ARTICLE

Study on the Dephenolization of wastewater of coal chemical industry

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Abstract: *Coal chemical wastewater contains large number of phenolic substances, which cause great harm to the environment. The dephenolization of wastewater from coal chemical enterprises was investigated. Through the combined treatment of oil removal, concentration, adsorption and other processes, the final processing results achieved the anticipated goal.*

INTRODUCTION

The main pollutants of coal chemical wastewater are ammonia, sulfide, phenolic substances, aromatic hydrocarbons and their derivatives. Coal chemical wastewater, to some degree, is a high concentration industrial wastewater, which is intractable because of its huge output, complex composition, large toxicity, high chromaticity and poor biodegradability. It contains many non-volatile phenolic compounds, such as phenol, methyl phenol, dimethyl phenol, naphthalene and so on [1-3], which are difficult to degrade and are highly biotoxic, and even can lead to protein denaturation.

In the process of denitrification of coal chemical wastewater, solvent extraction with two isopropyl ether and methyl isobutyl ketone is widely used in industry [4-7]. The process of extraction is mature, easily maneuverable, with a high rate of dephenolization (the removal rate of phenol and cyanide can reach 80% and 50% respectively), and the change of phenol content in wastewater has little effect on the extraction efficiency [8-12]. This process can also recover a large amount of phenoxide. However, the rate of dephenolization is often affected by the alkalinity of wastewater, and a small amount of extractant is dissolved in water.

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Further treatment is required to remove the extractant from the water. Therefore, the development of more efficient and economical dephenolization adsorption materials and the practicality of applying these materials remain the key points in the treatment process of the coal chemical wastewater [13-15].

At present, activated carbon, sulfonated coal and other porous materials are widely used as solid adsorbent. Macroporous resin is a new material with a high level of adsorptivity, which is attracting increasingly more attention and is being widely applied in many fields. Recently, the adsorption of phenol by porous acrylic polymer resin has been studied, which revealed it is more efficient in dephenolization process [16-20]. The specific surface area of resin plays a significant role in the adsorption process. Also, the temperature, pressure and flow rate of the tested system have a great influence on the rate of dephenolization. With the decreasing of temperature and increasing of pressure, adsorption of phenols on resin enhances. By contrast, phenols are desorbed under the condition of high temperature and low pressure during the resin purification process. This type of resin can be regenerated for reuse.

MATERIALS AND METHODS

The composition of raw wastewater is shown in Table 1.1.

Table 1.1 The composition of wastewater

No	pH	SS (mg/L)	COD (mg/L)	NH$_3$-N (mg/L)	Total Phenol (mg/L)	Volatile phenol (mg/L)	Oil (mg/L)	TDS (mg/L)
1	9.8	902	16320	3540	5540	4620	770	1440
2	9.0	2040	19920	3880	5800	5010	3180	668
3	9.8	2040	16120	2380	5200	4430	1060	4410
4	9.4	7270	16320	2210	5540	5350	1820	4860
Aver	9.5	4371	17170	2753	5520	4853	1708	2845

SS: Suspended Solids; COD: *Chemical Oxygen Demand; TN: Total Nitrogen;* TDS: *Total Dissolved Solids*

Pre-treatmen distillation

Firstly, oil in the wastewater was removed by a phase splitter, and the pH value of wastewater, after oil removal, is adjusted to 10~11. Then the light components, such as ammonia nitrogen and volatile phenols in alkali wastewater, were extracted by distillation.

Volatile phenol removal process

Since ammonia nitrogen has a relatively low boiling point, it was distilled from the system first, after which volatile phenols were distilled with water, because they form an azeotrope mixture.

Vapor was condensed into liquid, which was then collected for preparing coal water slurry. The remaining wastewater in tower kettle contains large amounts of non-volatile phenols, which need further processing.
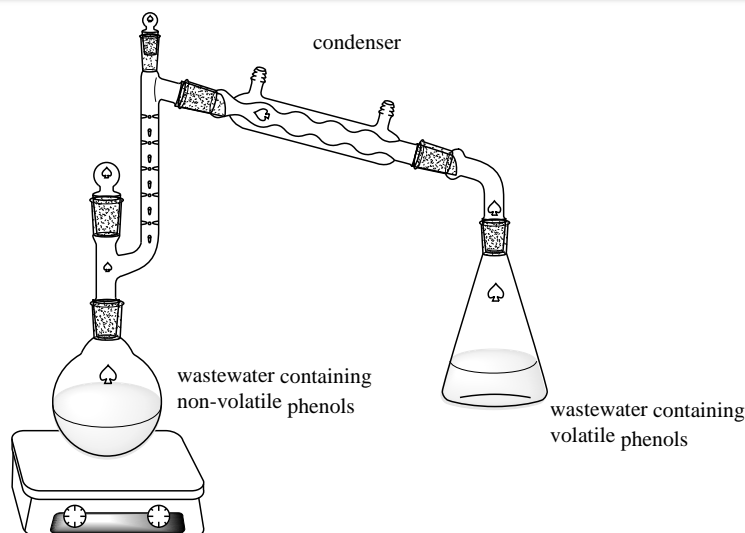
Figure 1.1 The simulation process of distillation of wastewater

The composition of wastewater before the rectification treatment is shown in Table 1.2.

