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Study on Walnut Shell for Treatment of Ammonia Nitrogen Wastewater

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Abstract

The waste biomass walnut shell was modified, and then used to treat ammonia nitrogen wastewater. The effects of wastewater pH, modified walnut shell amount, initial concentration of ammonia nitrogen and contract time on the treatment of ammonia nitrogen wastewater were studied. The results showed that within 3-9 range of pH, the removal of ammonia nitrogen from wastewater by modified walnut shell was suitable, and the maximum removal rate could reach 81%. Modified walnut shell treatment of ammonia nitrogen wastewater (concentration of 100mg/L) is suitable for the use of 10g/L. The initial concentration of ammonia nitrogen has a great influent on the removal of ammonia nitrogen in ammonia nitrogen wastewater. When the concentration of ammonia nitrogen increases to 300mg/L, the adsorption capacity can reach 9.33mg/L. The contract time of modified walnut shell for treatment of ammonia nitrogen wastewater was more suitable for 6 hours. The treatment of

ammonia nitrogen wastewater with modified walnut shell is mainly based on adsorption, as well as the chemical reaction of oxidation and reduction. The study provides a basis for wastewater treatment and reuse of waste materials.

Keywords: Walnut shell, Ammonia nitrogen, Wastewater

1. Introduction

Ammonia nitrogen exists in water mainly in the form of ammonium ion or free ammonia, which comes from fertilizer, feed, aquaculture and other production processes. A large amount of ammonia nitrogen wastewater discharged easily leads to water eutrophication, decrease of dissolved oxygen, death of aquatic organisms and destruction of aquatic ecosystem [1]. At present, the treatment of ammonia nitrogen wastewater mainly includes physicochemical and biological methods. Physicochemical treatment of consumables energy consumption, the existence of higher costs, materials need to be disposed of after treatment [2,3]. The cost of biological treatment is low, and there is no need to worry about recontamination after treatment, but biological treatment is greatly affected by temperature. Therefore, how to adopt an efficient and economical method for ammonia nitrogen wastewater treatment has always attracted much attention.

In today's society, the problem of resources and environment was increasingly reflected, and people's awareness of environmental protection was also growing. China's annual agricultural and forestry biomass production was huge, most of which were abandoned, only a small part of which was used as feed or fuel, resulting in waste of resources, increasing the environmental burden [4,5]. For walnut shell, because of its own characteristics, it had been used as filter material to treat wastewater, and there were many reports on this aspect [6,7]. China is the origin of walnut, and the output of Shanxi is second. Based on this, the walnut shell was used to treat ammonia nitrogen wastewater, and the treated walnut shell was used as nitrogen fertilizer to return to farmland. There were few studies in this field. Biomass modification can improve its performance, the influencing factors of ammonia nitrogen wastewater after walnut shell modification were studied, and its removal mechanism was analyzed. It was hoped to provide guidance for the development of efficient and economical

ammonia nitrogen wastewater treatment technology.

2. Materials and methods

2.1 Experimental material

Ammonia nitrogen waste water: The simulated ammonia nitrogen wastewater was used in the experiment. Ammonia standard storage solution of 10g/L (ammonia nitrogen content) was prepared with deionized water (prepared in laboratory) and ammonium chloride (analytical purity). It was closed storage at room temperature. The 10mL storage solution was diluted to deionized water to 1L, which was made up of ammonia nitrogen wastewater with a concentration of 100mg/L. Other concentrations of ammonia nitrogen wastewater were prepared using ammonia standard storage solution in the similar way.

Walnut shell: Walnuts were purchased from the farmers' market, origin Shanxi Fenyang. The walnut was broken and the shell was leaved. The walnut shell was washed with deionized water, boiled for 1hour, then the residue was removed, dried to constant weight in oven at 105℃, and then was broken to below 50 meshes, reserved after screening.

Modified walnut shell: 10g walnut shell powder (50 mesh) was put into a 1L beaker, phosphated using 200mL phosphoric acid its concentration was 1mol/L, then carbonized at 600℃ for 40 minutes, then washed with deionized water, adjusted pH to 7, oven dried at 50 ℃ for reserve [8].

