

Adsorption and Removal Performance of Waste Biomass for Pollutants in water under The Background of ''Double Carbon''

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Abstract: While the quality of the environment is gradually declining, non-renewable resources are also being continuously consumed. In the future, human beings may have to face the dual challenges of the continuous decline of the ecological environment and the gradual exhaustion of non-renewable resources. Therefore, it is of great significance for environmental protection and sustainable development of resources to develop waste renewable resources and apply them to environmental governance. The main purpose of this paper is to study the performance of waste biomass adsorption to remove pollutants in water based on the "two-carbon" background. In this paper, the typical antibiotics in the micro-polluted water body are taken as the research object, and the rice straw and corn stalk in the agricultural production process are used as the modified objects. Through the modification of acids and biological enzymes, it is clear that different modification conditions have a typical effect on the adsorption of biomass. The effect of antibiotics. The study showed that the adsorption capacity of TYL increased with the increase of reaction time. In 0-2H, the adsorption capacity of TYL increased the fastest, accounting for 60%-80% of the total adsorption. It continued to increase for 5-7 hours, but the speed became slow, and the adsorption amount reached the maximum value at 12H, and the adsorption tended to be balanced.

1. Introduction

There are a large number of natural renewable macromolecular substances in nature, which have different structures, shapes and components, and can be degraded by nature. Therefore, researchers

have begun to pay attention to the renewable biomass resources in nature. By modifying and processing them to prepare materials with various functions, it is not only a means to solve environmental pollution, but also fully realize the utilization of renewable resources. Industrial and agricultural production activities have caused a large amount of nitrate-containing wastewater to enter natural water bodies, causing serious harm to human health and the ecological environment, resulting in the degradation of aquatic biodiversity. There is an urgent need to develop a cost-effective biomass adsorption material and clarify its adsorption mechanism [1].

In a related study, Detho determined the percentage reduction of COD and ammonia nitrogen (NH3-N) by using coconut shell activated carbon (CSAC) and peat soil (PS) as economic composite adsorbents and partially reducing the amount of CSAC [2]. The method to determine the optimal conditions for composites is carried out using static batch processing techniques. The coefficient of determination values indicated that the Langmuir models for COD and NH3-N were consistent with the experimental data for decontamination. Manzur et al. assessed plant biomass, root length, and nitrogen concentration, and assessed intrinsic water use efficiency (iWUE) and its component net photosynthesis and stomatal conductance by carbon and oxygen isotopic analysis of shoot tissues [3]. It was found that both types of plants produced similar biomass under water-limited conditions. aimed to evaluate the potential of biosorption technology under more realistic conditions to remove toxic Pb(II), Cr(III) and Cr(III) from wastewater by utilizing locally available biosorbents such as produce jute stick powder (JSP) The Cd(II) ion [4]. Fourier transform infrared spectroscopy (FTIR) and scanning electron micrograph (SEM) analysis demonstrated that the surface of the biosorbent was porous with a heterostructure containing high internal space. The removal efficiency of the target metal mixture by JSP was optimized in terms of pH, initial metal concentration, shaking time and biomass dosage. The biosorption performance of JSP in various metal systems has an adsorption rate of more than 90% for the tested metal ions. Biomass regeneration efficiencies of up to 98% can be achieved using acid as eluent.

Based on the "two-carbon" background, this paper studies the performance of waste biomass adsorption to remove pollutants in water. This paper firstly analyzes the water pollution removal technology and introduces the water pollution treatment method. In this paper, the typical antibiotics in the micro-polluted water body are taken as the research object, and the rice straw and corn stalk in the agricultural production process are the modified objects. Through the modification of acids and biological enzymes, it is clear that different modification conditions can adsorb typical antibiotics on biomass. Influence, adsorption characteristics and mechanism of straw modification on typical antibiotics.

2. Design Research

2.1. Water Pollution Removal Technology

In response to the shortage of water resources and serious nitrogen and phosphorus pollution, the country has issued a series of water quality standards. In order to achieve this standard, the content of phosphate and nitrate in water should be reduced. There are mainly the following methods [5-6].

2.1.1. Chemical Precipitation Method

At present, chemical precipitation is mainly used for the removal of phosphate in water. Add the phosphorus removal agent to the wastewater with excessive phosphorus content, and the metal ions in the agent react with the phosphate to form a new substance, that is, insoluble phosphate precipitate. Effect of salt. The chemical precipitation method has the advantages of economical reliability, convenient operation, quick effect, and adaptability to a variety of water quality.

