Research status of anion in treating water by biomass adsorbent

Jinhui Yang\(^1\), Zengjiang Lei\(^1\), Yanghong Dai\(^2\), Bin Yang\(^3\), Chuanshu Li\(^1\), Yi Luo\(^1\) and Hong Yang\(^1\)

\(^1\)School of Civil Engineering, University of South China, Hengyang 421001, China;
\(^2\)CGNPC Nuclear Power Operation Co., Ltd., China, Shenzhen518000

Author brief introduction: Jinhui Yang, Professor, water treatment technology and theoretical research; E-mail: yanjinhui126@126.com

*Corresponding author: Zengjiang Lei, E-mail: 530566791@qq.com

Abstract. The biomass adsorbent is prepared by chemical modification of agricultural and forestry waste as raw materials, and has the characteristics of wide source, low price, fast and efficient, and degradable regeneration. It can not only reduce the environmental pollution, but also realize the green development concept of “treating waste by waste”. Biomass adsorbents have gradually become a research hotspot in water treatment theory and technology, and agricultural and forestry wastes that can be used as raw materials are increasing. According to the research status at home and abroad, the research on the treatment of anions by biomass adsorbents is reviewed. It is expected to provide reference for the further adsorption mechanism of postgraduate material adsorbents for anions and the rational utilization of agricultural and forestry wastes.

1. Introduction

Many pollutants from industrial and agricultural activities enter the natural water body and exist in the form of potential or significant toxic anions, causing different degrees of water ecological environment problems. Excessive nitrate and phosphate will directly lead to eutrophication of water, damage water ecosystem and deteriorate water quality [1]. The highly toxic dichromate and arsenite can not only damage water quality, but also enrich human body through biological enrichment, seriously damaging human health [2]. Although perchlorate does not produce acute toxicity, it still has serious consequences for water environment and human health [3].

Traditional methods to treat anionic pollutants in water include chemical precipitation, chemical reduction, electrochemical method, membrane separation, microbial method, adsorption and ion exchange technology, etc. [4]. Most of the traditional methods have some defects, such as incomplete treatment, high operation cost, secondary pollution and difficulty in promotion. Adsorption and ion exchange technology has obvious advantages in the treatment of anionic pollutants. In particular, the adsorption technology is based on the electrostatic effect, so that negatively charged anionic pollutants and positively charged substances and colloidal particles gather to form large particle precipitation. The main cost of adsorption technology comes from the cost of adsorbing materials. The development of green and affordable biomass adsorbents from agricultural and forestry wastes has become a research
hotspot in the field of material environment. At present, there have been studies at home and abroad. Biomass adsorbents are prepared from Luffa fruits, eucalyptus leaves, cassava straw and other agricultural and forestry wastes to treat wastewater containing heavy metals, adsorb dyes and remediate soil pollution. However, the research on the treatment of anionic pollutants in water is not enough, and the adsorption mechanism is still not very clear. According to the existing research at home and abroad, the material composition of agricultural and forestry wastes, the preparation methods and typical applications of biomass adsorbents were analyzed and summarized, hoping to provide theoretical reference for the follow-up study of the treatment of anions in water by biomass adsorbents.

2. The material composition of agricultural and forestry wastes
The analysis of the material composition of agricultural and forestry waste is one of the important theoretical bases for exploring and developing the rational utilization of agricultural and forestry waste. In general, the main components of agroforestry waste are cellulose, hemicellulose and lignin, as well as a small amount of pectin, ash, and protein. Agricultural and forestry wastes are simply divided into straw, leaves and husk, as shown in Table 1.

| agricultural and forestry wastes | composition (%) | reference |
|---------------------------------|-----------------|-----------|
| Rice straw                      | 43.3            | [5]       |
| Maize straw                     | 39.2            | [6]       |
| Paulownia leaves                | 45.3            | [7]       |
| Sycamore leaves                 | 42.5            | [8]       |
| Cotton shell                    | 48.7            | [9]       |
| Soybean skin                    | 67.6            | [10]      |

