Adsorption Characteristics of Macroporous Resin for Oil Removal from Desulphurization Wastewater on Board

Tie Li, Chen Chen, Qi Jin, Jiao Zhao, Xiaojia Tang and Yimin Zhu

Collaborative Innovation Center for Vessel Pollution Monitoring and Control, Dalian Maritime University, Dalian, Liaoning 116026, China

ntp@dlmu.edu.cn

Abstract. According to our previous results on the magnesium-based exhaust gas cleaning system (Mg-EGCS), PAHs and total oil content were the main factors affecting the COD in the wastewater. In this work, three kinds of adsorption materials were investigated and macroporous resin was selected for oil removal. The effects of the dosage of macroporous resin, adsorption time and the flow rate were studied, and thermodynamics equation was used to characterize the adsorption process. The results showed that macroporous resin is a good candidate for oil removal from desulphurization wastewater on board, and the COD after treatment can meet the discharge criteria set by the International Maritime Organization (IMO).

1. Introduction

A novel magnesium-based exhaust gas cleaning system (Mg-EGCS), which adopts magnesium oxide or magnesium hydroxide as absorbent, has been reported in our previous studies, and after a long time operation on board, Mg-EGCS has been proven to meet the IMO sulfur emission requirements [1]. However, due to the heavy fuel oil used in the diesel engine, the exhaust gas also contains unneglectable products from incomplete combustion, such as aromatic and naphthenic compounds, which would be washed into the wastewater in the desulphurization process. If such wastewater was discharged without treatment, it would cause serious seawater pollution.

The composition of the wastewater from the Mg-EGCS has been analyzed in our laboratory [2], and the results showed that the COD in the wastewater was beyond the limitation based on the washwater discharge criteria. The PAHs and total oil content were the main factors affecting the COD in the wastewater.

Various methods of oil removal have been developed. Among them, physical method was simple but only suitable for the wastewater which contained high oil content [3], while chemical method and biology method showed better oil removal efficiency, but the processes were usually complicated [4-6].

Adsorption method was commonly used for oily wastewater treatment [7]. The typical adsorption materials include activated carbon, fly ash, bentonite, cotton fibers adsorbent, ceramsite filter and adsorption resin, etc.

According to the characteristics of the desulphurization wastewater and the special requirements of the ship wastewater treatment, in this work, three kinds of adsorption materials were investigated and macroporous resin was selected for oil removal. The effects of the dosage of macroporous resin, stirrer speed and the flow rate were studied, and thermodynamics equation was used to characterize the adsorption process.

2. Materials and method

2.1. Preparation of simulated oil wastewater

The simulated oily wastewater was prepared as follows: certain amount of fuel oil was put into a beaker, and mixed with sea water; after stirring for 24 hours, the mixture was kept stand for 5 hours. It should be diluted to about 140 mg/L if the oil content in water is too high.

2.2 Properties of macroporous resin

The physicochemical properties of macroporous resin are shown in Table 1.

Table 1. The physicochemical properties of macroporous resins

Item	Parameters
Water content (%)	55～65
Particle size (μm)	250～600
Specific surface area (m^2/g)	590
Pore volume (mL/g)	1.3
Relative density	1.01
Apparent density (g/L)	680

2.3 Analysis methods

The COD was analyzed according to the standard methods (APHA, AWWA and WEF, 1999). The PAHs and total oil were determined by liquid chromatography (Agilent 1260) and infrared spectrometer (JDS-100, Jilin North Light Technology Co., Ltd., China), respectively. The oil removal rate D_0 was calculated as follows:

$$D_0 = \frac{\rho_0 - c_e}{\rho_o} \times 100\% \quad (1)$$

where ρ_0 is the initial oil concentration in water sample (mg/L), C_e is the equilibrium oil concentration (mg/L).

3. Results and discussion

3.1 Comparison of adsorption performance

Cotton fibers adsorbent 0.5 g, ceramist filter 3 g and macroporous resin 1.0 g were stirred with 50 mL of desulfurization wastewater with initial oil concentration of 18.638 mg/L in a beaker, respectively. After 3 hours, the residual oil content in the solution was measured. Such parallel experiments were repeated for 3 times.