2.1.2. Biological Treatment Method

Using the metabolism of microorganisms to remove nitrogen and phosphorus in water has the advantages of low cost and good treatment effect, and has good application prospects, but the treatment period is long, and the microorganisms after use will cause secondary pollution to the environment.

2.1.3. Membrane Separation Technology

Membrane separation technology refers to the technology in which some specific ions and particulate mixtures in water achieve selective permeation when passing through a semi-permeable membrane, and the driving force is generally voltage difference or concentration difference. Since the membrane separation method has relatively high requirements for the inlet water quality and only has the effect of removing specific substances, there are insurmountable obstacles to the removal and recovery of nitrogen and phosphorus by the membrane separation method. Usually biological methods are used together with membrane separation technology to achieve the effect of removing nitrogen and phosphorus.

2.1.4. Adsorption Method

The nitrogen and phosphorus are adsorbed by porous materials, and then removed by surface precipitation, ion exchange, etc., and then the removal and recovery of nitrogen and phosphorus are realized by adsorption-desorption. The adsorption method has the advantages of simple principle, high efficiency, strong adaptability, and no secondary pollution, and has good application prospects, but the adsorbent has problems such as high cost and low regeneration rate.

In summary, the operating conditions required for nitrogen and phosphorus removal by biological methods are relatively strict, and it is difficult for traditional processes to operate stably, which makes it difficult for effluent nitrogen and phosphorus to reach the standard stably, and is easily affected by water quality conditions and environmental factors. , the treatment effect of lower concentrations of nitrogen and phosphorus is poor. The precipitated substances produced by the chemical precipitation method may cause secondary pollution to the environment, and when the phosphate concentration is too high, a large amount of chemicals needs to be added, which will also pollute the ecology of the water body and lose the water purification effect. Membrane separation can remove specific pollutants in wastewater, especially macromolecular pollutants, through simple operations. However, the initial cost is high, the membrane is prone to blockage, there are relatively strict requirements for the water quality of the membrane, and it is inconvenient to replace. For the catalytic reduction method, the process conditions have high requirements, and it can only be used for specific waste water, such as highly hazardous radioactive waste water, and its investment and operation cost is high. Although nitrate can be quickly reduced to nitrogen, the catalyst selectivity is not easy to control., and prone to secondary pollution. The adsorption method has attracted a lot of attention of researchers due to its advantages of convenient operation, high efficiency and reliability, no secondary pollution, and good adaptability, and is widely used in the field of water treatment. The adsorption method can enrich the pollutants in the water to the surface of the adsorbent, can effectively achieve the enrichment of nutrients in the water, and can be used as a good carrier. When dealing with sudden pollution situations, adsorption method can also be used as the preferred method to achieve rapid removal of pollutants in water, which is a promising treatment method for nitrogen and phosphorus removal [7-8].

2.2. Processing Method

At present, physical (such as adsorption, air flotation, evaporative crystallization, solvent extraction, etc.), chemical (such as photocatalysis, chemical precipitation, chemical oxidation, electrochemistry, etc.) and biological (such as biological adsorption, biological flocculation, etc.) technologies have been applied to Deal with water pollution problems in different situations. Among them, adsorption methods exhibit significant advantages over other wastewater treatment technologies in terms of ease of operation, initial cost, flexibility, and effectiveness against a wide range of pollutants. Therefore, the adsorption process is considered as a potential and efficient method among all possible technologies for the treatment of colored wastewater. In addition to adsorption technology, photocatalytic degradation technology, as a clean technology, is also considered to be a very promising technology in existing organically polluted wastewater treatment methods [9-10].

Adsorption usually uses the attractive force of the adsorbent itself or the chemical bonds on the surface to achieve the immobilization of metal or organic molecules. Physical adsorption is generally unstable, the adsorption is weak, non-selective, and easily disturbed. Chemisorption is faster and more stable due to the action of chemical bonds. In practice, the two adsorption processes are not completely independent, and most adsorption processes are accompanied by two adsorption processes. This also means that the adsorption process does not require additional energy, and with the aid of the large specific surface area or rich functional groups of the adsorbent, the adsorbent can even achieve a removal effect of more than 99%. For some precious metal ions, it can also be recycled through adsorbents. Therefore, adsorption is widely used in organic or inorganic wastewater treatment processes.

