

Application of Traditional Chinese Medicine Residue and Its Derivatives in Sewage Treatment

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Abstract. As traditional Chinese medicine treatment has received extensive attention in the treatment of novel coronavirus in recent years, output of Chinese medicine residues (CMR) increases. The produced CMR may lead to secondary pollution and waste of resources improperly, but it also can bring huge benefits for environmental protection as a potential resource with high efficiency. This article analyzes the advantages and disadvantages of a variety of CMR treatment methods over these years, investigates and summarizes the previous literature from the aspect of wastewater treatment, then finds that CMR and their derived materials can efficiently and stably absorb some pollutants as new adsorbents after modified treatment. In this article, the pollutants were divided into two main categories: heavy metals and organic matter. Varieties of treatments were proposed and their feasibility of application to wastewater treatment. The mechanism for the pollutant removal is further analyzed, where the adsorption methods include physical and chemical types. Research on the application of the CMR in wastewater is still in its infancy in terms of practical applications, but this research has great potential for development. In the process of recycling and application of the CMR, economic benefits would be brought to society and treatment methods of wastewater would be improved. Future research should be orientated to the study of adsorption treatment of large flow rates and mixed wastewater with multiple pollutants.

Keywords: Chinese Medicine Residues, Composite Material, Wastewater Treatment, Organic Pollutants, Heavy metal.

1. Introduction

In the context of the novel coronavirus epidemic, new treatments are being developed around the world to treat coronavirus patients. Among the many treatments, Chinese herbal therapy has received a lot of attention. With the industrialization of Chinese herbal medicine production, the production of Chinese medicine residues (CMR) produced by the process of concocting and processing Chinese herbal medicine has also risen sharply [1]. The CMR is a solid waste, which still contains rich nutrients, such as cellulose lignin, crude protein, crude fat, amino acids and polysaccharides. The treated residue can be used as a good adsorbent or raw material for adsorption. However, the current methods of disposal are still mostly simple and crude, such as landfill, composting and incineration, and if care is not taken, the organic compounds and bacteria in the residue may affect the surrounding environment through water or soil transportation. Therefore, it is necessary to develop a new way to use the CMR to reduce the negative effects.

And recently, the potential of CMR in wastewater treatment has been discovered by several scholars, and a series of advances in the use of CMR for the treatment of heavy metal and organic pollutions in wastewater have also been made. For example, by using oxygen-limited pyrolysis, Cai et al. prepared biochar by pyrolysis of CMR and found it is a kind of good adsorption of tetracycline in solution [2]. After preparing biochar using CMR. Zhang et al. loaded nano zero-valent iron on CMR biochar and found that the composite had good adsorption effect on methylene blue [3]. Tao et al. used the residue of magnolia officinalis as a raw material to expose more adsorption sites for the

copper ion adsorption by inoculating *Phanerochaete chrysosporium* [4]. It's feasible that recycling CMR and applying it for the treatment of different pollutants such as heavy metal or organic pollutants can show a good prospect for development.

As a result, to recycle CMR and achieve the dual goals of green treatment of CMR and establishing circular economy, this article will analyze the research progress since 2015 about how CMR has been treated for organic pollutants and heavy metals in wastewater, and look at the use of CMR resourcefulness in wastewater treatment.

2. The CMR application and treatment status

2.1. Centralized landfill and incineration

Landfills, incineration and piles were born very early and widely used, which usually transportation the residue from the producing area to remote mountains and fields [5]. The disadvantages of this type of treatment method are also notable. After precipitation or geological transportation, the CMR may cause pollution to nearby water bodies and soil.

2.2. Soil substrate mixture

The CMR is rich in crude fat, protein and amino acids, alkaloids and other substances, as shown in Figure 1. There are a number of scientific results indicating that CMR can be used in agricultural cultivation after processing. For example, suitable fermented CMR was selected and added to the culture substrate proportion, which effectively promoted the growth of vegetation [6]. Chen et al. used cowdung and mushroom residue with CMR as substrate for watermelon cultivation improved the yield of it [7]. However, when it was used for soil fertilization, the amount of CMR needs to be strictly controlled, otherwise it can lead to excessive heavy metal content in the soil then cause secondary contamination.

2.3. Paper making

Wang et al. observed the cellulose structure within *Ganoderma lucidum* by electron microscope scanning and infrared spectrometry method, then matched it to bleached broadleaf wood pulp [8]. What the research made is a kind of paper whose tensile index and burst index are excellent. These papers could be used for packaging Chinese herbs, and other applications.

