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Treatment of pretreated coal gasification wastewater (CGW) by magnetic polyacrylic anion exchange resin

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ABSTRACT

A magnetic polyacrylic anion exchange resin, NDMP, was employed to treat the pretreated Lurgi coal gasification wastewater (CGW). The effects of some factors such as resin dosage, adsorption time and the CGW molecular weight distribution as well as resin recyclability on the COD removal by NDMP were investigated. An economic and effective condition for the treatment of CGW by NDMP resin was a pH of 10, resin concentration of 8.0 g/L and adsorption time of 10 min. The molecular weight distribution showed the COD of CGW was mainly concentrated on small organic molecules in the fraction MW < 500 Da, and both of small organic molecules and macromolecular organic substances can be effectively absorbed onto NDMP. A mixture of 1% NaCl and 1% NaOH was found to be highly efficient for the regeneration of NDMP resin. This study reveals the high efficiency and reusability of NDMP for removing the organic matter of coal gasification wastewater, and shows its great potential application in industrial wastewater.

1. Introduction

In China, the rapid development and wide application of coal gasification technology has played an significant role in the new energy resource market in recent decades due to the fact that the coal is the most important part of energy structure [1]. Coal gasification wastewater (CGW) generated from coal gasification process contains high concentrations of phenolic compounds, thiocyanate and ammonium [2], and those substances may lead to serious effects on nature circumstances.

Genarally, the CGW is treated by a physico-chemical pretreatment and subsequent biological treatment to reduce the concentration of phenols and ammonium [3,4]. Some new adsorption materials, such as activated carbon and so on, have been used in this field. In this system, CGW is firstly pretreated through ammonia stripping and phenol solvent extraction [5,6]. Then, flocculation and adsorption can be used to reduce organic load and toxic impact on biological units. Though flocculation has effective performance in removing particulate organic matters [7], its shortage is also obvious due to the fact that flocculation shows no efficient result for the removal of COD and ammonium [7]. As for the adsorption of activated carbon, the regeneration is the crucial problem due to difficulty and costly reproducing of adsorption materials. Furthermore, the reduction of effluent COD to a level below 200 mg/L remains difficult [8], as well as the refractory compounds still remains high in CGW [5,6].

Recently, magnetic polyacrylic anion exchange resin, a new-type ion exchange resin, has been developed to remove organic contaminants with diverse chemical properties, and the new technology presents great potential for wastewater treatment. The resin beads can self-agglomerate under the magnetic force for quick and effective separation in completely mixed contactors processes because of the magnetized component within their structure [9]. Additionally, it has high resistant to organic fouling and can be effectively regenerated without noticeable capacity loss [10].

Until now, few works have evaluated the effects about the removal of organic pollutants in industrial wastewater by utilizing ion exchange resin [10,11]. Hence this study was aimed to investigate the effective removal for organic effluents in CGW, based on adsorption by magnetic polyacrylic anion exchange resin NDMP.

2. Materials and methods

2.1. Materials

The coal gasification wastewater (CGW) was collected from a Lurgi Gasifier located in Yunnan province, China. After the

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Table 1
The typical properties of the Lurgi coal gasification wastewater.

Indicators	COD (mg/L)	NH_3-N (mg/L)	pH	Color	Odor
Values	6500 ± 1000	460 ± 80	8.5 ± 1.0	Dark brown	Pungent

pretreatment of phenol extraction and ammonia stripping, the obtained samples of CGW have the following typical characteristics (shown in Table 1). The wastewater was dark brown in color with a pungent odor, and it contained high COD and ammonia with the concentration of about 6500 mg/L and 460 mg/L, respectively.

The magnetic resin NDMP was supplied by Nanjing University (China). The preparation processes and physicochemical properties of NDMP resin were described in the previous report [10]. The preparation of NDMP resin required polymerization, aminolysis, and alkylation. The NDMP resin with a small particle size has a polyacrylic matrix, quaternary amine functional group and a macroporous structure [12]. The resin was rinsed repeatedly with distilled water and dried at 60 °C in a vacuum before adsorption experiments.

2.2. Experimental

In the first phase of the work, the effect of pH on the COD removal was determined. In the test, conical flasks were filled up with 100 mL of unfiltered raw water, dosed with 0.800 g NDMP resin, and mixed at 160 rpm at 25 °C for 3 h with the pH of the solutions varying from 7.0 to 11.0, which was adjusted by using HCl aqueous solution (1 mol/L) or NaOH aqueous solution (1 mol/L).

Secondly, the effects of resin dosage and contact time on the COD removal of CGW were investigated. 100 mL of unfiltered wastewater was introduced into a series of 250 mL conical flasks at 160 rpm at 25 °C for 1 h with NDMP resin dosage varying from 0.200 to 10.0 g after the pH of raw water was adjusted to 10. For kinetic tests, 0.800 g NDMP resin and 100 mL of raw wastewater were introduced into conical flasks at 160 rpm at 25 °C. Samples were withdrawn from beakers at predetermined time intervals (2, 4, 6, 8, 10, 30, 60, and 120 min) for COD measurement.

