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ScienceDirect
Mining Science and Technology 20 (2010) 0778–0781
MINING SCIENCE AND TECHNOLOGY
www.elsevier.com/locate/jcumt

Adsorption of oil from waste water by coal: characteristics and mechanism

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Abstract: The work described here was focused on exploring the potential application of coal to purification of oily waste water. Coal was added to oily waste water as an adsorbent and then removed through a flotation process. This allowed economical and highly efficient separation of oil from the waste water. The absorption time, coal type, coal particle size distribution, pH value and oil concentration were investigated. The results indicate that oil absorption by a coal increases for a period of 1.5 h and then gradually tends toward an equilibrium value. It appears that the absorption capacity of anthracite is more than that of lean coal or lignite, given the same coal particle size distribution. The absorption capacity of a coarse coal fraction is less than that of finer coal, given the same of coal type. The absorption capacity of anthracite decreases slightly as the pH increases from 4 to 9. The adsorption of oil on anthracite follows the Freundlich isothermal adsorption law: given initial oil concentrations of 160.5 or 1023.6 mg/L the absorption capacity was 23.8 or 840.0 mg/g. The absorption mechanism consists of two kinds of absorption, a physical process assisted by a chemical one.

Keywords: oily wastewater; waste water; separation; coal; oil; adsorption; mechanism

1 Introduction

Oily waste water is one of the most serious environmental issues created by production in oil fields. The treatment of oily waste water is important not only from an economic view point but also in terms of ending the pollution of water resources. Commonly used technologies for treating oily waste water include physical treatment, physical chemistry, chemical de-emulsifying, biochemistry and electrochemistry[1-4]. However, application of these techniques has been limited for both technical and economic reasons. A flotation process has been attracting much recent attention from scholars because of its high separation efficiency, low capital investment and operational costs. Some new types of flotation devices and some new methods for quick and highly efficient separation of oily waste water have been developed[5-9].

Currently, many oil fields in China have entered a medium-high water-cut stage during their mid to late phase of oil extraction. The development and application of the polymer-flooding technology in oil fields has resulted in the production of water containing a large amount of high molecular weigh polymer that is highly emulsified and has a high water-phase viscosity. This makes treatment of the polymer-flooding waste water considerably more difficult.

Hao Z T et al. used fly ash as an adsorbent to adsorb oil from oily waste water[10]. Oil removal efficiencies reached 70%~80% in that scheme and the adsorption process fit an S-shaped isothermal adsorption law. Yan L H et al. reported that the adsorption process follows the Freundlich isothermal adsorption law when fly ash was used as an adsorbent for separation of oil from oily waste water at room temperature[11]. The results showed that the residual oil concentration in the waste water would not be too high when the adsorption process was helped by stirring. However, the recovered oil can not be recycled effectively when fly ash is used as the adsorbent.

The objective of this study was to explore the potential application of using coal to treat oily waste water. The oil can first be separated from the waste water with a novel method where the coal is used as an oil adsorbent and then the coal-oil mixture is separated from the waste water by flotation economically and with high efficiently. As a result, oil removal from waste water was successfully performed and the recycled oil could then be used as fuel, namely a coal-oil-water multiphase fuel. The adsorption of oil droplets onto a coal particle surface from oily waste water was also studied.

Received 07 December 2009; accepted 08 March 2010

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doi: 10.1016/S1674-5264(09)60280-5

2 Experimental

2.1 Materials

The oily waste water was polymer-flooding water. Samples were obtained from the Shengli Gudao Oil Field, China. The initial oil mean concentration in the water was 246.40 mg/L. The oil droplet size distribution was analyzed with a laser particle size analyzer (LS-100Q). About 13.4% of the oil droplets were 1 μm in diameter or smaller and about 99.1% were 10 μm or smaller. The oily waste water is very difficult to separate because of the small mean size of the droplets that consist of emulsified oil and polymer.

The coals used as sorbent in the experiments were Yongcheng anthracite from Henan province, China, Anyang lean coal from Henan province, China and Wuhai lignite from Inner Mongolia province, China. These coal samples were ground into fine particles for 8 minutes using a XMB-67 ball mill. Then they were screened with a bushing screen into fractions of particle size +0.5–1.0, +0.125–0.5, +0.074–0.125, +0.046–0.074 and –0.046 mm.