Photocatalytic degradation technology is to generate electron-hole pairs (e--h+) through the action of light on the surface of the catalyst. When the incident light is larger than the energy band gap (Eg) of the photocatalyst, it will excite the catalyst surface to generate e- and h+. Subsequently, e- will convert the contacted O2 into superoxide radical (·O2-); h+ will oxidize hydroxyl or water on the surface, thereby generating hydroxyl radical (OH). The generated active substances such as OH, O2- and h+ will mineralize organic macromolecules to produce harmless organic small molecules or harmless CO2 and H2O final products, thereby achieving the degradation of pollutants. In addition, photocatalytic technology can also achieve the reduction of some high-valence metal ions (such as Cr(VI), U(VI), etc.) through the generated e-, so as to weaken or eliminate the generation of high-valence metal ions. harm. Therefore, photocatalytic technology has received attention in the degradation of organic wastewater (such as dyes, medicines) and the reduction of metal ions [11-12].

2.3. Adsorption Kinetic Model

It is mainly used to describe the adsorption process of antibiotics by adsorbents, and the rate-controlling process includes material transfer and chemical reaction. Commonly used are the first- and second-order Lagrangian kinetic equations, which are used to describe the time-varying rate law of antibody adsorption in the adsorption medium, and the first- and second-order Lagrangian kinetic equations in Equation 1 and Equation 2. The adsorption process and rate-controlling agent in antibiotics, calculated from the adsorption data using the internal diffusion model of the particle, is Equation 3.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

$$q_t = k_i t^{0.5} + Cond \tan t \tag{3}$$

Among them, qe(mg/kg) is the saturated adsorption capacity, qt(mg/kg) is the adsorption capacity at time t, k1(l/h) is the first-order Lagrangian kinetic reaction rate, $k2(g)/\mu g$ /min) is the Lagrangian kinetic adsorption process constant, kt (mg/(g h1/2))) is a constant, which is related to the particle diffusion rate, and Constant is a constant, which is related to the thickness of the adsorbent boundary layer.

3. Experimental Study

3.1. Adsorption Experiment

3.1.1. Adsorption Kinetics Experiment

In order to study the removal rate and interaction of TYL in water by the modification of straw materials by strong acid, adsorption kinetics experiments were carried out. into a 30m1 glass centrifuge tube, pour 20m1 of TYL (Tylosin) solution with a concentration of 5ppm, weigh and seal them separately, put them in a constant temperature of 25 °C, and react in a shaker with a rotation speed of 150r/min to avoid light. Set the mS adsorption TYL blank reference. The sampling time was set as reaction 15min, 30min, 1h, 3h, 5h, 7h, 12h and 24h, and two parallel samples were made for each node. Use a 0.45µm disposable filter head connected to a syringe to sample 1 ml of the reaction solution and store it in a 1.5 ml brown chromatographic bottle for detection and analysis.

3.1.2. Adsorption Isotherm Experiment

Dilute the TYL mother liquor with ultrapure water to prepare TYL solutions with concentrations of 1ppm, 5ppm, 10ppm, 20ppm and 30ppm in sequence, add a certain amount (0.02-0.07g) of C-mS, S-mS and N-mS respectively, and place them at a constant temperature. 25°C, 150r/min vibration under the condition of 12H (according to the kinetic experiment, the 12H adsorption reaches equilibrium), sample into the chromatographic bottle for detection, the number of parallel samples in each group is 2, and set the MS (mass spectrometer) adsorption blank as a reference experiment.

3.1.3. The Effect of pH on Adsorption

In order to investigate the effect of solution pH on the adsorption process, the adsorption experiments of H-mS on TYL under different pH conditions were carried out. The pH of the background solution was adjusted to 3, 5, 7, 9, and 11 with HnO3 and KOH, to dilute the TYL stock solution to 10 ppm, and 0.03 g of C-mS, S-mS, and N-mS, then poured 25m1 of 10ppm TYL solutions of different pH prepared above, placed at a constant temperature of 25 $^{\circ}$ C, vibrated for 12H under the condition of i50r/min, and connected a syringe with a 0.45 μ m-disposable filter to sample 1m1 of the reaction solution in Refrigerate in a 1.5ml brown chromatographic bottle for detection and analysis. The number of parallel samples and blank reference were similar to other experiments.

3.1.4. Adsorption Thermodynamic Experiment

Dilute the TYL mother liquor with ultrapure water to prepare TYL solutions with concentrations

of 1ppm, 5ppm, 10ppm, 20ppm and 30ppm in sequence, add a certain amount (0.02-0.07g) of C-mS, S-mS and N-mS respectively, and keep them at a constant temperature. 15 °C, 25 °C and 35 °C, under the condition of 150r/min, shake to equilibrium sampling to be detected in the chromatographic bottle; the number of parallel samples and blank reference are the same as the above experiments.