2.4. Preparation of different functional materials

Because of its good electrical conductivity, biochar prepared from the CMR is often used as electrochemical energy storage material, structural skeleton or battery anode. Such biochar materials still have irreplaceable electrical conductivity, while such carbon materials are slightly deficient in specific surface area and electroactive sites. For example, Guo et al. had used hydrothermal method to make biochar composites of CMR as anodes for lithium batteries in loaded SnS nanosheets [9]. Similarly, Sun et al. transformed CMR into microporous carbon and made it an advanced electrochemical energy storage material [10].

2.5. Preparation of functional materials

Due to its unique porosity, adsorption properties, pH and other properties, the performance of the CMR for the treatment of environmental pollution and adsorption of pollutants has been recognized by numerous scholars. For example, the CMR can be compounded with nano iron and zeolite to obtain the most suitable CMR compound for the treatment of rare earth soil structure, verifying the practicality of this technology. And the activated carbon can be produced from the waste residue of two traditional CMR (*Panax ginseng* and *Medicago sativa*) after adding zinc chloride as an activator. The adsorption efficiency of the prepared activated carbon for copper, lead and other metals is significantly improved, so it can be put into the treatment of heavy metal pollution of sewage.



Figure 1. CMR application and treatment status

3. Application of the CMR in sewage treatment

3.1. Removal of organic pollutants

Most of the sources of organic pollutants in sewage are sewage discharged from the petroleum industry, dyeing and textile industry, aquaculture, and food processing industries. Organic pollutants will cause serious damage to the environment after entering the ecological environment. For example, the printing and dyeing sewage discharged from the dyeing and textile industry contains a large number of dyes, and the sewage from the breeding industry contains antibiotics and pesticides. A diverse of different organic pollutants will worsen water quality and represent a major threat to the entire aquatic ecosystem by raising the water's chemical and biological oxygen demands. By bioconcentration, organic pollutants that enter the water and penetrate the food web and food chain can endanger human life and health.

Sun et al. produced sodium dodecyl sulfate (SDS)-modified angelica dahuricae residues materials with different impregnation ratios by mixing angelica dahuricae residue with different amounts of the SDS [11]. Experiments were conducted on various SDS impregnation ratios, adsorption pH and adsorption times of materials derived from angelica dahuricae. It was discovered that a 1:1 SDS impregnation ratio and a pH of 10.5 produced the best results for adsorption capacity. The modified angelica dahuricae residues materials can be characterized by different instruments. The results show the impregnation of angelica dahuricae residues materials by SDS and the adsorption of methylene blue. The methylene blue adsorption by angelica dahuricae residues materials is not a pore filling effect. The modified angelica dahuricae residues materials exhibit pseudo-second-order model-conforming methylene blue adsorption, demonstrating that chemical adsorption dominates the process of adsorption. The point of zero charge of angelica dahuricae residue materials is greatly impacted by the SDS impregnation ratio. Coumarin is present in significant amounts in angelica dahuricae. Methylene blue is a potent electron acceptor, and the ring-opening of coumarin produces the electron-donating group cis-o-coumaric acid under alkaline circumstances. The π - π bonds between the benzene rings creates a charge transfer complexes when methylene blue comes into touch with the modified angelica dahuricae residues, which stabilizes the structure. Methylene blue changed from liquid to solid and stayed in the modified angelica dahuricae residues materials. After desorption

of modified angelica dahuricae residues materials with hydrochloric acid as regenerating agent, the adsorption capacity of modified angelica dahuricae residues materials to methylene blue has almost no change, showing that the adsorption of modified angelica dahuricae residues materials to methylene blue has high reversibility, with the feasibility of industrial production promotion.

Zhang et al. used CMR recovered from pharmacies, and pyrolyzed them at 900 °C for 4 hours in a vacuum environment to prepare CMR-based biochar [12]. Magnesium hydroxide modified biochar is prepared by loading magnesium hydroxide on CMR biochar. XRD detection of untreated CMR, magnesium hydroxide modified biochar and reactive blue 19 (RB-19) shows that there are magnesium hydroxide characteristic peaks on the modified biochar that neither untreated CMR nor RB-19 appear, indicating that hydroxide magnesium has been loaded on modified biochar. Biochar's specific surface area was somewhat bigger before the alteration than it was after, and part of the pores were plugged by the loaded magnesium hydroxide, according to the BET data. The results also revealed that the adsorption of RB-19 on modified biochar exhibited both spontaneous and endothermic features, and that the adsorption model of RB-19 was more in accordance with the Langmuir model. Electrostatic interactions, pore filling, electron-donor-acceptor interaction, and hydrogen bonding are a few examples of possible adsorption processes. It has been demonstrated that adding alkali to biochar materials can enhance the CMR biochar's ability to adsorb organic pollutants.

