as the research object, and the experimental results are shown in Table 4. From the table we can see that the *Eichhornia crassipes* of Cu enrichment in the amount of 1 > 2 > 3 generation; *Nymphaea tetragona* of heavy metal enrichment in the amount of 10 weeks, 12 weeks > 8 weeks > 6 weeks > 4 weeks. Therefore, the enrichment of Cu in mature plants was larger than that of seedlings, which was the same as that of Lavid et al. research results [32].

With the growth of plants, the content of the three main components (lignin, cellulose, hemicellulose) in the plants also changed. To further study the quantity variation of heavy metal accumulation in plants in different growth periods, three main components (cellulose, lignin, and hemicellulose) contents were observed and analyzed, and the results are shown in Table 5. It can be seen that in all periods of growth, *Eichhornia crassipes* and *Nymphaea tetragona* in the cellulose content was the highest, and the cellulose content increased at different rates. By comparing hemicellulose content in different growth periods, we found that the semi cellulose increased with prolonging the incubation period. When it reached a certain value, hemicellulose content decreased in spite of the prolonged culture time. Comparing lignin content in different growth periods, we found that lignin content of the *Eichhornia crassipes* and *Nymphaea tetragona* increased in different degrees with prolonging culture time, and then tended to be stable in the end. Combined with the different growth period of *Eichhornia crassipes* and *Nymphaea tetragona* of Cu enrichment and the three component changes, we found that the changes in the pigment of aquatic plants on Cu enrichment are the same as those of the aquatic plant in wood. The concentration of the plant is related to the content of lignin in plants. In order to further study the impact on the accumulation of heavy metal when lignin content is changed, we propose changing the content of lignin in the plant by means of chemical and biological engineering. Previous studies have found that lignin is synthesized in higher plants through the phenylpropanoid pathway and lignin-specific pathway. Three main monomers were generated by phenylalanine, which is amino, hydroxy, methylation, and redox reactions. p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol were aggregated to form p-hydroxyphenyl lignin, guaiacyl lignin, and syringyl lignin. Finally, under the catalysis of peroxidase (POX) and laccase (LAC), various lignin monomers were polymerized into high molecular lignin [33-36]. Domestication and cultivation of aquatic plants: A certain amount of phenylalanine was added during the cultivation of *Eichhornia crassipes*, and its concentration was 1 g/L, and every morning and evening at 8:00, the water portion was given a spraying of 0.1g/L amino acid

Table 4. Contents of three major components of different plant ages and concentrations of heavy metals.

	Eichhornia crassipes			*Nymphaea tetragona*				
	1st	2nd	2rd	4 weeks	6 weeks	8 weeks	10 weeks	12 weeks
Accumulation (mg/kg)	54.5	82.7	97.4	35.7	47.2	60.8	62.1	62.7
Cellulose (%)	16.75	19.31	25.26	19.43	23.57	28.41	30.22	33.19
Hemicellulose (%)	12.82	14.52	14.17	10.77	16.34	17.52	15.97	15.24
Lignin (%)	7.92	10.80	13.02	9.07	11.15	13.91	14.55	14.58
Accumulation/lignin	7.639	7.657	7.481	3.936	4.104	4.371	4.268	4.300

Table 5. The content of lignin and the concentration of Cu in water under external environmental stress.

	0 d	5 d	10 d	15 d
Accumulation (mg/kg)	93.8	104.2	113.0	118.6
Lignin content (%)	12.81	13.74	15.47	16.30
Accumulation/ lignin	7.322	7.140	7.304	7.239

solution for one time, which was continued to be carried out on days 0, 5, 10, and 15. And they were transferred to the common nutrient solution for one week before the test. The experimental results are shown in Table 5. It can be seen that after phenylalanine culture, the lignin content in *Eichhornia crassipes* increased and the lignin content in plants increased with the increase of induction time; the accumulation of heavy metals by *Eichhornia crassipes* was also increased. Therefore, the lignin content in the *Eichhornia crassipes* was further promoted to Cu accumulation. The reason may be that lignin is a lot more negative with the group of polycyclic macromolecule organic matter, which has a strong affinity for high valence metal ions.

