ISSN: 2414-1895 DOI: 10.6919/ICJE.202308_9(8).0002

Study on the Performance of Modified Biochar in Treating Oily Sewage from Ships

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Abstract

With the rapid development of China's economy and foreign trade, the shipping industry with large volume and low freight rate is also growing. With the increasing number and tonnage of ships, the pollution of a large number of ship oily sewage to the marine environment is becoming more and more serious. How to treat ship sewage efficiently and conveniently has become a top priority. In recent years, biochar has attracted much attention in the field of sewage treatment due to its rich pore structure and efficient adsorption performance. In this paper, ship heavy oil was selected as the target pollutant, and hydrochloric acid was used as the modified solution. The single factor experiment was used to explore the repair and treatment of ship oily sewage by modified biochar. The main conclusions are as follows: Under the optimal modification conditions of 30°C, 2 mol/L modified solution concentration and 16 h modification time, the acid modification method can greatly increase the specific surface area and pore volume of biochar. The adsorption efficiency of oil pollution has been greatly improved, providing a maximum adsorption capacity of about 14.86 g/g. The research on biomass conversion in this paper can not only promote the development of agricultural waste recycling, but also alleviate the pollution and environmental damage of ship sewage to marine ecology.

Keywords

Biochar; Corn Straw; Ship Oily Sewage; Environmental Governance.

1. Introduction

The pollution of ship oily sewage to the ocean is very serious, and the input channels are diverse. Because of its stable structure, it is easy to remain in the marine environment for a long time [1], but the current treatment effect is not ideal. Therefore, the treatment of ship sewage has become an urgent task. The specific methods and characteristics of the current treatment of oily sewage from ships are shown in Table 1.

Table 1. Method and characteristics of oil-containing sewage

Class	Specific methods	Feature
Physical methods	Adsorption method, Sedimentation method	Low cost, Wide source, General removal effect
Chemical process	Dispersant method, Electrochemical method	Technology is simple, High cost, Easy to cause secondary pollution
Biological process	Microbial method, Activated sludge method	High efficiency, Good effect, Environmental friendly

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In a variety of treatment methods, the correct and efficient treatment of these sewage is very important. Although the removal effect of physical adsorption method is slightly lower than that of chemical method and biological method, it is more easily accepted by people because of its simple treatment process, wide source of raw materials, low cost and no secondary pollution to seawater. It has become the most commonly used method for treating oily sewage from ships.

The raw materials for the preparation of biochar are extremely extensive, and most crops and biomass in nature can be used [2]. According to statistics, the annual output of crop straw alone has exceeded 700 million tons, accounting for about 20~30% of the world 's total straw. However, most of them are abandoned and buried or burned in the open air, which does not achieve the resource utilization of plant waste and causes a certain degree of environmental pollution [3]. The preparation of biochar happens to be an effective use of these plant wastes and helps to mitigate global issues such as global warming, soil improvement, resource recycling and carbon storage [4]. Biochar is a carbon-rich product obtained by thermochemical conversion of biomass under oxygen-limited or anaerobic conditions. At present, biochar materials can be divided into pretreatment method and post-treatment method from the preparation method [5]. From the preparation environment, there are mainly anaerobic pyrolysis and oxygen-limited pyrolysis. From the preparation of carbonization temperature and heating rate to classify, mainly gasification pyrolysis, hydrothermal carbonization and microwave pyrolysis [6]. Porous biochar has attracted much attention due to its excellent pore structure, attractive physical and chemical properties, low cost and wide source. Igalavithana et al found that the presence of nitrogen and sulfur in biochar is the main reason for the high CO2 adsorption capacity [7]. The micropores formed by potassium hydroxide can also further improve the adsorption capacity of biochar to CO2, while the combined activation of potassium hydroxide and CO2 cannot improve the micropores and CO2 adsorption capacity of biochar. The preparation of biochar by pyrolysis is a current research hotspot. The preparation of biochar by microwave and hydrothermal methods will be the future research direction. In addition, new biomass energy can be developed by gasification technology [8]. Biochar also has the characteristics of high pH value, high specific surface area, high carbon content and rich functional groups. It can be applied to soil improvement, water pollutants [9].