Which cellulose accounts for more than 40% of all components. Because there are a lot of cell walls in agricultural and forestry wastes, the main component is the fiber structure formed by cellulose. The chemical properties of cellulose are similar to polyols, and the glucose ring in its structure is composed of b-d-furan glucose group [11]. With three active hydroxyl groups, it can produce esterification reaction, etherification reaction, acetylation reaction, hydrolysis reaction, etc., which has become the theoretical basis for the preparation of biomass adsorbent by chemical modification of agricultural and forestry wastes. Hemicellulose has a smaller molecular weight than cellulose, but its structure is more complex than cellulose. Because hemicellulose carries a large number of reducing groups, hemicellulose has a certain degree of reducibility. In addition, the active hydroxyl group, alkoxyl group and other functional groups on hemicellulose give it similar properties to cellulose. The lignin content is second only to cellulose, and lignin contains several different types of hydroxyl groups and C = C double bonds, making it highly reactive.

3. Types and Preparation Methods of Biomass Adsorbent
Agricultural and forestry wastes without modification have a certain adsorption capacity for heavy metals, which is mainly due to the large number of carboxyl and hydroxyl functional groups with electronegativity in cellulose, hemicellulose and lignin, and have strong electrostatic effect on heavy metal cations. The chemical properties of agricultural and forestry waste are modified by physical & chemical method to give full play to its application value, wider application scope and higher adsorption efficiency. At present, agricultural and forestry wastes are often used to prepare the following three biomass adsorbents to treat anionic pollutants in water: Porous biomass adsorbent [12], Biomass loaded with metal adsorbent [13].

3.1. Porous biomass adsorbent
Porous biomass adsorbent is activated carbon obtained by activation reaction at high
temperature (200°C-900°C) using Agricultural and forestry wastes as raw material [14]. The common activation methods include physical activation, chemical activation and microwave heating. The activated gases commonly used in physical activation methods are single or mixed gases such as N2, CO2, and water vapor. Yu Junfeng [15] in the activation temperature of 850°C, such as activation of CO2 gas conditions, with sawdust charcoal as raw material to produce activated carbon, measured the specific surface area of 296 m2/g. ZnCl2, K2CO3 and NaOH are commonly used as activators in chemical activation. It is found that the temperature of chemical activation reaction is lower than that of physical activation, and the specific surface area of activated material is larger. Miao et al. [16] prepared soybean straw activated carbon with ZnCl2 as activator. The specific surface area was 2,271 m2/g. Microwave heating is a new heating method which has the advantages of uniform heating, short reaction time and energy saving.

3.2. Biomass loaded with metal adsorbent

Biomass loaded with metal adsorbents are modified by chemical reactions to the surface of agricultural and forestry waste, introducing positively charged metal ions or metal oxides. Commonly used metal ions include Fe(III), Zn(II), Mg(II), and some rare earth metal ions. Alonso et al. [17] prepared activated carbon with corn shavings as raw materials, respectively using six different compounds of AlCl3, Cu(OH)2, FeSO4, KCl, MgCl2 and Mg(OH)2 as supporting metals. The adsorption efficiency of arsenates, phosphates and nitrates was studied. It was found that the porosity of all metal bearing biochar was improved and the adsorption efficiency was enhanced. Chen Jing et al [18] used MgCl2, FeCl3 and mixed solution of the two to modify the ammonia-nitrogen wastewater prepared by Nanzhu. The results showed that the properties of the material changed greatly after modification, the pore distribution was uneven and the pore size increases; The synergistic modification of Mg(II) and Fe(III) had the best adsorption effect. This may be due to the electrostatic attraction of the supported metal ions and anions such as ammonia nitrogen, which improves the adsorption efficiency.

4. Application of biomass adsorbent to the treatment of anions in water

According to the different types of anionic pollutants, the application of biomass adsorbents can be divided into three aspects: (1) Adsorption treatment of eutrophic anions NO3-, PO43- etc; (2) Adsorption treatment of highly toxic anions Cr(VI), As(V), As(III), etc.