Conclusions

The uptake and accumulation effect of Cu^{2+} by eight kinds of aquatic plants (i.e., *Juncus effusus*, *Acorus calamus*, *Eichhornia crassipes*, *Sagittaria sagittifolia*, *Arundina graminifolia*, *Echinodorus major*, *Nymphaea tetragona*, and *Pistia stratiotes*) were studied. The findings in this research implied that (differential accumulation pattern was noted for copper) the accumulation of copper was different in different aquatic plants. *Eichhornia crassipes* and *Pistia stratiotes* are the best; *Arundina graminifolia*, *Nymphaea tetragona*, and *Acorus calamus* are second best; and Juncus effuses, *Sagittaria sagittifolia*, and *Echinodorus major* are the worst. The enrichment ratio of roots, stems, and leaves is different in the various plants. *Juncus effusus* mostly accumulated in stems, *Sagittaria sagittifolia* and *Acorus calamus* mainly accumulated in the roots, and the distribution of Cu is similar in the root of *Echinodorus major*. Different aquatic plants have Cu enrichment at different rates, among which the adsorption rate of the *Eichhornia crassipes*, *Pistia stratiotes*, *Echinodorus major*, and *Nymphaea tetragona* is higher than that of *Juncus effusus*, *Arundina graminifolia*, *Sagittaria sagittifolia*, and *Acorus calamus*. When different aquatic plants reach the adsorption equilibrium, pH value is different. The concentration of Cu in aquatic plants was also related to the content of lignin in plants, and the higher the content of lignin, the greater the amount of Cu.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 31000269) and the Education Department Foundation of Fujian Province (No. JB13039).

References

1. LUO X., LEI X., CAI N., XIE X., XUE Y., YU F. Removal of heavy metal ions from water by magnetic cellulose-based beads with embedded chemically modified magnetite nanoparticles and activated carbon, ACS Sustainable Chemistry & Engineering, **4**, 3960, **2016**.
2. FAKHRI A., KAHI D.S. Synthesis and characterization of MnS_2/reduced graphene oxide nanohybrids for with photocatalytic and antibacterial activity, Journal of Photochemistry and Photobiology B: Biology, **166**, 259, **2017**.
3. FAKHRI A. Adsorption characteristics of graphene oxide as a solid adsorbent for aniline removal from aqueous solutions: Kinetics, thermodynamics and mechanism studies, Journal of Saudi Chemical Society, **21**, S52, **2017**.
4. GUPTA V.K., AGARWAL S., TYAGI I., SOHRABI M., FAKHRI A., RASHIDI S., SADEGHI N. Microwave-assisted hydrothermal synthesis and adsorption properties of carbon nanofibers for methamphetamine removal from aqueous solution using a response surface methodology, Journal of Industrial and Engineering Chemistry, **41**, 158, **2016**.
5. FAKHRI A. Assessment of Ethidium bromide and Ethidium monoazide bromide removal from aqueous matrices by adsorption on cupric oxide nanoparticles, Ecotoxicology and Environmental Safety, **104**, 386, **2014**.
6. FAKHRI A., KHAKPOUR R. Synthesis and characterization of carbon or/and boron-doped CdS nanoparticles and investigation of optical and photoluminescence properties, Journal of Luminescence, **160**, 233, **2015**.
7. FAKHRI A., BEHROUZ S. Comparison studies of adsorption properties of MgO nanoparticles and ZnO-MgO nanocomposites for linezolid antibiotic removal from aqueous solution using response surface methodology, Process Safety and Environmental Protection, **94**, 37, **2015**.
8. FAKHRI A., BEHROUZ S. Improved uptake of steroid hormone from aqueous solution using γ-Fe_2O_3/NiO nanocomposites, Journal of Industrial and Engineering Chemistry, **26**, 61, **2015**.
9. MISHRA V.K., TRIPATHI B.D. Concurrent removal and accumulation of heavy metals by the three aquatic macrophytes. Bio Technol, **99**, 7091, **2008**.
10. CHEN X.Y., KUO D.H. Nanoflower bimetal CuInOS oxysulfide catalyst for the reduction of Cr(VI) in the dark, ACS Sustainable Chemistry & Engineering. **5**, 4133, **2017**.
11. LU Q., HE Z.L., GRAETZ D.A., STOFFELLA P.J., YANG X. Phytoremediation to remove nutrients and improve eutrophic stormwaters using water lettuce (*Pistia stratiotes* L.) Environmental Science and Pollution Research, **17**, 84, **2010**.
12. FU F., WANG Q. Removal of heavy metal ions from wastewaters: A review, Journal of Environmental Management. **92**, 407, **2011**.