The effects of oil removal of various adsorbent materials on desulfurization wastewater were showed in Table 2. The oil removal rate of cotton fibers adsorbent and ceramist filter was 8.62% and 4.05%, respectively, which was less than that of macroporous resin with the oil removal rate of 51.22%.

Table 2. The adsorption performance of various adsorbent materials on desulfurization wastewater

Adsorbent material	cotton fibers adsorbent	ceramist filter	macroporous resin
Residual oil content	17.045	17.826	9.295
C_e(mg/L)	16.832	18.295	8.931
	17.221	17.532	9.051
Average C_e(mg/L)	17.032	17.884	9.092
Removal rate (%)	8.62	4.05	51.22

3.2 The adsorption experiments of macroporous resin

3.2.1 The effect of the dosage of macroporous resin. In order to determine the effect of oil removal, the dosage of macroporous resin was kept as 4.0, 5.0, 6.0, 7.0, 8.0, 12.0, 16.0, 24.0, 28.0, 36.0, 44.0 and 60.0 g/L, respectively, and the experimental conditions were kept as the initial oil concentration of 140 mg/L and the stirrer time of 4 hours.

As shown in Figure 1, the oil removal rate increased with the increase of the macroporous resin dosage, and the removal rate reached 94% when the dosage was increased to 44.0 g/L. As the dosage of macroporous resin raised from 4.0 to 8.0 g/L, a significant increase of the removal rate could be observed. While in the range of 12.0 g/L to 44.0 g/L, there was only a slight increase of the removal rate.

When the dosage was in the range of 4.0 ~ 8.0 g/L, the macroporous resin can be fully contacted with the water by stirring, therefore, the oil removal rate increased rapidly. When the dosage increased from 12.0 g/L to 44.0 g/L, the density of macroporous resin decreased, which cannot fully contact with water.

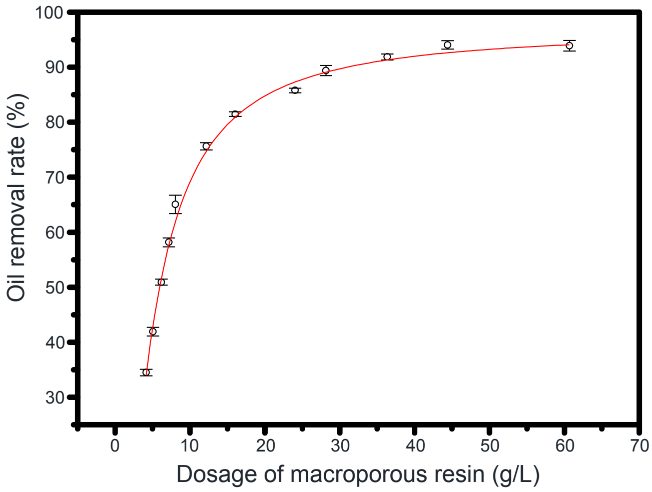

Figure 1. The effect of the dosage of macroporous resin.

3.2.2 The effect of adsorption time. Figure 2 showed the effect of adsorption time on the oil removal rate, when it was varied from 60 to 240 min. The other parameters were kept constant for all trials with the initial oil concentration of 140 mg/L, dosage of macroporous resin of 7.0 g/L and a stirring speed of 1,100 rpm. The maximum oil removal rate reached to 58% with the adsorption time of 165 min, then only a slight increase of removal rate was observed with further increase of the adsorption time.