Du et al. prepared biochar from angelica dahuricae radix slag as raw material, and loaded nano-zero-valent iron and graphene oxide on angelica dahuricae radix slag biochar to prepare multifunctional magnetic biochar [13]. The synthesized magnetic biochar has plenty of pore structures and high specific surface area. The adsorption effect is greatest when the pH is 7, the biochar is pyrolyzed at 700°C, and 1% of graphene oxide is added. Pore filling, hydrogen bonds, π - π electron-donor-acceptor interaction, and electrostatic interaction are the fundamental adsorption procedures, demonstrating that physical and chemical adsorption dominates in determining the process rate of adsorption. After five cycles, the removal rate exceeded 70%, showing good regeneration. Magnetic biochar is conducive to reducing the difficulty of later recovery, reducing the need for centrifugation, filtration, and other steps to recover non-magnetic biochar in the past, and facilitating large-scale promotion.

Shang et al. used Astragalus mongholicus residue as raw material, and placed it at different temperatures for oxygen-limited conditions to obtain astragalus biochar at different temperatures [14]. Greater specific surface area, richer pore structures, and more active site adsorption for ciprofloxacin (CIP) adsorption are characteristics of higher pyrolysis temperature-produced biochar. The Astragalus mongholicus residue biochar adsorption process on CIP was a process of chemical adsorption, according to the isotherm of adsorption. It has been demonstrated that it is feasible to create biochar materials using CMR as the raw material and then utilize those materials to adsorb antibiotics from sewage.

Wang et al. prepared zinc-biochar composites by adding $ZnCl_2$ to the residues of flueggea suffruticosa residue for pyrolysis and carbonization [15]. The zinc-biochar had a bigger specific surface area and more numerous pore structure than the original Chinese medicine residue biochar, according to the SEM data. The adsorption models on zinc-biochar for tetracycline (TC), oxytetracycline (OTC) and chlortetracycline (CTC) are more similar to the Langmuir model, which indicates that the mechanism of adsorption is monolayer adsorption. The adsorption is a spontaneous process, and the antibiotics such as TC are adsorbed through hydrogen bonding and electrostatic interaction. The composite biochar's adsorption capacity for TC and CTC declined as the Ca^{2+} content in the adsorption environment rose, but the adsorption capacity of OTC increased. It is assumed that Ca^{2+} neutralized the anions on the adsorbent surface, and it decreased the adsorbent's electrostatic repulsion to OTC. The study shows that the concentration of some ions will affect the adsorption effect. As a result, in the subsequent large-scale application and promotion, the concentration of various ions in the sewage needs to be considered to avoid the high concentration of some ions affecting the adsorption effect.

3.2. Removal of Heavy Metals

Wastewater discharged from various industrial production activities, such as electroplating factories, tanneries, textile factories, pigment and dye factories, paint production factories, wood processing factories, photographic film factories, and oil refineries, is the main source of heavy metals in wastewater. If these heavy metals in these sewages are not properly disposed of, it will bring serious damage to environment. The low concentration of heavy metals ions in nature will enter human body through bioconcentration and food webs, which will bring irreversible harm to human health.

Shang et al. used co-precipitation method to prepare magnetic biochar by using dahuricae residue as raw material [16]. The results indicated that the surface of the prepared astragalus membranaceus residue magnetic biochar was covered with iron oxide particles. In the environment of low pH ($\text{pH} < 2$), the adsorption effect of astragalus membranaceus residue magnetic biochar on Cr^{6+} was the best. The adsorption capacity peaked at pH 2, which was also critical for the removal of Cr^{6+} . The pseudo-second-order model and the Langmuir adsorption isotherm model both provided good fits to the batch sorption data. It shows the great potential of drug residue biochar as an adsorbent, and magnetic biochar is also convenient for subsequent recovery and processing.