Main reagents: Sodium reagent solution (determination of ammonia nitrogen), sodium hydroxide solution (regulation of pH), hydrochloric acid solution (regulation of pH), ammonium chloride solution (preparation of wastewater), potassium sodium tartrate solution (determination of ammonia nitrogen), phosphoric acid solution (modified walnut shell) and so on, were all prepared with analytical pure drug.

2.2 Experimental instrument

The pH meter (model ZD-2), electronic balance (model FA21045N), high-speed centrifuge (model 52A), six stirrer (model JJ-4), constant temperature drying box (model 101-2), magnetic stirrer (model 85-2A), speed regulating oscillator (model HY-4), spectrophotometer (model 722), scanning electron microscope (model JSM-6510A), infrared spectrometer (model VECTOR-22), etc.

2.3 Experimental method

The simulated ammonia nitrogen wastewater was prepared with ammonia standard storage solution, and then the simulated ammonia nitrogen wastewater was treated with modified walnut shell powder. The effects of pH, dosage of modified walnut shell powder, concentration of ammonia nitrogen in simulated ammonia nitrogen wastewater and contact time between wastewater and modified walnut shell powder on ammonia nitrogen removal performance were studied. Moreover, scanning electron microscopy and infrared spectroscopy were used to investigate the micro characteristics of modified walnut shell powder before and after treating ammonia nitrogen wastewater, and the mechanism of removing ammonia nitrogen from wastewater by modified walnut shell was analyzed.

2.4 Determination method

Samples were collected from the sample wastewater. After centrifugation, the supernatant was used to determine ammonia nitrogen. Nash reagent method was used to determine ammonia nitrogen [1].

3 Results and discussion

3.1 Effect of pH

Twelve conical bottles of 250mL were added with modified walnut shell powder of 1g and 100mL ammonia nitrogen wastewater (100mg/L) respectively. The pH was adjusted from 1 to 12. At room temperature, after shaking for 6 hours, then centrifugation was carried out through 3000rpm for 5 minutes, and then the supernatant was used to determine the concentration of ammonia nitrogen. The effect of pH on ammonia nitrogen removal was investigated. The results were shown in Figure 1.

