Preparation of a coal cinder-zeolite ball and its adsorption performance for ammonia nitrogen

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Abstract. Coal cinder and zeolite have been widely studied in wastewater treatment. However there are some problems with the materials, such as low mechanical strength, poor water resistance, difficult recovery of coal cinder, and poor stability, easy powder, high price of zeolite. To resolve these problems, a coal cinder-zeolite ball was developed with modified PVA adhesive. Then the adsorption performance and thermal regeneration for ammonia nitrogen were studied. The results showed that the adsorption process of the sorbent had a good match with pseudo-second-order kinetic model and Langmuir equation; the adsorption capacity of ammonia nitrogen calculated from Langmuir equation was 0.18mg/g， which was larger than that obtained from coal cinder alone. And the sorbent has a good regeneration performance. and the best parameters of regeneration in the process of experiments was 170℃, 4h. Under this condition, the regeneration efficiency reached 74%.

Introduction

Ammonia nitrogen is one of the predominant pollutions in water and can lead to water eutrophication, which is also an important pollution emission index in Liaohe estuary wetland. Liaohe estuary wetland is the last barrier of the pollutants

flow into the sea, the high concentration of ammonia nitrogen in wetland water not only threaten coastal wetland ecological environment, but also cause the increase of pollutants flux and accelerate the eutrophication of coastal water[Kuang Deshun,2010]. Therefore, it is necessary to research on the methods of removing ammonia nitrogen effectively, which is of great significance to the protection of coastal wetland and coastal environment.

Coal cinder is widespread solid waste from indusrial manufacture and daily life in China, and the main chemical composition is SiO_2, Al_2O_3, Fe_2O_3, CaO, Sulfur, magnesium and carbon etc[Wang S,2006].Because of its porous structure, large surface area and low price,coal cinder has been widely used in wastewater treatment process, so as to realize the resource utilization of solid waste, which can play a role in the removal of heavy metals, ammonia nitrogen[Alinnor,2007][ChenLirong,2013]. However, there are some disadvantages in the use of cinder, such as low mechanical strength, not resistant to water, uneasy to recovery, and its direct use may lead to aluminum , lead, chromium and other heavy metals dissolution, which may bring secondary pollution to water bodies. Zeolite is another adsorption material, with frame shape structure, rich pores, and large surface area (400 ~ 800 m^2/g) [Gao Junmin,2001], which adsorb ammonia nitrogen. Besides the regeneration performance is good. Studies have shown that [Tang Dengyong, 2011] [Sprynskyy,2005]natural zeolite has a good removal effect of ammonia nitrogen, but its price is high, which limits its wide application in a certain extent.

Therefore, this study prepared coal cinder-zeolite honeycombed sorbent, using modified PVA adhesive, hydrochloric acid modified coal cinder and zeolite as raw materials. To investigate the adsorption performance of ammonia nitrogen, adsorption kinetics and adsorption isotherm experiments were carried out; and using adsorption experiments to evaluate the regeneration performance, so as to get a kind of new water treatment material with low price, high mechanical strength, and resistance to shock loading.

Materials and Methods

Experimental materials.

Boiler combustion coal cinder; Natural zeolite(Guangzhou, China); Polyvinyl alcohol(1799); succinic acid(AR);Hydrochloric acid(AR); Ammonium chloride(AR).

Grinder(DF-4,ZhejiangZhongke Building Material Equipment Co. Ltd.); Scanning electronmicroscope (JSM-840,JEOL); Horizontal oscillator (LRH-250-G250L, Shaoguan Taihong medical machinery Co. Ltd.); Drying box(DHG-9140, Shanghai Jinghong

Experimental Equipment Co. Ltd.); UV VIS spectrophotometer(The 18 series, Beijing Purkinje General Instrument Co. Ltd.).

Experimental methods.

1) Preparation of modified PVA adhesive

The PVA (1799) was dissolved under the condition of 90 ^oC water bath, then succinic acid was added when water bath temperature was 85 ^oC. The solution was stirred well and cooling to room temperature[Chen Lin,2012]. The rate of PVA (w:v) was 7%.

2)The preparation of coal cinder-zeolite ball

The cinder(20 mesh) was modified using HCl(6 mol/L) soaking for 24 h, and washed close to neutral, and then dried. Then the coal cinder and zeolite(20 mesh) was mixed with the ratio of 2:1, then suitable amount of modified PVA adhesive was added into that mixture. The coal-zeolite ball about 3 cm in diameter was made in ball machine, and then the ball was dried under the condition of 70 ^oC, soaked in water for 2 ~ 3 weeks, taken out and dried again and then can be used.