4.1. Eutrophic anions NO3-, PO43-

Eutrophication of anions NO3-, PO43-, etc., the most direct harm is to cause eutrophication of water, resulting in the wanton propagation of algae in water, occupying the living resources in water, reducing the oxygen content in water, and damaging the water ecosystem. At the same time, NO3 enters the human body and is transformed into highly toxic NO2 through a series of reactions, seriously threatening human health. Therefore, it has become an urgent problem to seek cheap and efficient adsorbent to treat eutrophic anions in water. Song et al [19] used a corn stover to prepare a biomass adsorbent for the removal of NO3 in aqueous solution. Studies have shown that the performance is good in the pH range of 6.0–9.0, PO43- and SO42- have competitive adsorption to NO3-, and the maximum adsorption amount of NO3- is 102.04mg/g. Zhang et al. [20] modified the residue of sphagnum sphagnum extract with Fe(III) to study the adsorption property of PO43-. It was found that the modified adsorbent had the highest removal efficiency of PO43- at pH value of 5, the initial concentration of Fe(III) was 0.072mol/L, and the pH of PO43-solution was 3. The maximum removal efficiency was 82%. As the pH increases, the adsorption efficiency gradually decreases.

4.2. Highly toxic anions Cr(VI), As(V), As(III)

The highly toxic anions Cr(VI), As(V) and As(III), also known as heavy metal anions, are highly destructive to water environment and human health, and are listed as indicators for water quality testing pollutants in various countries. Due to the great harm of such anions, the study on them has been fully reported. Lin et al. [21] fixed FeOOH on the root powder of water hyacinth to prepare biodegradable
biomass adsorbent to improve the adsorption performance of arsenic in aqueous solution. The experiments showed that the adsorption rate and capacity of As(V) and As(III) were significantly enhanced by FeOOG, and the saturated adsorption capacity of As(V) and As(III) was 9.43mg/g and 5.65mg/g respectively within 50 minutes. Regeneration by 0.4 mol/L NaOH solution did not show significant loss of adsorption capacity after 6 cycles of utilization. Hao Linlin et al [22] chemically modified wood chips and coffee grounds to obtain modified biomass adsorbents, and studied their adsorption characteristics and mechanism of arsenic in water. It is found that the modified wood scrap adsorbent has the best adsorption effect when the pH range is 5-6, and the maximum adsorption amounts of As(V) and As(III) are 46.1 and 13.2mg/g, respectively. Therefore, it is a hot spot for subsequent research to introduce a suitable functional group to prepare a novel biomass adsorbent which can be recycled under acidic conditions, and it is stable and efficient.

5. Summary and Scope

Through the study on the treatment of anions by a large number of biomass adsorbents, it is known that biomass adsorbents with low cost, wide sources and renewable resources are becoming the object of extensive attention of scholars. Since the porous structure of agricultural and forestry wastes contains a large number of carboxyl groups, hydroxyl groups and other active groups, anionic pollutants can be better removed. The adsorption effect of the biomass adsorbent is mainly affected by factors such as temperature, pH, initial concentration and adsorption time. Modified agricultural and forestry wastes can obtain better adsorption capacity, and the main mechanisms for adsorbing pollutants are ion exchange, electrostatic interaction, and complex adsorption.

Although reports on the treatment of anionic pollutants in water by biomass adsorbents have increased rapidly, there are still some problems that have not been well solved. For example, how to select the modification method and determine the best modification process; The modification mechanism and adsorption mechanism of biomass adsorbent are not yet clear. The harmlessness treatment means of the adsorbed materials are not yet clear. The forming and practical application of biomass adsorbents have not been studied. Although there are still many problems and challenges, the use of agricultural waste as a biomass adsorbent can not only reduce the environmental burden, but also achieve the goal of “disposal of waste”. In the future environmental governance, it will have a broad space for development.