There are a wide range of raw materials for the preparation of biochar, and the internal structure formed under different pyrolysis time and temperature also has great changes : Kong [10] used a slow pyrolysis preparation process at a pyrolysis temperature of 400~600°C, and the holding time was 30~90 min to prepare palm kernel shell biochar. Akhtar et al achieved carbon conversion of biomass of date palm and high-rate algal pool (microalgae) by slow pyrolysis (400~600°C) [11]. Manya et al prepared biochar by slow pyrolysis of corn straw, grape buds and olives [12]. Compared with other preparation methods, it was found that the carbon produced by the slow pyrolysis process was more stable. Yang et al found that rapid pyrolysis is to rapidly heat biomass (103~104°C/s) to a higher reaction temperature (about 500°C under normal pressure), so that biomass macromolecules are pyrolyzed and converted into biochar [13]. Yang et al used fluidized bed rapid pyrolysis to prepare biochar [14]. Studies have shown that biochar has more functional groups and new functional groups such as C-H, deformation vibration, and makes biochar more stable through rapid pyrolysis.

In this paper, based on the research status of biochar at home and abroad, based on the background of increasing marine pollution caused by ships, according to the characteristics of ship oily sewage and biomass, heavy oil is taken as the target pollutant, and biochar is prepared with the characteristics of corn straw biochar in physical properties, yield and adsorption efficiency. The changes of adsorption capacity of biochar at different temperatures, different modified solution concentrations and modified time were investigated. The biochar samples before and after modification were analyzed by characterization, and the modification conditions were optimized by adsorption experiments to study the performance of modified biochar in treating oily sewage from ships.

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2. Materials and Methods

2.1 Preparation of Biochar

The prepared corn stalk raw materials were thoroughly washed with deionized water, and the impurities such as dust were removed by filtration. The excess water was removed by placing it in a constant temperature drying oven. The dried raw material samples were crushed and finally powdered, using a 100 mesh sieve. Then the prepared biochar raw materials were evenly placed in a crucible and placed in a muffle furnace for thermal cracking reaction. The target temperature was set at 400°C, and the maximum temperature maintenance time was 45 min. After the reaction was completed, the sample was cooled to below 70°C, and the preparation of biochar materials was initially completed. The prepared biochar samples are shown in Fig.1.

Fig.1 The finished biochar sample

2.2 Modification of Biochar Materials

After the initial preparation of biochar, in order to ensure the efficient adsorption of oil pollution, biochar needs to be modified. The purpose is to give biochar some specific functions without destroying the adsorption capacity of biochar, so as to enrich its internal functional groups, increase the pore structure and specific surface area, thus changing the chemical properties of biochar and improving the adsorption performance. The common methods mainly include load method, acid-base modification method, oxidation modification method, surfactant modification method, etc. Because the acid-base modification method is easy to operate and the modification effect is obvious, but the alkaline solution will destroy the molecular structure of biochar to a certain extent, this experiment intends to use the acid modification method to modify the biochar material.

In order to carry out the next modification experiment, several biochar samples with corn straw as raw material were prepared for use.

A certain mass of HCl solution was weighed at 10°C, 20°C, 30°C, 40°C, 50°C, and the samples were immersed in the solution and stood for 18 h. The optimum modification temperature was obtained by experiment.

The hydrochloric acid solutions of 0.5 mol/L, 1 mol/L, 1.5 mol/L, 2 mol/L and 2.5 mol/L were prepared respectively. Under the optimal modification temperature, the samples were immersed in the solution and allowed to stand for 18 h. The optimum concentration of hydrochloric acid modified solution was obtained by experiment. A certain mass of the best concentration of hydrochloric acid modified solution was weighed and soaked for 12 h, 14 h, 16 h, 18 h, 20 h, 22 h and 24 h respectively under the best modified temperature environment. The best modified soaking time was obtained from the experiment.

2.3 Adsorption Experiment after Biochar Modification

According to the experimental data obtained by controlling the single factor experiment, combined with the best modification time, the concentration of the modified solution and the modification temperature, the final adsorption experiment of corn straw charcoal was carried out, and the

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maximum adsorption capacity D after modification was measured. If D>d, it is proved that modification is helpful to improve the adsorption efficiency of biochar, and the maximum adsorption capacity of corn straw charcoal for adsorbing oily wastewater is obtained.

3. Results and Discussion

3.1 Scanning Electron Microscope Analysis of Biochar(SEM)

After the modification, the modified corn straw carbon was analyzed by scanning electron microscopy. It can be seen from the image that the modification experiment significantly increased the pore size and pore volume inside the biochar. These changes will greatly improve the adsorption efficiency of biochar on oil pollution. The scanning electron microscope image (a) of corn straw before modification and the scanning electron microscope image (b) of modified corn straw are compared as shown in Fig.2.