3) Adsorption kinetic experiment

The 600ml water was prepared with ammonium chloride(10 mg/L). The three coal cinder-zeolite balls were placed in the water, and then were shocked constantly at 25 ^oC. The samples were collected at fixed time. According to concentration of ammonia nitrogen in the simulation water, the adsorption of ammonia nitrogen was calculated.

$$q_e(q_t) = \frac{(c_0 - c_t)v}{m} \quad (1)$$

q_e is the equilibrium adsorption quantity, mg/g; q_t is the adsorption quantity of adsorption when time is t, mg/g; c_o is initial concentration of ammonia nitrogen in water samples, mg/L; c_t is concentration of ammonia nitrogen in water samples at adsorption time t, mg/L; v is the volume of solution, mL; m is the quality of coal-zeolite ball, g.

4) Isothermal adsorption experiment

The 200 ml simulation ammonia nitrogen water was prepared with ammonium chloride. The concentration of water was 2, 4, 6, 8, 10, 15, 20, 25 mg/L, respectively. One coal cinder-zeolite ball was added into each water sample and shocked constantly at 25 ^oC for 24 h. The concentration of ammonia nitrogen adsorption equilibrium was determined and the adsorption of ammonia nitrogen was calculated.

5) Thermal regeneration performance of the sorbent

The 200ml simulation water was prepared with ammonium chloride(10 mg/L). The influence of the regeneration time and temperature for the regeneration efficiency were studied, under the conditions of 2,4,6h at 170^oC, and70,120,170 ^oC for 4h.

Results and Discussion

Characterization of coal cinder-zeolite ball.

The specific surface area of the coal cinder before and after pretreatment were 13.509m^2/g, 22.141 m^2/g, respectively. Because in the process of pretreatment, metals may leach out, and hydrochloric acid may react with Sulfide, alumina, etc[Teng Zonghuan,2007]. Then the internal structure gets more loose, and the porosity increases. SEM of coal cinder-zeolite ball is shown in figure1. There are rich pores on the sorbent surface, and the uneven structure can provide larger surface area and more adsorption sites for the adsorption of ammonia nitrogen in water.

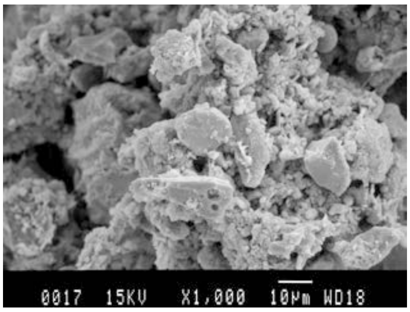
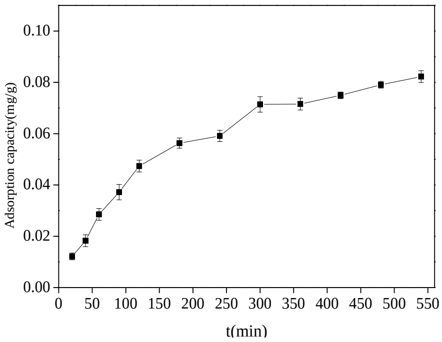


Fig.1 SEM of coal cinder-zeolite ball

Adsorption kinetics.

The process of adsorption kinetic was measured, and the results was showed in figure 2.The adsorption rate was relatively fast in the first 300min, and then slowed down gradually.



To better understand the mechanism of the adsorption process of ammonia nitrogen by coal cinder-zeolite ball, the experimental data were fitted with pseudo-first order kinetic model and pseudo-second order kinetic, respectively. The kinetic parameters obtained from the straight line fitting for ammonia nitrogen were showed in Table 1.

Table 1 Kinetic parameters obtained from the straight line fitting for ammonia nitrogen

	q_e(mg/g)	k_1(min^{-1})/ k_2(g/(mg·min)	R^2
pseudo-first order model	0.0812	0.00663	0.988
pseudo-second order model	0.106	0.0558	0.992

As seen from Table 1, the linear regression analysis of the second order rate equation gave a high R^2 value, which suggested that the sorption of ammonia nitrogen follows the pseudo-second order model. The same conclusion was also obtained from the study on the adsorption effect of ammonia nitrogen using fly ash [Uğurlu,2011].The pseudo-second order model is based on the assumption that the adsorption rate is controlled by the chemical adsorption mechanism[Ho,1999].So the adsorption process of ammonia nitrogen by the sorbent was affected by the chemical properties of sorbent and pollutants.