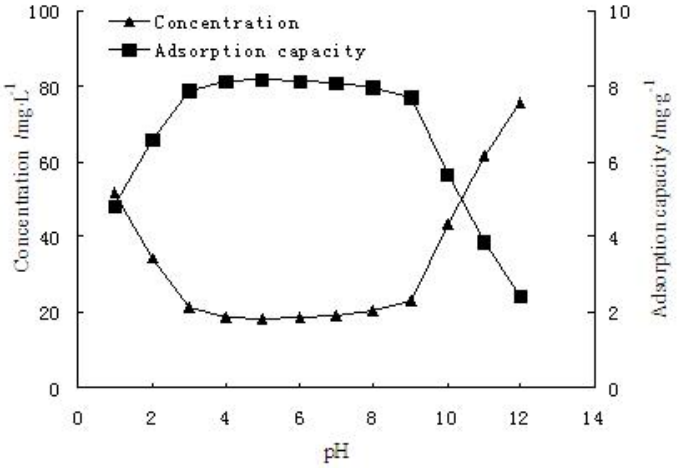

Figure1. Effect of pH on walnut shell

As can be seen from Figure 1, when pH was less than 3 or more than 9, the ammonia nitrogen adsorption capacity of modified walnut shell was relatively small, and the ammonia nitrogen concentration in the wastewater was still higher, above 20mg/L, the removal of ammonia nitrogen in the wastewater was not ideal. The reasons were analyzed. Ammonia nitrogen in wastewater was mainly formed by ammonia and inorganic ammonia. When the wastewater was neutral or alkaline, ammonia nitrogen was affected by both ammonia and inorganic ammonia. When the wastewater is acidic, ammonia nitrogen was mainly affected by inorganic ammonia. Therefore, when pH was less than 3, the concentration of H^+ in wastewater was higher, and H^+ and NH_4^+ in wastewater were apt to compete for adsorption sites, which was not conducive to the contact between ammonia nitrogen and modified walnut shell surface, and was not conducive to the removal of ammonia nitrogen. When the pH was higher than 9, ammonia was the main form of ammonia because of the alkalinity of the wastewater. Molecular ammonia was not easy to combine with the surface of modified walnut shell and was not conducive to the removal of ammonia nitrogen. Moreover, the sodium ions in strong alkali also competed with the adsorption sites of NH_4^+. Therefore, it was considered that the modified walnut shell was suitable for removing ammonia nitrogen from wastewater within 3-9 range of pH, and the maximum removal rate can reach 81%. In the next experiment, the pH of simulated wastewater was adjusted to about 7.

2.2 Effect of walnut shell dosage

Eight conical bottles of 250mL were added with modified walnut shell powder of different quality (one of which was not added), and 100mL ammonia nitrogen wastewater (100 mg/L)

was added. The adjusted pH was 7. At room temperature, after shaking for 6 hours, then centrifugation was carried out through 3000rpm for 5 minutes, and then the supernatant was used to determine the concentration of ammonia nitrogen. The effect of walnut shell dosage on ammonia nitrogen removal was investigated. The results were shown in Figure 2.

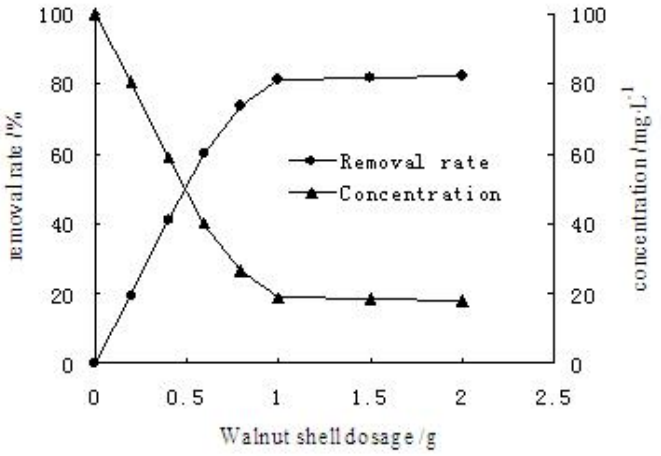

Figure2. Effect of walnut shell dosage on adsorption

From the figure 2, it can be seen that the removal rate of ammonia nitrogen was higher and higher with the increase of the dosage of modified walnut shell powder. When the dosage was increased to 1g (that was, the concentration of 10g/L), the removal rate of ammonia nitrogen was no longer significantly increased, and remained at about 81%. At this time, the concentration of ammonia nitrogen in the wastewater was reduced to below 20mg/L. The reasons were analyzed. When the dosage of modified walnut shell powder was relatively small, with the increase of the dosage of modified walnut shell powder, the effective surface area contacting with ammonia nitrogen in wastewater will also increased, which was conducive to the removal of ammonia nitrogen. When the dosage of modified walnut shell powder was too large, the interaction between modified walnut shell powders may cause resistance or barrier, the contact opportunity between ammonia nitrogen and powder surface was affected, so the removal rate of ammonia nitrogen had not increased significantly [9]. Therefore, it was considered that it is appropriate to use modified walnut shell powder to treat ammonia nitrogen wastewater with the concentration of 100mg/L at the dosage of 10g/L.

2.3 Effect of ammonia nitrogen concentration

Nine conical bottles of 250mL were added with modified walnut shell powder of 1g and simulated ammonia nitrogen wastewater of 100mL with different concentrations respectively. The adjusted pH was 7. At room temperature, after shaking for 6 hours, then centrifugation was carried out through 3000rpm for 5 minutes, and then the supernatant was used to determine the concentration of ammonia nitrogen. The effect of ammonia nitrogen concentration on the removal of modified walnut shell was investigated. The results were shown in Figure 3.