Increased surface area and improved adsorption performance are achieved by the inoculation of *Phanerochaete chrysosporium* on drug residues [17]. *Phanerochaete chrysosporium* was inoculated into the discarded magnolia officinalis residues and fermented. In this way, the lignin in magnolia officinalis residues is decomposed and the specific surface area is enlarged. The specific surface area of the magnolia officinalis residues after fermentation reached $1.013 \text{ m}^2/\text{g}$, which was 2.57 times that before the fermentation. Under the same conditions, the adsorption rate of Magnolia officinalis residues for Cu^{2+} after 14 days of fermentation was 3.15 times higher than that of unfermented, showing better adsorption performance. Cu^{2+} was more effectively adsorbed on the used materials, which is consistent with Freundlich equation and suggests that the existing functional groups can affect the adsorption capacity. The results show that Cu^{2+} interacted with several functional groups on the used materials throughout the adsorption procedure. After several experiments with adsorption and regeneration, fermented Magnolia officinalis residues still maintained its good adsorption performance. It is fully proved that the use of CMR as adsorbent material is cheap and efficient, and it is feasible to inoculate specific microorganisms to enhance the adsorption capacity of traditional Chinese medicine residues, which has the potential for popularization and application.

The rich cellulose content in CMR has attracted the interest of some scholars. Qiu et al. selected radix astragali residue as raw material, extracted cellulose as the precursor, and prepared a double-network hydrogel [18]. The theoretical adsorption value of Pb^{2+} on the chemically modified double-network hydrogel reaches 994.5 mg/g , which is 5 times that of the unmodified hydrogel. The findings of the thermodynamic calculations demonstrate that chemical adsorption and ion exchange constitute the majority of the total adsorption process. After the actual wastewater adsorption test, it was found that the modified double-network hydrogel has high selectivity for the adsorption of Pb^{2+} . At the same time, after repeated adsorption and regeneration experiments, the modified hydrogel still maintained a high adsorption capacity for Pb^{2+} . It is proved that it is feasible to develop high-selective adsorbents for some heavy metal elements from CMR.

Chen et al. used CMR and chicken manure as raw materials, pyrolyzed and carbonized in a nitrogen atmosphere, added potassium dihydrogen phosphate, and then pyrolyzed again to prepare phosphorus-modified biochar [19]. The capacity of phosphorus-modified biochar to adsorb Pb^{2+} increases when pH rises in a certain range. The reason is that at higher pH, the surface of phosphorus-modified biochar is deprotonated, so that more active sites on the surface can be combined with Pb^{2+} , and the adsorption performance is enhanced. The pseudo-second-order kinetic model's R^2 was higher than the pseudo-first-order kinetic model's, but both models' R^2 values were higher than 0.99. Therefore, the adsorption process of Pb^{2+} by phosphorus-modified biochar has chemical adsorption and physical adsorption. The results show that it is feasible to prepare heavy metal adsorbents with CMR and chicken manure. Phosphorus also played a considerable role in the chemical modification

of biochar and created a fresh idea for the creation of high-performance adsorbents from CMR and another biomass.

Chen et al. used Chuanxiong rhizome residue and Chinese wolfberry residue as raw materials to test their adsorption capacity for chromium ions [20]. It was found that the removal percentage of Cr^{6+} from the Chinese wolfberry residue and Chuanxiong rhizome residue were greater than 85% and 98%, respectively, at a lower pH (2-4) and the starting value of 0.05 g/L. The overall removal process is mainly reduction and adsorption, and Cr^{6+} is reduced to Cr^{3+} on the surface of the residue. The Cr^{3+} ion produced on the residues surface interacts with Cr-binding groups to form complexes. This study confirmed the feasibility of removing Cr^{6+} by reducing Cr^{6+} to Cr^{3+} . Additionally, the abundance and low cost of CMR indicate considerable promise for the creation of inexpensive adsorbents.

4. Adsorption mechanism analysis with CMR for organic pollutants and heavy metals

As shown in Figure 2, the main methods of adsorption of organic pollutants by CMR derived materials include pore filling, π - π stacking, hydrogen bonding and electrostatic interaction. CMR materials contain a large amount of lignin, cellulose, hemicellulose and other components. High temperature pyrolysis and other methods can help to increase the specific surface area of CMR materials, thereby exposing more active sites to adsorb organic pollutants. Shang et al. used astragalus mongholicus residue as raw material, and prepared biochar at different temperatures. It was found that the biochar materials produced under situations of greater temperature had bigger specific surface areas and more pore structure [14]. The enormous specific surface area and many pores let biochar materials physically adsorb organic pollutants more effectively. However, the kinds and quantities of various functional groups on the biochar surface will decrease as the pyrolysis temperature increases. There are several different functional groups, such as $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$. However, the adsorption capacity of some CMR materials for organic pollutants depends on the functional groups of the used materials. The decrease in the number and type of functional groups may have a negative impact on effects of adsorption. Some scholars have prepared materials with better adsorptive properties by modifying the CMR materials with the addition of substances such as alkali, salts, or surfactants to increase their specific surface area, surface functional groups, or decrease the electrostatic repulsion of the adsorbent materials on the adsorbed materials.