Table 1.2 Material balance wastewater composition before removal of phenol

Constituent	Unit	Raw wastewater	Bottom water	Top water
	°C	145	149	131.96
NH_3-N	mg/L	1601.3	0.2	52195.3
Total Phenol	mg/L	5673	5635	5707

Non-volatile phenol removal process

The wastewater from the tower kettle was passed through a resin absorber tower. Non-volatile phenols were adsorbed effectively by resin. Qualified water was obtained by adsorption. With the combination of waste water, which come from the top of the distillation tower, this qualified water can be used in preparing coal water slurry.
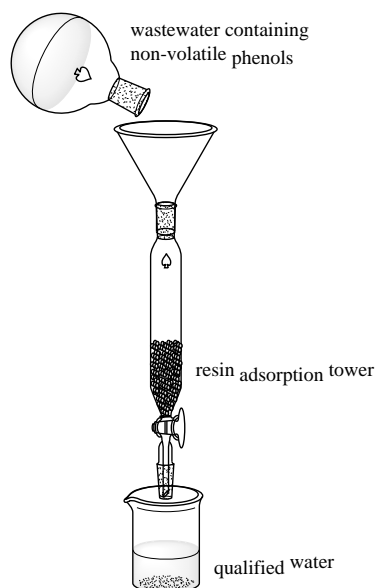

Figure 1.2 The process of dephenolization

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Reagents and laboratory equipment

Beaker with scale iodine 50 ml, 100 ml, 500 ml bottles, funnel, glass tube container, bracket, flow rate regulator, rectifying column, heating apparatus were used for the experiments.

The TG analysis was measured on Mettler TGA2. N_2 adsorption-desorption isotherms and FT-IR spectra were performed on a Micromeritics ASAP 2460 and Thermofisher IS50, respectively.

Adsorption resin and reagents used: commercial D201 resin, 5% NaOH solution, hydrochloric acid, methanol.

Preparation of adsorbent: The preparation method of YSP-NJ (05-C) NHB sulfonated modified adsorption resin - for removing impurities, 200 g of D201 macroporous adsorption resin was immersed by methanol for 24 hours and subjected to subsequent filtration. The sample was washed with water until there was no more ethanol in the filtrate. Then 4% wt hydrochloric acid was added to the system slowly, the stirring was kept for 5 hours, after which the resin was washed with water until the solution became neutral. Following which, 4% wt. sodium hydroxide solution was added to the system slowly while stirring the solution. Thereafter, the sample was kept for 5 hours and then it was washed with water until it became neutral. The final sample was obtained through drying.

RESULTS AND DISCUSSION

TG results

The results of thermogravimetric analysis of the prepared adsorption material is illustrated in Fig. 2.1. The TG curve shows that there are four main steps of the weight loss. The first part of the TG curve below 115°C was related to the removal of physically adsorbed water and it contributed to around 42% of the total weight loss. There was much more weight loss than the reported results [21]. It may be due to the different water content of the adsorbent. The high water content was favourable for maintaining the pore structure. Dehydration causes central pipe which leads to poor adsorption performance. [24]. The weight loss at 115 to 400°C was about 4.39%. This indicated that the basic structure of D201 resin remains the same, which shows better thermal stability than other resin [21]. The third part at 400-600°C was attributed to the breakage of polystyrene chains (19.46% weight loss). Finally, the step above 600°C can be assigned mainly due to dehydroxylation (1.18% weight loss).
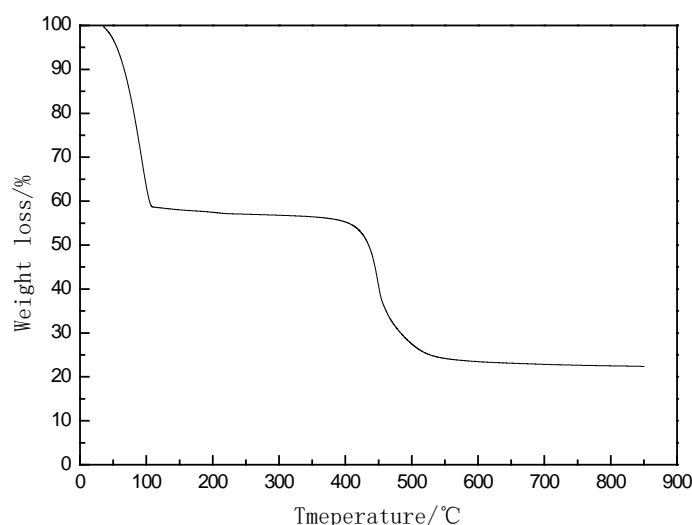