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references

[1] Xiao-nan ZHANG, Qiu-ping GUO, Xiao-xue SHEN, et al. Water quality, agriculture and food safety in China: Current situation, trends, interdependencies, and management[J]. Journal of Integrative Agriculture, 2015, 14(11):2365-2379.
[2] Jobby R, Jha P, Yadav A K, et al. Biosorption and biotransformation of hexavalent chromium [Cr(VI)]: A comprehensive review.[J]. Chemosphere, 2018, 207:255-266.
[3] Xie Y, Ren L, Zhu X, et al. Physical and Chemical Treatments for Removal of Perchlorate from Water—A Review[J]. Process Safety & Environmental Protection, 2018, 116: 180-198.
[4] Xu X, Gao B, Jin B, et al. Removal of anionic pollutants from liquids by biomass materials: A review[J]. Journal of Molecular Liquids, 2016, 215:565-595.
[5] Shuang-Qi Tian, Ren-Yong Zhao, Zhi-Cheng Chen. Review of the pretreatment and bioconversion of lignocellulosic biomass from wheat straw materials[J]. Renewable and Sustainable Energy Reviews, 2018, 91:483-489
[6] Zhang K, Chen T. Dried powder of corn stalk as a potential biosorbent for the removal of iodate from aqueous solution[J]. Journal of Environmental Radioactivity, 2018, 190:73-80.
[7] Liu W X, Li J X, Wang J L, et al. Adsorption characteristics of modified paulownia leaf sorbent on lead and cadmium in water [J]. Journal of agro-environmental science, 2014, 33(06):1226-1232.
[8] Ren X F. Adsorption of typical dyes and 2,4-dichlorophenol in water by modified leaves of Chinese parasol [D]. Henan: Zhengzhou University, 2014.
[9] Mariappan R, Vairamuthu R, Ganapathy A. Use of chemically activated cotton nut shell carbon for the removal of fluoride contaminated drinking water: Kinetics evaluation[J]. Chinese Journal of Chemical Engineering, 2015, 23(4):710-721.
[10] Yingjie Dai, Qiya Sun, Wensi Wang, et al. Utilizations of agricultural waste as adsorbent for the removal of contaminants: A review[J]. Chemosphere, 2018, 211:235-253.
[11] Ramesh M, Palanikumar K, Reddy K H. Plant fibre based bio-composites: Sustainable and renewable green materials[J]. Renewable & Sustainable Energy Reviews, 2017, 79:558-584.
[12] Ao W, Fu J, Mao X, et al. Microwave assisted preparation of activated carbon from biomass: A review[J]. Renewable & Sustainable Energy Reviews, 2018, 92:958-979.
[13] Gautam R K, Mudhoo A, Lofrano G, et al. Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration[J]. Journal of Environmental Chemical Engineering, 2014, 2(1):239-259.
[14] Danish M, Ahmad T. A review on utilization of wood biomass as a sustainable precursor for activated carbon production and application[J]. Renewable & Sustainable Energy Reviews, 2018, 87:1-21.
[15] Yu Junfeng, Yu Zhimin. Preparation and process optimization of activated carbon by CO2 activated sawdust carbon [J]. Environmental science guide, 2013, 32(4):1-5.
[16] Miao Q, Tang Y, Xu J, et al. Activated carbon prepared from soybean straw for phenol adsorption[J]. Journal of the Taiwan Institute of Chemical Engineers, 2013, 44(3):458-465.
[17] Alba Dieguez-Alonso, Andrés Anca-Couce, Vladimír Frišták, et al. Designing biochar properties through the blending of biomass feedstock with metals: Impact on oxyanions adsorption behavior[J]. Chemosphere, 2019, 214:743-753.
[18] Chen Jing, Li Weimin, Ding Wenchuan, et al. Removal of ammonia nitrogen from water with Fe/Mg modified bamboo charcoal [J]. Chinese journal of environmental engineering, 2015, 9(11):5187-5192.
[19] Song W, Gao B, Xu X, et al. Adsorption of nitrate from aqueous solution by magnetic amine-crosslinked biopolymer based corn stalk and its chemical regeneration property[J]. Journal of Hazardous Materials, 2016, 304:280-290.
[20] Zhang R, Leiviska T, Taskila S, et al. Iron-loaded Sphagnum moss extract residue for phosphate removal[J]. Journal of Environmental Management, 2018, 218:271-279.
[21] Lin S, Yang H, Na Z, et al. A novel biodegradable arsenic adsorbent by immobilization of iron oxyhydroxide (FeOOH) on the root powder of long-root Eichhornia crassipes[J]. Chemosphere, 2018, 192:258-266.
[22] Hao Linlin. Study on preparation of modified biomass material and its adsorption and treatment of arsenic in water [D]. Heilongjiang: Harbin Institute of Technology, 2017.