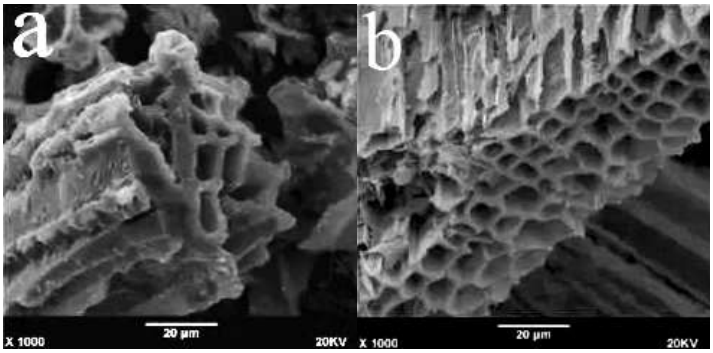

Fig.2 Scanning electron microscopy of corn straw charcoal before and after modification

3.2 Ftir Spectroscopic Analysis (FTIR)

After the modification of HCl solution, it can be seen from the above conclusions that in the range of 3500~3100 cm-1, the modified corn straw biochar has a slower downward trend than before the modification, and the N-H type stretching vibration occurs in the -OH stretching vibration region. At 2360 cm-1, there are three-bond and cumulative double-bond stretching vibration regions, -N=C=O stretching vibration occurs, and C-H groups are generated. The chemical structure of the modified corn straw charcoal has changed, the chemical functional groups are more abundant, and its adsorption capacity is further improved [15]. The infrared spectrum analysis of corn straw charcoal before and after modification is shown in Fig.3.

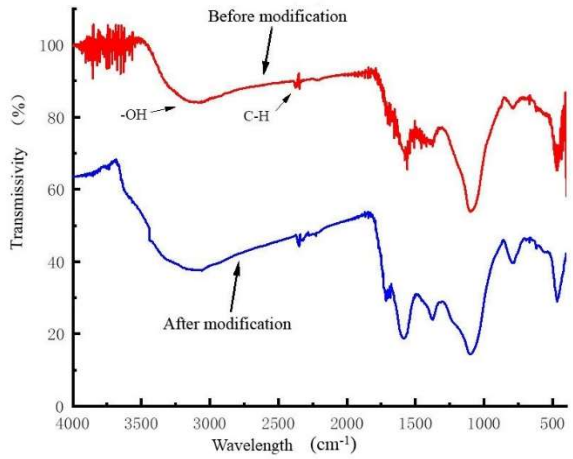

Fig.3 Infrared spectrum analysis and comparison of corn stover charcoal before and after modification

ISSN: 2414-1895 DOI: 10.6919/ICJE.202308_9(8).0002

3.3 Explore the Best Modification Temperature

The effect of different modification temperatures on the adsorption effect of corn straw charcoal is shown in Fig.4. The hydrochloric acid solution of a certain quality was weighed at 10°C, 20°C, 30°C, 40°C, 50°C and the samples were immersed in the solution and stood for 18 h. After the modification is completed, the mixture of the sample and the filtrate is placed in the funnel and filtered, and the filtrate is continuously washed with a large amount of water until the filtrate is neutral, and then the biochar sample is dried and collected for use. The modified corn straw charcoal was subjected to an oil-water mixture adsorption experiment, and the adsorption amount was recorded and made into the above image. The image can be obtained. When the ambient temperature is 30°C, the adsorption amount is 14.214 g/g. The modification temperature has little effect on the modification effect. Combined with the actual application scene temperature, the experimental results show that the modification effect is the best at 30°C.