Figure 2.1 TG curve of the adsorbent

FT-IR results

FT-IR was used to analyze the composition of the adsorbent and the FT-IR spectra is displayed in Fig. 2.2. The strong peak at 3361.26 cm^{-1} indicates the stretching frequency of N-H groups. The medium peak at 2922.73 cm^{-1} indicates the presence of -CH$_2$- from styrene. The characteristic vibration bands at 1604.05 cm^{-1}, 1506.02 cm^{-1} and 1419.91 cm^{-1} were ascribed to the existence of aromatic rings. From IR spectra it can be inferred that there is no chemical reaction during polymeric phases. The aromatic skeleton and quaternary ammonium group remain intact. The results of the FT-IR study are consistent with the reported literature [22].
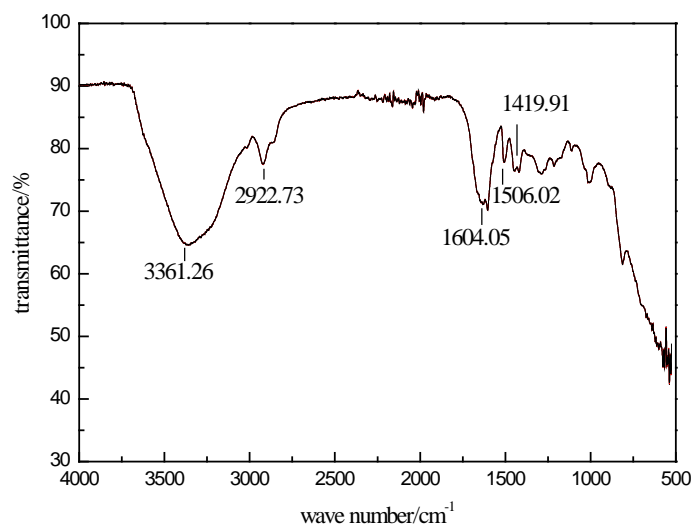

Figure 2.2 FT-IR spectrogram of adsorbent

N$_2$ adsorption-desorption

N$_2$ adsorption-desorption isotherms of adsorbent material is presented in Fig. 2.3. In the low pressure area (p/p$_o$<0.1) isotherm rises rapidly, which indicates the existence of microporous structures. The curve is not closed in this area, it may be due to the excellent swellability of the adsorbent. The adsorbing molecule are stuck the during desorption. In the relative pressure (p/p$_o$) range of 0.1~0.9, adsorption isotherm and desorption isotherm do not coincide.

There is an obvious presence of hysteresis loop because of capillary condensation of mesoporous. In the high pressure area (p/p$_o$>0.9), isotherms rise rapidly indicating the existence of macroporous structures. The adsorption-desorption isotherm is consistent with the literature [23].
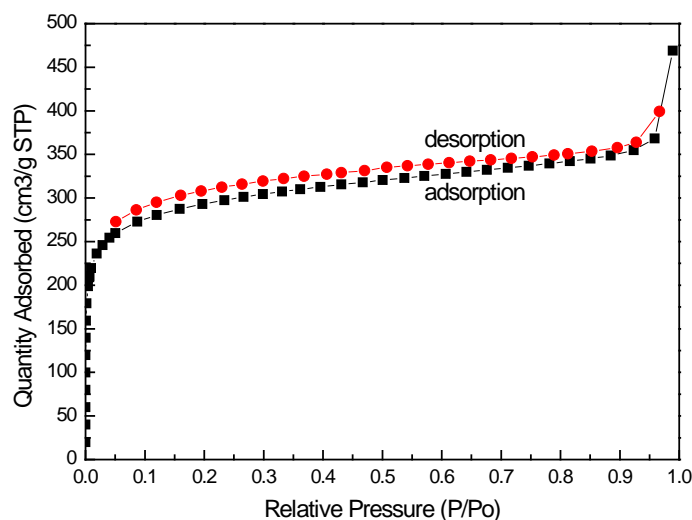
Figure 2.3 N₂ adsorption-desorption isotherms of adsorbent