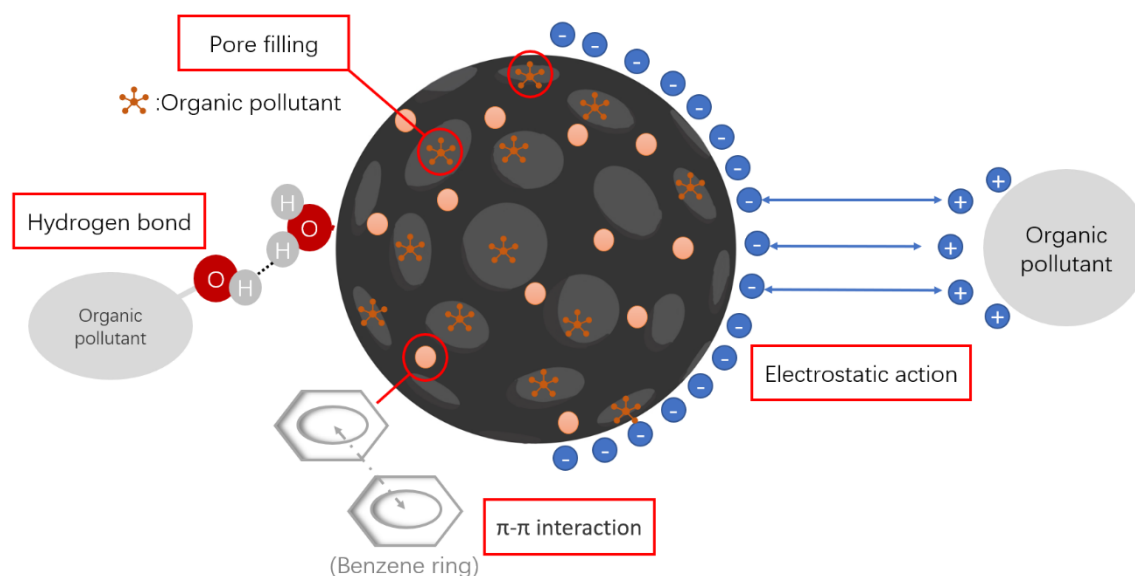


Figure 2. Adsorption mechanism of CMR-based materials for organic pollutants

Precipitation, ion exchange, redox, electrostatic adsorption and complexation are the main adsorption mechanisms of heavy metals from CMR materials, as shown in Figure 3. On the surface of CMR materials, there are several types and different functional groups that are crucial for heavy metal removal. Co-precipitation is through the combination of phosphate and sulfate on the surface of CMR materials with heavy metal ions, so that the heavy metal is precipitated on the CMR materials surface, and the adsorption process is completed. Ion exchange refers to the exchange of cations and heavy metal ions on the CMR materials surface, thus completing the adsorption of heavy metals. Chen et al. modified biochar cotyrolized from chicken manure and CMR by using potassium dihydrogen phosphate so that phosphate radicals were loaded on biochar and combined with Pb^{2+} , to adsorb Pb^{2+} [19]. At the same time, after the co-pyrolysis of chicken manure and CMR, the biochar has a large amount of K^+ on the surface. K^+ and Pb^{2+} undergo ion exchange to complete the adsorption. There are several different functional groups, such as $C=C$ and $C\equiv C$. Heavy metal adsorption can be completed by complexing $-OH$ with heavy metal ions to create complexes. The electrostatic adsorption is influenced by pH of the environment. When the pH of the solution exceeds the zero-charge point of the adsorbent, which is deprotonated and becomes negatively charged, which adsorbs positively charged heavy metal cations. On the surface of the substance, protonation occurs when pH lower than the point of zero charge, the surface carries a positive charge and adsorbs anions. The redox principle is to reduce high-valence heavy metal cations to less toxic low-valence ions, and then adsorb them. Chen et al. used Chuanxiong rhizome residue and Chinese wolfberry residue to adsorb Cr^{6+} [20]. And it was found that a redox reaction occurred during the adsorption process. Cr^{6+} oxidizes the phenolic hydroxyl groups on the drug residues to quinones, and at the same time is reduced to Cr^{3+} , forming complexes attached to the drug residues surface.