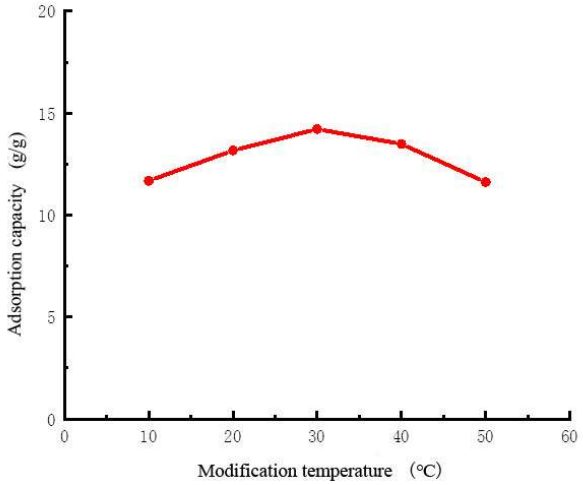

Fig.4 Effect of modified temperature on adsorption effect of maize straw chard

3.4 Explore the Best Modified Solution Concentration

The effect of the concentration of different modified solutions on the adsorption effect of corn straw biochar is shown in Fig.5. The hydrochloric acid solutions of 0.5 mol/L, 1 mol/L, 1.5 mol/L, 2 mol/L and 2.5 mol/L were prepared respectively. The samples were immersed in the solution at 30°C and allowed to stand for 18 h.

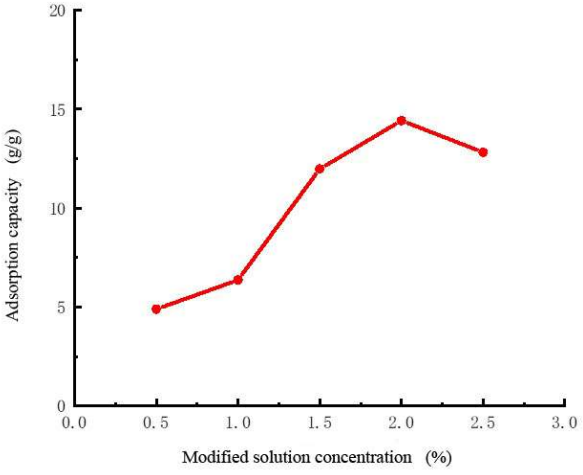

Fig.5 Effect of modified solution concentration on adsorption effect of corn straw charcoal

ISSN: 2414-1895 DOI: 10.6919/ICJE.202308_9(8).0002

After the modification is completed, the mixture of the sample and the filtrate is placed in a funnel for filtration, and a large amount of water is continuously rinsed until the filtrate is neutral. The dried filter residue has been modified to complete the corn straw charcoal and collected for later use. The modified corn straw charcoal was subjected to an oil-water mixture adsorption experiment, and its adsorption amount was recorded and made into the above image. According to the image, the adsorption amount increased rapidly when the concentration of the modified solution was 1~1.5 mol/L, and when it reached 2 mol/L, the biochar adsorption amount did not increase significantly. It is speculated that when the concentration of the modified solution reaches this node, the internal chemical groups are fully modified, and the expansion and growth of the pore structure reach the limit. Therefore, the adsorption capacity does not change significantly in the subsequent adsorption experiments. The modification effect was the best when the hydrochloric acid solution was 2 mol/L.

3.5 Explore the Best Modification Time

The effect of different modification time on the adsorption effect of corn straw charcoal is shown in Fig.6. A certain quality of hydrochloric acid solution was weighed and soaked for 12 h, 14 h, 16 h, 18 h, 20 h, 22 h and 24 h at 30°C. After the modification is completed, the mixture of the sample and the filtrate is placed in a funnel for filtration, and a large amount of water is continuously rinsed until the filtrate is neutral. The dried filter residue has been modified to complete the corn straw charcoal and collected for later use. The modified corn straw charcoal was subjected to oil-water mixture adsorption experiments, and the adsorption amount was recorded and made into the above image. According to the image, the adsorption capacity reached 13.997 g/g after the modification time reached 16 h. When the modification time was prolonged, the adsorption capacity increased little. It is speculated that the internal chemical properties of corn straw biochar can be fully changed during the modification time of 16 h, and the subsequent modified soaking time has no significant improvement on the optimization of internal structure. The modification effect is the best when soaking for 16 h.

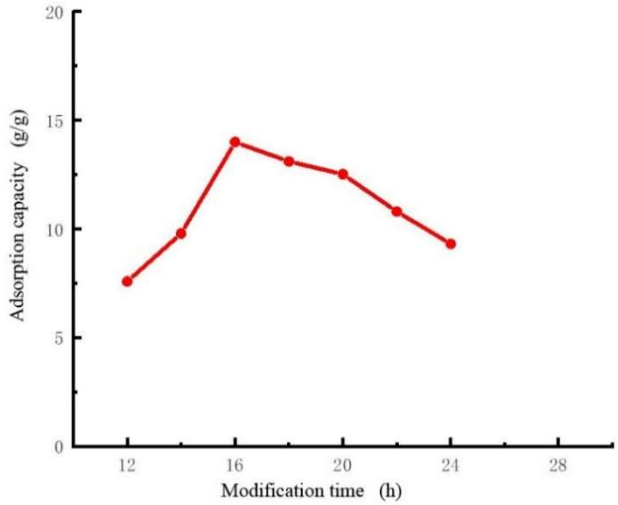

Fig.6 Effect of modification time on the adsorption effect of corn straw charcoal

3.6 Adsorption Experiments Before and after Modification

In this experiment, heavy oil was used as the target pollutant to verify the adsorption performance of corn straw biochar before and after modification. The biochar samples before and after modification are shown in Fig.7.