2.2 Methods

2.2.1 Oil concentration measurement and the absorption capacity calculation

The oil concentration of the waste water was determined by UV spectrophotometry (UV2602).

The adsorption capacity for crude oil was calculated using Eq.(1)

$$\Gamma = (C_0 - C_e) \times v / m \qquad (1)$$

where Γ is the superficial adsorption capacity; C_0 the initial concentration of crude oil in the oily waste water; C_e the equilibrium concentration of crude oil in the waste water; and m the quantity of coal added to the sample.

2.2.2 Equilibrium absorption time

In a typical experiment 0.25 g of anthracite, the lean coal or the lignite was used for each trial. The coal was first added to a 250 mL conical flask along with 50 mL of oily waste water. The mixture was then mixed with a thermostatically controlled oscillator at (25±1) °C. The mixing time was programmed from 0 to 3.0 h. Finally, the oil concentration of these samples was measured after absorption by the coal. The results are presented in Fig. 1.

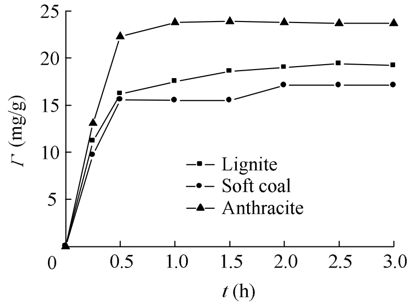

Fig. 1 Absorption as a function of time

Fig. 1 shows that absorption equilibrium occurs later than 1.5 hours after initial contact. Thus, a 3.0 h contact time was chosen as being most suitable by experiment. The absorption process of each of the three coals may be divided into two stages, a quick and a slow absorption stage. The absorption capacity during the quick absorption stage is more than 90% of the total absorption capacity. The absorption gradually comes to equilibrium during the slow, final absorption stage.

2.2.3 Selection of coal type and particles size

0.25 g samples of anthracite, the lean coal or the lignite were used. The particle sizes of the samples were –0.046, –0.074 +0.046, –0.125+0.074, –0.5+ 0.125 or –1.0+0.5 mm. The coal sample was put into a 250 mL conical flask along with 50 mL of oily waste water. Then the mixture was mixed in a thermostatically controlled oscillating bath at (25±1) °C for 3.0 h. The results are shown in Fig. 2.

2.2.4 pH value

0.25 g anthracite samples with a particles size of –0.074+0.046 mm were used for this part of the work. The coal sample was added to a 250 mL conical flask along with 50 mL of oily waste water. Then the pH of the mixture was adjusted by adding either $NH_3·H_2O$ or HCl to it. The flask was mixed in a thermostatically controlled oscillating mixer at (25±1) °C for 3.0 h. The results are shown in Fig. 3.

2.2.5 Oil concentrations

Samples with different oil concentrations in the water were prepared at a pH value of 7.0. Again, 0.25 g of anthracite, particle size +0.046–0.074 mm, were placed in a 250 mL conical flask along with 50 mL of oily waste water. This mixture was mixed in the thermostatically controlled oscillating mixer at (25±1) °C for 3.0 h. The results from this trial are shown in Fig. 4.

3 Results and discussion

3.1 Effect of coal type and particles size on the absorption capacity

Fig. 2 shows that the absorption capacity of anthracite exceeds that of the lean coal and the lignite for each particle size. The equilibrium adsorption capacities of anthracite, lean coal and lignite were 24.4, 18.6 and 20.7 mg/g, respectively, when the particle size was –0.046 mm.

The coarser lean coal had greater absorption capacity than the coarser lignite. For example, the equilibrium adsorption capacities of lean coal and lignite were 11.3 and 9.3 mg/g respectively when the particle size was –1.0+0.5 mm. However, the absorption capacity of the lean coal is less than the lignite when the particle size was smaller. For example, the adsorption capacities of the lean coal and the lignite were 14.1 and 17.8 mg/g respectively when the particle size was