Fig. 2.4 shows the pore size distributions of adsorbent, which were calculated by the DET method. As shown, the distribution of diameter of most holes was more concentrated in 5-20 nm and 300-1000nm. This is consistent with the result of N₂ adsorption-desorption isotherms of adsorbent material.
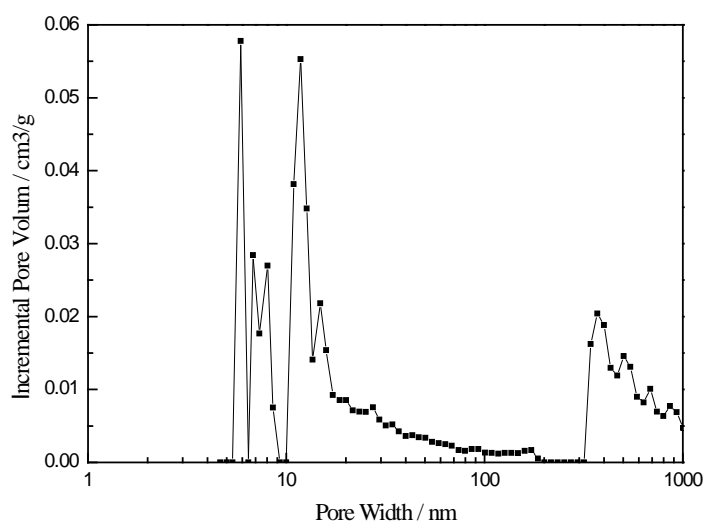

Figure 2.4 Pore size distribution of sample

As shown in Fig. 2.5, the holes with diameter of 5-20 nm were the largest contributors to specific surface area of the sample, which was more than 780 m2/g. This is consistent with the result of pore size distribution. Large specific surface area is beneficial to the adsorption process.
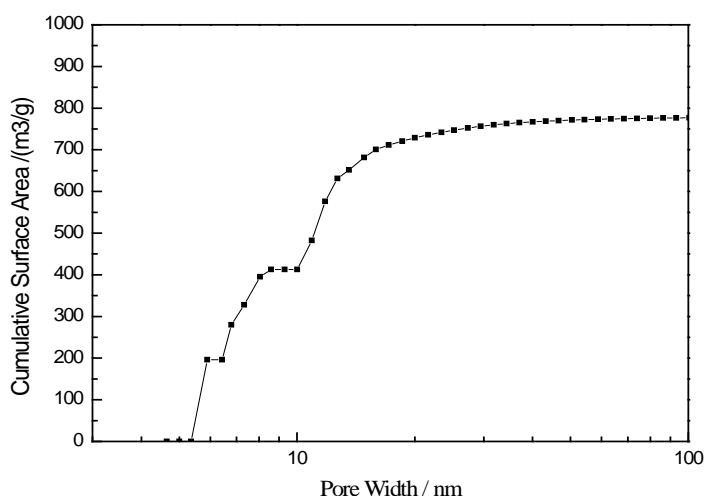
Figure 2.5 Cumulative surface area of adsorbent

The composition of raw materials reveal that the characteristic pollutants of wastewater are ammonia nitrogen, volatile phenol and total phenol. A large amount of oil in the wastewater will affect the performance of the adsorption resin. The adsorption resin is costly and if high concentration pollutants are absorbed directly, the resin saturates rapidly, resulting in shorter regeneration cycle, increased resin loss and large amount of adsorption resin. Therefore, in this experiment, the oil in the wastewater was removed first by simple filtration, after which such components as ammonia nitrogen and volatile phenol were removed by distillation.

Table 1.2 shows that the NH3-N and volatile phenol in the wastewater are effectively removed by distillation. The content of ammonia nitrogen in a reboiler at the bottom of the wastewater tower is only 45mg/L, and the non-volatile phenol is treated by resin adsorption. The results are shown in Table 2.1.

Table 2.1 The quality of the wastewater after adsorption

Analyze project	Raw water	Sample 1	Sample 2	Sample 3	Sample 4	Average	Removal rate
Phenol（mg/L）	5520	128	183	242	302	213.75	96.13%
Oil（mg/L）	1708	10.3	10.4	11.1	13.5	11.325	99.34%
COD（mg/L）	17170	349	384	435	476	411	97.61%

In the process of resin regeneration, alkaline waste liquid and waste gas containing phenols would be generated. The regenerated tail gas is absorbed by water circulation, and the nitrogen can be discharged directly. When it reaches a certain concentration level, it can be used to prepare coal water slurry, so as to realize resource utilization [25-26].

CONCLUSIONS

(1) The combined process of pre-treatment, distillation, adsorption of dephenolization is used to treat coal chemical wastewater, which can not only reduce air pollution caused by volatile phenol in wastewater, but can also greatly reduce the concentration of pollutants in discharged wastewater. The ratio of removing phenolic substances in the raw water is 96.13% under the optimal conditions. It shows a higher removal rate than the traditional method such as solvent extraction (80%).

(2) This technology partially evaporated waste water concentrated in distillation tower, and less power is spent.

Furthermore, evaporated water and water resources can be used for the slurrying of coal.

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