3.2. Material Preparation

The original raw-LC was immersed in deionized water for 720 min to remove impurities and then dried at 50 °C. LC/h-ZIF-8 composites were prepared by two methods.

Deposition method: A typical procedure is to transfer 2-MIM (2.0g) and raw LC into 20.0 mL of deionized water (DIW). The suspension was dispersed with ultrasound for 10 min and stirred for 120min. Then 2.5mL of waste water was added to the suspension and stirred at room temperature for 120min. Among them, the composite materials were prepared with different quality LC (0.06~0.18g), and the best quality of LC (loofah) was investigated. By comparing the mass of LC (mass LC) and LC/h-ZIF-8 (mass LC/h-ZIF-8), the ratio of h-ZIF-8 loaded to LC was obtained, and the calculation formula is: ratio) = (mass LC/h-ZIF-8-massLC)/mass LC×100%. Finally, after washing with deionized water, it was dried at 50 °C and named as raw-LC/h-ZIF-8.

In addition, the catalytic performance of raw-LC/h-ZIF-8 was optimized: (1) the raw LC was pretreated with NaOH solutions of different concentrations (0.03~0.7mol L-1); (2) the raw LC was pretreated with h-ZIF-8 composites prepared at different temperatures (25 $^{\circ}$ C~85 $^{\circ}$ C) The composites prepared under optimal conditions were named LC/h-ZIF-8.

Solvothermal method: The steps are the same as the deposition method, but the solvent is methanol (MT), after the final mixture of 2-MIM, LC and waste liquid is completed, the mixed solution is transferred to the tetrafluoroethylene liner of the stainless steel autoclave at 120 React at 720mim at $^{\circ}$ C. After the reaction was completed, the samples were washed with distilled water and ethanol, and then dried at 50 $^{\circ}$ C (named LC/h-ZIF-8H).

4. Experiment Analysis

4.1. Preliminary Experiments on Adsorption of Modified Straw Materials

In order to optimize the experimental conditions and improve the experimental efficiency, the TYL adsorption and removal effects of different biomass under different modification conditions were pre-tested. First, select 5m of nitric acid modified 10H n-rS, N-mS and n-WS for pre-adsorption experiments, respectively weigh 0.05g of the above modified materials into a 30m1 glass centrifuge tube, pour 25m1 of 20ppm TYL initial solution, and put Shake in a constant temperature shaker, set two parallel samples for each group of samples, and set a blank experiment for the adsorption of TYL by unmodified straw materials corresponding to the test conditions. Sampling 1 ml of the reaction solution through a 0.45µm disposable filter needle and put it in a 1.5 ml brown chromatographic bottle for detection and analysis. The TYL concentration of the solution after the reaction was detected by HPLC, and compared with the blank experiment, the adsorption capacity of TYL by different modified biomasses was obtained as shown in Table 1.

It can be seen from the figure 1 that mS has the strongest ability to adsorb TYL after modification. In the subsequent experiments, mS was selected as the main material for modification and experimentation.

StalkBefore modificationAfter modificationStraw461557Maize8741526Wheat398409

Table 1. Adsorption comparison of TYL by different modified straws



Figure 1. Comparative analysis of adsorption of TYL by different modified straws

4.2. Adsorption Kinetic Analysis

The change trend of the adsorption amount of T-mS and T-rS on TYL in solution with the increase of reaction time is as Table 2:

Table 2. Fitting of adsorption kinetics of TYL on enzyme-modified straw materials

Conditions	Q _{eexp} (mg/kg)	Pseudo-first-order			Pseudo-second-order		
		q _e (mg/kg)	K1(1/h)	\mathbb{R}^2	q _{eexp} (mg/kg)	$K^2 \times 10^{-4} (1/h)$	\mathbb{R}^2
MS	1531	529	0.84	0.78	1534	26.1	0.99
RS	1393	401	0.66	0.75	1328	16.1	0.99
T-RS	1952	1305	0.88	0.87	1876	14.2	0.99
T-MS	2112	1541	0.79	0.73	2229	16.7	0.99

It can be seen from the figure 2 that the adsorption capacity of TYL increases with the increase of reaction time. In 0-2H, the adsorption capacity of TYL increased the fastest, accounting for 60%-80% of the total adsorption. It continued to increase for 5-7 hours, but the speed became slow, and the adsorption amount reached the maximum value at 12H, and the adsorption tended to be

balanced. The saturated adsorption capacity of TYL by different straw materials was in the order of T-mS>T-rS>mS>rS. Among them, the maximum adsorption amount of T-mS (2109 mg) is 1.5 times that of the minimum adsorption amount of rS (1390 mg/kg), and T-rS (1949.5 mg/kg) is 1.4 times that of rS. This shows that the TYL adsorption capacity of the enzyme-modified corn stalk material has been greatly enhanced, and it has played a good role in promoting the adsorption of TYL.