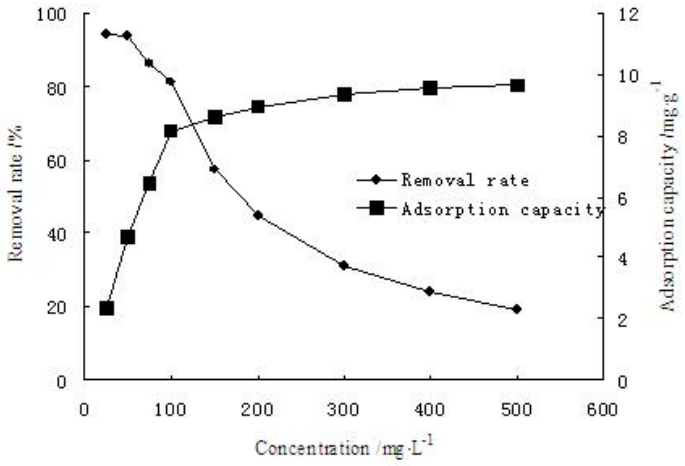

Figure3. Effect of ammonia nitrogen concentration

As can be seen from Figure3, ammonia nitrogen concentration in simulated ammonia nitrogen wastewater affected the removal of modified walnut shell. With the increase of initial concentration of ammonia nitrogen, the removal rate of ammonia nitrogen in wastewater decreased. The adsorption capacity of modified walnut shell powder to ammonia nitrogen increased with the increase of ammonia nitrogen concentration. When the concentration of ammonia nitrogen increased to 300mg/L, the adsorption capacity of modified walnut shell powder to ammonia nitrogen didn't increase significantly, which basically reached adsorption saturation, the adsorption capacity was about 9.33mg/g. The reasons were analyzed. Because of the limitation of adsorption capacity of modified walnut shell, the removal rate of ammonia nitrogen inevitably decreased after increasing the initial concentration of ammonia nitrogen, and the increase of initial concentration of ammonia nitrogen made enough ammonia nitrogen to compete for the active sites on the adsorption surface, so the adsorption capacity of modified walnut shell increased, but it was not an unlimited increase. To a certain extent, ammonia nitrogen ions also repelled each other, and

there were no more active sites to bind to ammonia nitrogen. Therefore, the effective adsorption surface of modified walnut shell was determined, and the removal of ammonia nitrogen from wastewater by modified walnut shell was probably due to the surface monolayer adsorption.

2.4 Effect of contact time

In order to ensure adequate sampling times, the test results and test results were not affected. Two 500mL conical bottles were added with modified walnut shell powder of 2g, and then 200mL ammonia nitrogen wastewater (100mg/L) was added. The adjusted pH was 7. At room temperature, after shaking for 12 hours, during the shaking process, the ammonia nitrogen concentration was determined by sampling at different times (the interval time was shorter in the earlier period, and the interval time was longer in the later period). Then samples centrifuged through 3000rpm for 5 minutes, and then the supernatant was used to determine the concentration of ammonia nitrogen. The effect of contact time between modified walnut shell powder and ammonia nitrogen in wastewater on the removal of ammonia nitrogen from wastewater was investigated. The results were shown in Figure 4.