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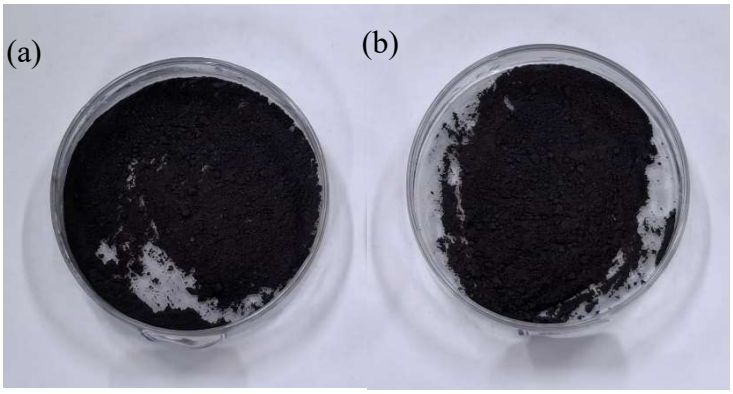

Fig.7 (a)Unmodified biochar samples, (b)Modified biochar samples

The biochar prepared from corn straw at 400°C was modified at 30°C, the hydrochloric acid modification solution was 2 mol/L, and the modification time was 16 h. The modified sample was washed with a large amount of pure water to neutral, filtered and dried. The oil-water mixture with a concentration of 10% was prepared and slowly stirred for 10 min by a magnetic stirrer, 2 g of biochar sample was placed in a non-woven filter bag and placed in the oil-water mixture for 20 min, waiting for the adsorption to be completed. The oil absorption capacity was calculated to be about 14.86 g/g, which was a large increase from the maximum adsorption capacity of about 6.58 g/g before modification, with an increase of 125.84%. The biochar adsorption experiment is shown in Fig.8.

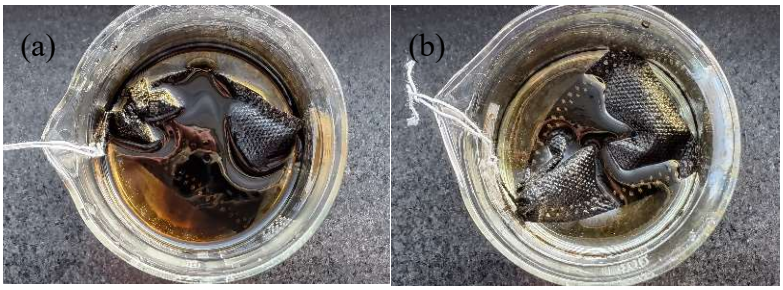

Fig.8 (a) Adsorption effect of unmodified biochar, (b)Adsorption effect of modified biochar

4. Conclusion

In this paper, by combining the characteristics and treatment methods of oil in ship oily wastewater, using natural crop biomass carbonization technology, biochar prepared by pyrolysis of straw as raw material, HCl as modified solution, hydrochloric acid modified biochar was prepared, and the biochar before and after modification was characterized and analyzed. Adsorption experiments were conducted to investigate the effects of raw materials, adsorption conditions and modification conditions on the adsorption efficiency of biochar. Finally, through the single factor experiment, it is concluded that under the environment of 30°C, hydrochloric acid solution is 2 mol/L, and the soaking time is 16 h, the chemical structure of corn straw biochar has undergone the optimal change for the adsorption of oil pollution, which greatly increases the pore structure and specific surface area. The maximum adsorption capacity is about 14.86 g/g, and the modification effect is the best. The experimental results show that biochar has better adsorption capacity and can treat ship oily wastewater more efficiently.

Acknowledgments

This work was funded by; Introduction and Education Plan of Young Creative Talents in Universities of Shandong Province (500076), China (KJ2018BBA015).

ISSN: 2414-1895 DOI: 10.6919/ICJE.202308_9(8).0002

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