The influence of molecular weight distribution of CGW on organic matters removal by NDMP resin was also investigated. Ultrafiltration (UF) was performed at 25 °C using a 300 mL Stirred Cell (MSC300, Shanghai Mosu Science Equipment Co., Ltd., China) with an exposed surface area of around 50 cm^2. With the pressure of 0.2 MPa, nitrogen was applied over the liquid in the stirred cell. After that, wastewater samples were filtered through two Poly (ether sulfones) membranes in turn with the nominal molecular weight cut-offs (MWCOs) including 5000 Da and 500 Da, subsequently. After ultrafiltration, three UF samples were obtained: a 5000 Da retentate sample, called as "MW > 5000 Da"; one sample which passed by the 5000 Da membrane, but was rejected by the 500 Da membrane, denominated as "500 < MW < 5000"; and another one 500 Da permeate sample, named as "MW < 500 Da".

The reusability of NDMP resin was assessed by investigating the regeneration performance. 100 mL of raw wastewater and 0.800 g resin were introduced into conical flasks at 160 rpm at 25 °C, the resin was filtered after adsorption equilibrium. A mixed aqueous solution containing 1% NaCl and 1% NaOH was used for regeneration [12]. Desorption experiments were conducted at 25 °C, with 100 mL of desorption solution and filtered resin in conical flasks. The cycles of adsorption/desorption were repeated for 25 times, and the regeneration time of NDMP resin was extended for the last 5 cycles.

The COD removal amount of CGW (R_t, mg/L) and the adsorption capacity of NDMP (Q_t, mg/g) were respectively calculated using Eqs. (1) and (2):

$$R_t = C_0 - C_t \quad (1)$$

$$Q_t = V \times \frac{R_t}{W} \quad (2)$$

where C_0 (mg/L) and C_t (mg/L) represent the initial concentration and a specified concentration at time t (min), respectively. V is the volume of solution (given in liters), and W is the weight of the dry resin (given in grams).

2.3. Analysis methods

The COD was determined according to the standard method [13]. The pH was measured using an acidity meter (PHS-3C, Shanghai INESA Scientific Instrument Co., Ltd., China). All chemicals used were of analytical reagent grade. Deionized water producted by a laboratory water purification system (RO DI digital, Shanghai Hitech Instruments Co., Ltd, China) was used for stock solution preparations and dilutions. An incubator shaker (HZQ-X300C, Shanghai Yiheng Scientific Instruments Co., Ltd., China) was used for oscillation in adsorption experiments.

3. Results and discussion

3.1. Effect of solution pH

The variation of solution pH resulted in remarkable change on the COD adsorption performance by NDMP resin. As shown in Fig. 1, both of the adsorption capacity for NDMP and COD removal amount increased sharply with solution pH enhancing from 7.0 to 10.0, and reached maximum values of 360.5 mg/g and 2883.8 mg/L, respectively, then decreased slightly with solution pH continually increasing to 11.0. The result indicated a high pH condition may contribute to the COD removal of CGW by NDMP. Since the CGW comprised a substantial amount of phenolic compounds, the effects of pH on phenol adsorption should be considered. Similar results were shown for phenol adsorption by active carbon [14]. A low pH would introduce additional protons occupying the effective adsorption sites by its electrostatic interaction with amino groups, which suppressed phenol adsorption [15]. The adsorbing species at a pH of 10 is mostly anionic since the pKa value for phenol is 9.89. Meantime, repulsion between the anionic phenolates and the surface layer resulted in reducing in phenol adsorption at pH > 10.0 [14]. Moreover, the tertiary amine groups of NDMP resin were deprotonated, which significantly decreased the anion exchange capacity [12]. The COD adsorption performance by NDMP resin

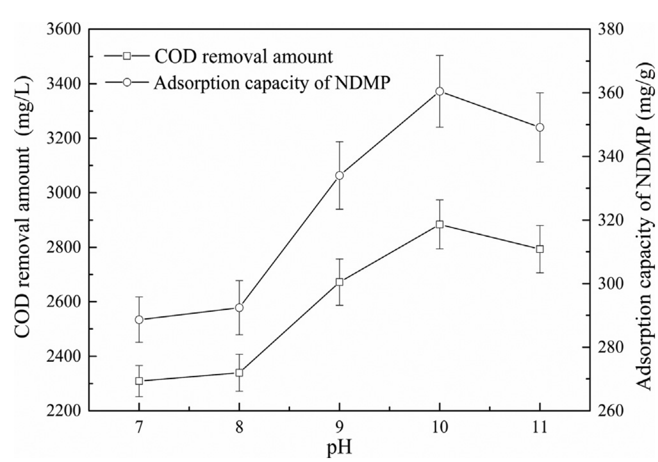

Fig. 1. Effect of pH on COD adsorption of CGW.