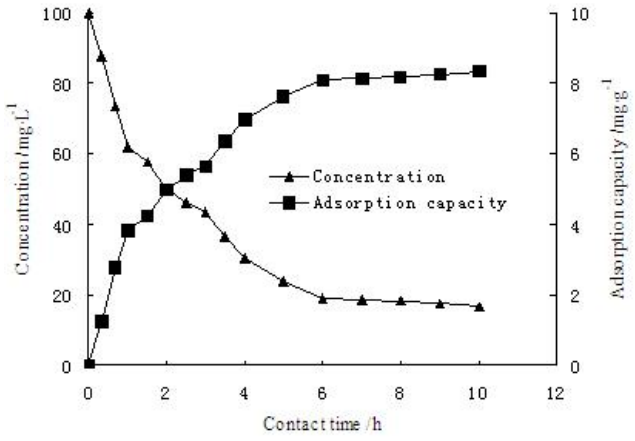

Figure4. Effect of contact time

As can be seen from Figure 4, the concentration of ammonia nitrogen in wastewater decreased rapidly with the extension of contact time, and the adsorption capacity of modified walnut shell to ammonia nitrogen increased rapidly, especially within the first hour. when the contact time reached about 6 hours, the concentration of ammonia nitrogen in wastewater decreased no longer obviously, the adsorption capacity of modified walnut shell was basically saturated. The reasons were analyzed. At the beginning of the experiment, a large amount of ammonia nitrogen ions in the wastewater can fully contact a large number

of active sites on the surface of the modified walnut shell, so the adsorption capacity of the modified walnut shell became larger, the removal rate of ammonia nitrogen increased and the concentration of ammonia nitrogen decreased quickly. After the contact time continued to extend, especially after more than 6 hours, the modified walnut shell surface became smaller. Surface adsorption was basically saturated, because adsorption was dynamic equilibrium, small changes in adsorption capacity was normal, but didn't increase significantly, the concentration of ammonia nitrogen in wastewater didn't continue to decline. The reason why there was no temperature effect test was because for wastewater, increasing the temperature will lead to increased energy consumption and waste, so discussed at room temperature was more appropriate. Therefore, the suitable contact time of modified walnut shell for ammonia nitrogen wastewater treatment was 6 hours.

2.5 SEM electron microscopy analysis

A certain amount of modified walnut shell powder after treatment of ammonia nitrogen wastewater was obtained, then dried at 105℃ and weighed. A small amount of modified walnut shell powder was scanned by SEM. The surface morphology was analyzed and compared with that before treatment. The results were shown in Figure 5.

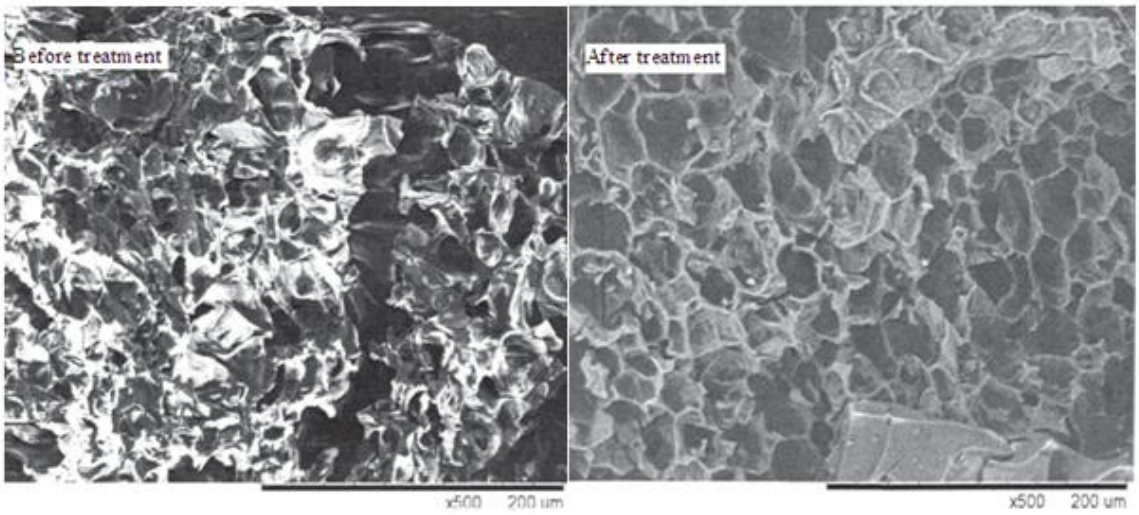

Figure5. SEM diagram of modified walnut shell

As can be seen from Figure 5, the SEM images before and after treatment were obviously different. The surface of modified walnut shell after treatment of ammonia nitrogen wastewater was smooth, the edges and corners became blurred after treatment, and the pores were much less than before treatment. The reasons were analyzed. It may be due to

the adsorption of ammonia nitrogen on the surface of the modified walnut shell and the filling of the voids. It may also be due to the change of the surface morphology of the walnut shell caused by stirring in the ammonia nitrogen wastewater during the treatment of the ammonia nitrogen wastewater, resulting in the change of the surface groups of the modified walnut shell [10].