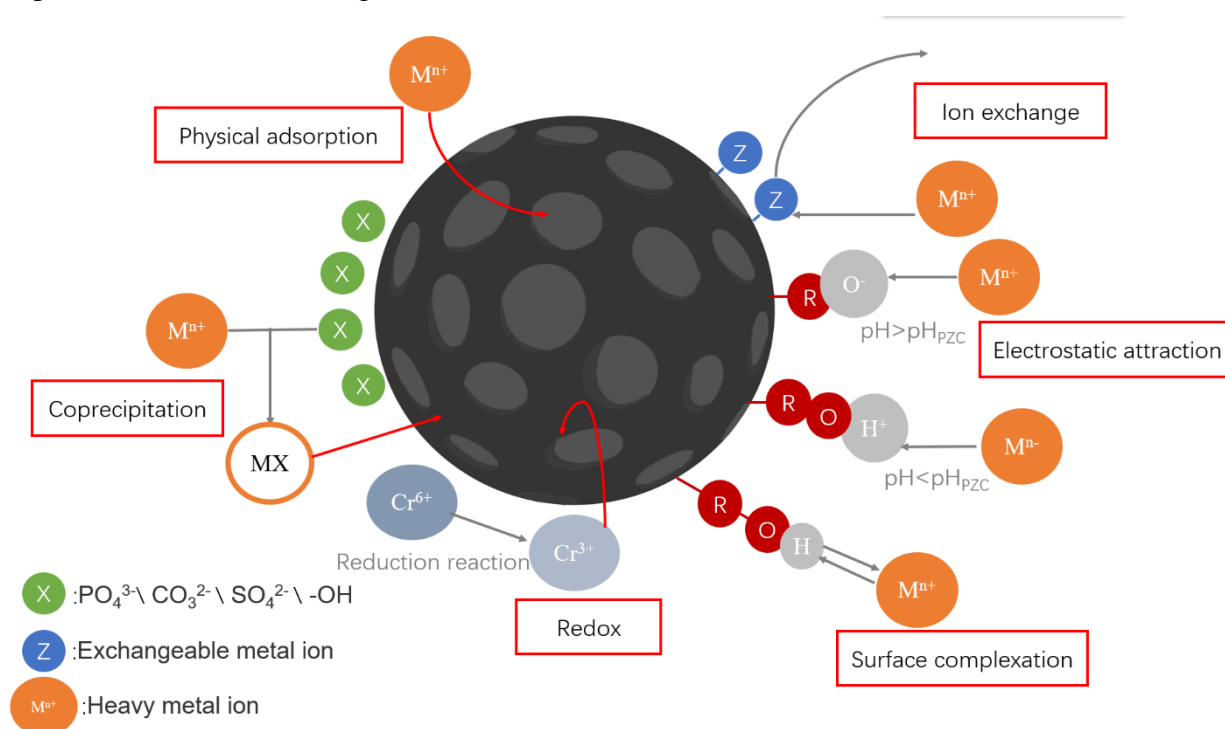


Figure 3. Adsorption mechanism of CMR-based materials for heavy metal ion

5. Conclusions

New coronavirus has brought Chinese medicine and herbal medicine into the limelight. On the other hand, as a kind of solid waste of CMR, how to dispose of it properly is a key point. The traditional disposal methods of solid waste (piling, landfill and incineration) are prone to secondary pollution of the environment. At the same time, the treatment of different pollutants in wastewater is also in urgent need of a new method to guide the application. By treating waste with waste, recycling and resourcing

the CMR for application in wastewater treatment, it is conducive to achieving the dual goals of green treatment of CMR and building a circular economy. There is a great potential to recover and resource the CMR and apply it to the adsorption treatment of different pollutants in wastewater according to the existing research results. It is feasible to further increase the adsorption performance of the herbal residue material by such operations as modification of the material, and the preparation of the magnetic material also facilitates the subsequent recycling process. Based on the different nature and structure of the two pollutants, there are differences between the mechanism of adsorption of CMR materials to the two pollutants, then to achieve the best adsorption effect, choosing the best material preparation according to the needs of different pollutants is necessary.

At present, the research on the adsorption effect of CMR materials still stops at the laboratory stage. Few scholars have tested and developed the actual adsorption capacity of CMR for industrial and domestic wastewater, and the research on mixed wastewater with multiple pollutants is at an early stage, so there is not enough research and industrial production for practical applications. Future research should be orientated to the study of adsorption treatment of large flow rates and mixed wastewater with multiple pollutants.

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