Adsorption isotherm.

Under the condition of 25℃, isothermal liner equation of ammonia nitrogen removal by coal cinder-zeolite ball was shown in figure5. The experimental data were fitted with Langmuir equation and Freundlich equation, respectively. The parameters obtained from the straight line fitting were listed in the table 2.

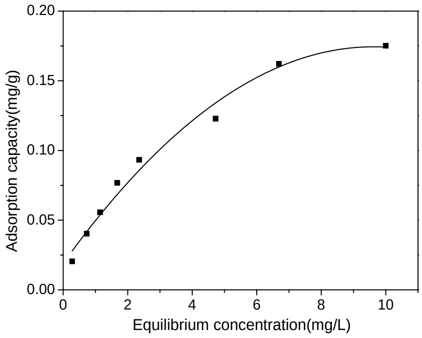


Fig.5 Isothermal liner equation of ammonia nitrogen removal by coal cinder-zeolite honeycombed sorbent

Table 2 Adsorption equation parameters obtained from the straight line fitting for ammonia nitrogen

Freundlich			Langmuir		
K_F (mg/g)	n	R^2	q_{max} (mg/g)	b(L/mg)	R^2
0.0494	1.642	0.981	0.1798	0.444	0.991

As seen from the table2, Langmuir isotherm model fit more for the adsorption process(R^2≥0.99) than Freundlich isotherm model (R^2≥0.98). Therefore, ammonia nitrogen adsorption in the sorbent surface mainly is monolayer adsorption and heterogeneous adsorption reaction[Alshameri,2014] [Yin,2007]. And the adsorption capacity of ammonia nitrogen calculated from Langmuir equation was 0.18mg/g, which was larger than that obtained from coal cinder alone(0.030mg/g)[Zheng Yue,2011].

Thermal regeneration performance of the sorbent.

1) The influence of the regeneration time

Under the condition of 170℃, regeneration time was design with 2,4,6h.As seen from figure8, the regeneration efficiency were 64%,74%,61%, respectively. The best regeneration efficiency was obtained when the regeneration time was 4h.The regeneration efficiency was decline with the the regeneration time prolong. It is due to the high temperature environment in a long time will lead to the collapse of the pore structure, and decrease of specific surface area[Bai Yujie,2012].

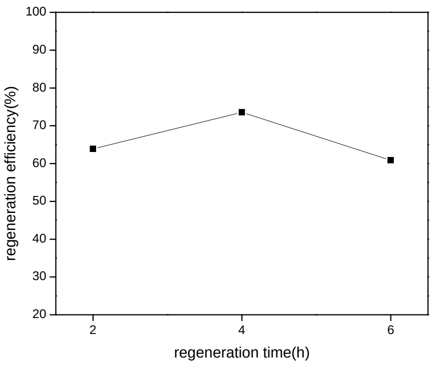


Fig.8 The influence of the regeneration time for the regeneration efficiency

2) The influence of the regeneration temperature

When the regeneration time was 4h, the regeneration temperature was designed with 70℃,120℃,170℃.

The regeneration efficiency were 57%,72%,74%, respectively. The regeneration efficiency increased with the regeneration temperature increasing. While the regeneration efficiency was hardly to promote as regeneration temperatures get higher.

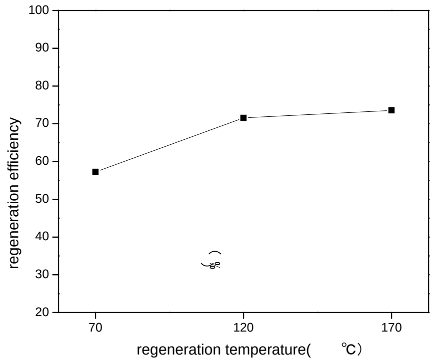


Fig.9 The influence of the regeneration temperature for the regeneration efficiency

Conclusion

The coal cinder-zeolite honeycombed sorbent has a large amount of pores on the surface and the uneven structure can provide larger surface area and more adsorption sites for the adsorption of ammonia nitrogen in water. The adsorption process fit well with pseudo-second order model and Langmuir isotherm model, which indicates a complicated chemical adsorption process. In addition ammonia nitrogen adsorption in the sorbent surface mainly is monolayer adsorption. And the adsorption capacity of ammonia nitrogen calculated from Langmuir equation was 0.18mg/g. And the sorbent has a good regeneration performance. The regeneration efficiency could achieve 74% under the regeneration condition of 170 ℃,4h.

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