2.6 FTIR infrared analysis

The FTIR diagram of the modified walnut shell powder before and after treatment of ammonia nitrogen wastewater was shown in Figure 6.

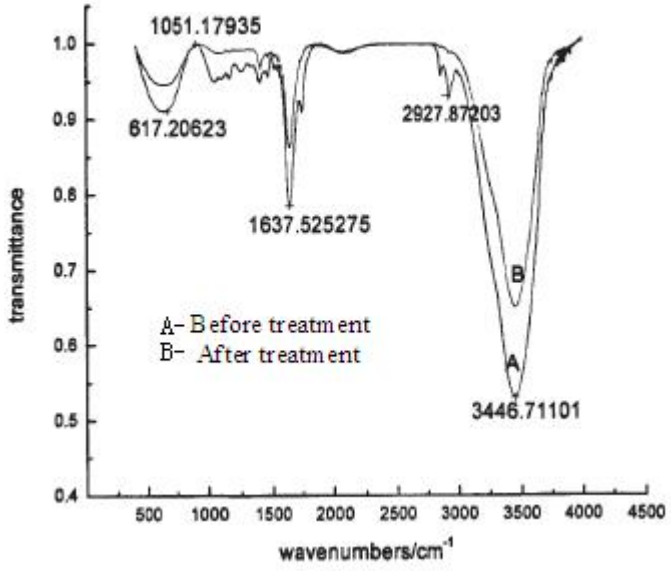

Figure6. FTIR diagram of modified walnut shell

As can be seen from Figure 6, the FTIR spectra of modified walnut shell before and after treatment of ammonia nitrogen wastewater were different. The absorption peak frequency, intensity and location all changed. The wave band 3446cm^{-1} appeared in the absorption band with low wave number offset. The characteristic peaks were shifted, but not obvious, and there were no different absorption peaks. It can be considered that the process was not only physical adsorption. In addition, some characteristic peaks became blurred and the strength decreased, indicating that walnut shell structure changed during the treatment [11]. It can

be concluded that the modified walnut shell mainly adsorbs ammonia nitrogen wastewater, and also has the chemical reaction process of oxidation and reduction.

3 Conclusions

1) Within 3-9 range of pH, the modified walnut shell was suitable for removing ammonia nitrogen from wastewater, and the maximum removal rate could reach 81%. The dosage of 10g/L was suitable for the treatment of ammonia nitrogen wastewater (100mg/L) by modified walnut shell. The initial concentration of ammonia nitrogen in ammonia nitrogen wastewater had a great influence on the removal of ammonia nitrogen. When the concentration of ammonia nitrogen increased 300 mg/L, the adsorption capacity increased no longer obviously, and the adsorption capacity could reach 9.33 mg/g. The contact time of modified walnut shell for ammonia nitrogen wastewater was 6 hours.

2) The surface of modified walnut shell became smooth, the edges and corners became blurred, the pores were reduced, and the surface groups were also changed. Modified walnut shell mainly adsorbed ammonia nitrogen wastewater, and also had the chemical reaction process of oxidation and reduction.

3) Modified walnut shell was used to treat ammonia nitrogen wastewater. On the one hand, waste biomass was fully utilized to solve the problem of ammonia nitrogen wastewater treatment; on the other hand, the treated materials did not need regeneration and reuse, so they could be used as agricultural fertilizers to return to the field directly, which not only solved the problem of adsorbent disposal, but also solved the problem of reusing ammonia nitrogen wastewater and waste biomass.

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