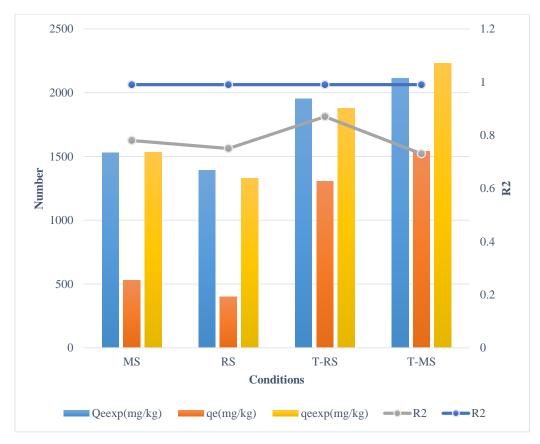


Figure 2. TYL adsorption kinetics fitting analysis diagram

In order to better describe the adsorption process of H-mS to TYL, Lagrangian first-order and second-order kinetics were introduced to fit the adsorption kinetic data. The adsorption model has been described in the second part. According to The data were fitted by formula (1) and formula (2) respectively, and the obtained adsorption parameters are shown in Table 3.

Conditions	Q _{eexp} (mg/kg)	Pseudo-first-order			Pseudo-second-order			
		q _e (mg/kg)	K1(1/h)	\mathbb{R}^2	q _{eexp} (mg/kg)	$K^2 \times 10^{-4} (1/h)$	\mathbb{R}^2	
MS	1531	529	0.91	0.77	1534	26.1	0.99	
RS	2202	1105	0.81	0.78	2236	10.1	0.99	
T-RS	2103	1012	0.80	0.80	2011	8.2	0.99	
$T_{-}MS$	2153	1020	0.76	0.70	2001	14.7	0.00	

Table 3. Fitting of adsorption kinetics of TYL on straw materials

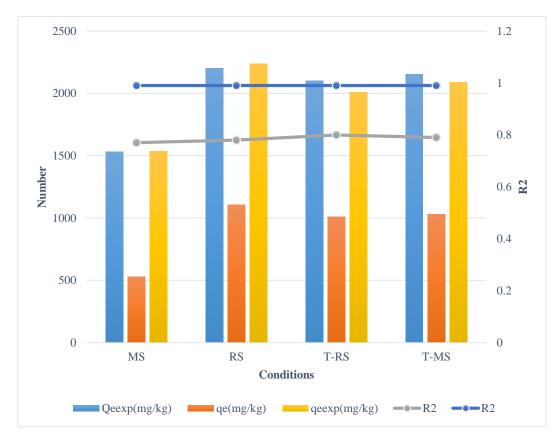


Figure 3. Fitting analysis diagram of adsorption kinetics of TYL on straw materials

The % value obtained by the first-order kinetic simulation is relatively small, which is quite different from the % measured by the experiment, and the correlation coefficient is obviously smaller than that of the second-order kinetic simulation data, and the correlation coefficient f of the second-order kinetic simulation is close to 1, which can be more efficient. The adsorption kinetic data of TYL in mS and H-mS are well fitted. It can also be seen from the figure 3 that compared with the first-order kinetic model, the second-order kinetic model has a better fitting effect on the adsorption kinetic data. , the rate control of the adsorption process may be dominated by chemical action.

5. Conclusion

Studies have shown that agricultural waste biomass mainly contains a large amount of cellulose, and cellulose itself has abundant functional groups (such as carboxyl groups, hydroxyl groups) and special structures (such as network, porous or hollow), so they can become the field of wastewater treatment. Strong candidate [13-15]. Moreover, the biomass material itself comes from nature, so it does not show any toxicity to the environment and organisms, and is extremely friendly. At the same time, the mechanical strength of biomass can be used as a carrier for other materials. By combining with other functional materials, the inherent adsorption properties of biomass materials can be exerted, and the structure of biomass materials can be used to realize many nanoscale functional materials. Dispersion and separation from aqueous solutions, thus combining the advantages of the two and overcoming the disadvantages of the two. Therefore, it is an effective measure to achieve sustainable development to apply the widely distributed biomass material components in the field of wastewater treatment.

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Data Availability

Data sharing is not applicable to this article as no new data were created or analysed in this study.

Conflict of Interest

The author states that this article has no conflict of interest.

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