13. GHADERIAN S.M., ALI A., RAVANDI G. Accumulation of copper and other heavy metals by plants growing on Sarcheshmeh copper mining area, Iran. Journal of Geochemical Exploration, **123**, 25, **2012**.
14. KLINK A., MACIOŁ A., WISŁOCKA M., JÓZEF K. Metal accumulation and distribution in the organs of *Typha latifolia* L. (cattail) and their potential use in bioindication. Limnologica, **43**, 164, **2013**.
15. YE X., QIU S. Phytoremedication of Pb-Cd combined pollution by three aquatic plants, Chinese journal of Environmental Engineering, **4**, 1023, **2010**.
16. WANG Q., CHENG S. Review of phytoremediation of havet metal polluted water by macrophytes, Environmental Science & Technology, **33**, 96, **2010**.
17. PAN Y., WANG H., GU Z., XIONG G., YI F. Accumulation and translocation of heavy metals by macrophytes, Acta Ecologica Sinica, **30**, 6430, **2010**.
18. BARAKAT M.A. New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry, **4**, 361, **2011**.
19. MOHAMMADI S., SOHRABI M., GOLIKAND A.N., FAKHRI A. Preparation and characterization of zinc and copper co-doped WO_3 nanoparticles: Application in photocatalysis and photobiology, Journal of Photochemistry and Photobiology B: Biology, **161**, 217, **2016**.
20. FAKHRIA A., TAHAMI S., NAJI M. Synthesis and characterization of core-shell bimetallic nanoparticles for synergistic antimicrobial effect studies in combination with doxycycline on burn specific pathogens, Journal of Photochemistry and Photobiology B: Biology, **169**, 21, **2017**.
21. FAKHRI A., POURMAND M., KHAKPOUR R., BEHROUZ S. Structural, optical, photoluminescence and antibacterial properties of copper-doped silver sulfide nanoparticles, Journal of Photochemistry and Photobiology B: Biology, **149**, 78, **2015**.
22. FAKHRI A., NEJAD P.A. Antimicrobial, antioxidant and cytotoxic effect of Molybdenum trioxide nanoparticles and application of this for degradation of ketamine under different light illumination, Journal of Photochemistry and Photobiology B: Biology, **159**, 211, **2016**.
23. CHEN X.Y., ABDULLAH H., KUO D.H. CuMnOS nanoflowers with different Cu^+/Cu^{2+} ratios for the CO_2-to-CH_3OH and the CH_3OH-to-H_2 redox reactions, Scientific. Reports**.** **7**, 41194, **2017**.
24. CHEN X.Y., KUO D.H., LU D.F. N-doped mesoporous TiO_2 nanoparticles synthesized by using biological renewable nanocrystalline cellulose as template for the degradation of pollutants under visible and sun light, Chemical Engineering Journal **295**, 192, **2016**.
25. SALEM Z.B., LAFFRAY X., ASHOOUR A., HABIB A., LOTFI A. Metal accumulation and distribution in the organs of Reeds and Cattails in a constructed treatment wetland (Etueffont, France). Ecological Engineering, **64**, 1, **2014**.
26. ZHAO F., XI S., YANG X., YANG W., LI J., GU B., HE Z. Purifying eutrophic river waters with integrated floating island systems. Ecological Engineering, **40**, 53, **2011**.
27. BRAECKEVELT M., REICHE N., TRAPP S., WIESSNER A., PASCHKE H., KUSCHK P., KAESTNER M. Chlorobenzene removal efficiencies and removal processes in a pilot-scale constructed wetland treating contaminated groundwater. Ecological Engineering, **37**, 903, **2011**.
28. BASÍLICO G., CABO L., FAGGI A. Impacts of composite wastewater on a Pampean stream (Argentina) and phytoremediation alternative with Spirodela intermedia Koch (Lemnaceae) growing in batch reactors. Journal of Environmental Management, **115**, 53, **2013**.
29. FAVAS P.J.C., PRATAS J., VARUN M., D'SOUZA R., PAUL M.S. Accumulation of uranium by aquatic plants in field conditions: Prospects for phytoremediation. Science of the Total Environment, 470-471, 993, **2014**.
30. LIAN J.J., XU S.G., HAN C.W. Absorption characteristics of molybdenum by reed and cattail, Environmental Science, **32**, 3335, **2011**.
31. YAN S., LIANG D., PEN X. A research on the tolerance Purification Ability of Eight Aquatic Plants in Heavy Metal Cu Contamindted Sewage, China Environmental Science, **10**, 166, **1990**.
32. LAVID N., BARKAY Z., TELOR E. Accumulation of heavy metals in epidermal glands of the water lily (Nymphaeaceae). Planta, **212**, 313, **2001**.
33. BAUCHER M., HALPIN C., PETIT-CONIL M., BOERJAN W. Lignin: Genetic engineering and impact on pulping. Critical Reviews in Biochemistry and Molecular Biology, **38**, 305, **2003**.
34. BOERJAN W., RALPH J., BAUCHER M. Lignin biosynthesis. Annual Review of Plant Biology, **54**, 519, **2003**.
35. KONG H., GUO A., GUO Y., LIU E., HE L. Advances in study of lignin biosynthesis and its genetic manipulation, Tropical Agricultural Engineering, **4**, 431, **2009**.
36. LI J., ZHANG Q., NIU Z., LU M., DOUGLAS C.J. Advances in study of lignin biosynthesis and Genetic Engineering Modification. World Forestry Research, **20**, 29, **2007**.