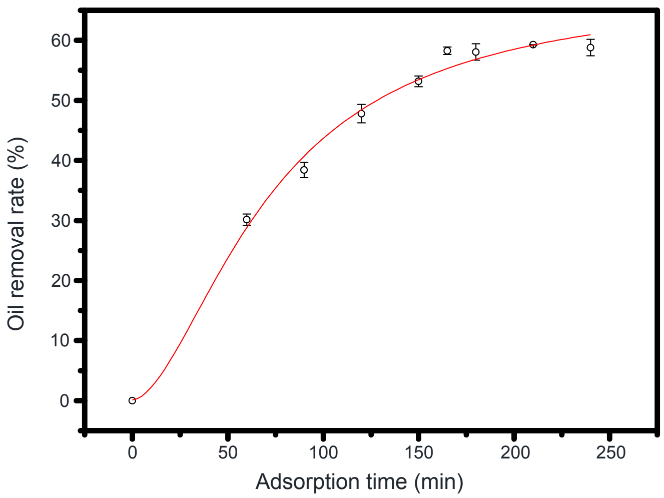

Figure 2. The effect of the adsorption time.

3.2.3 The effect of flow rate. The macroporous resin was packed in a chromatographic column with an inner diameter of 20 mm and a height of 400 mm. The flow rate was adjusted to 4.5 mL/min, 7.5 mL/min and 10 mL/min, respectively. Then the oil content was measured every ten minutes. In each batch of experiment, the macroporous resin and the initial oil concentration were kept as 10 g and 140 mg/L, respectively. The effect of flow rate on the oil removal rate was shown in Figure 3.

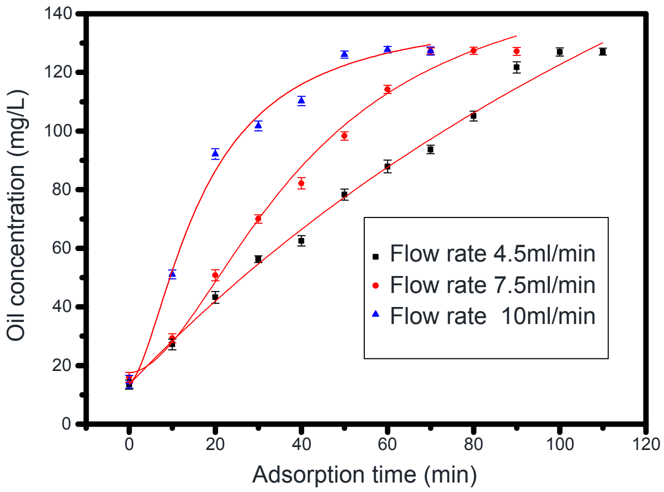

Figure 3. The effect of the flow rate

It can be seen from Fig. 3 that the permeation time decreased with the increase of the flow rate from 4.5 mL/min to 10 mL/min. When the flow rate was 4.5mL/min, 7.5 mL/min and 10 mL/min, the penetration time was 90 min, 70 min and 50 min respectively. The decrease of the flow rate will increase the contact time with the macroporous resin, and be helpful for the absorption of oil.

3.2.4 Adsorption isotherm. Various isotherm equations have been used to describe the equilibrium nature of adsorption, including the Freundlich and Langmuir equations.

The Langmuir isotherm which is applicable for monomolecular layer adsorption, has been extensively used for characterizing the adsorption of heavy metals, dyes, and organic pollutants [8]. This isotherm is described as homogeneous adsorption, assuming that all the adsorption sites have equal adsorbate affinity and that the adsorption at one site does not affect the adsorption at an adjacent site [9-11]. The Langmuir isotherm is used to obtain a maximum adsorption capacity produced from the complete monolayer coverage of the adsorbent surface. The isotherm equation is represented as:

$$q_e = \frac{bQ_m C_e}{1 + bC_e} \quad (2)$$

where Q_m and b are coefficients, q_e is the weight adsorbed per unit weight of adsorbent, and C_e is the oil concentration in the water at equilibrium. The value of Q_m and b were obtained from slope and intercept of linear curve presented in Figure 4.

The Freundlich isotherm is given by the following equation:

$$q_e = KC_e^{1/n} \quad (3)$$

By taking logarithms of both sides of equation (3) and rearranging, equation (4) was obtained.

$$\log q_e = \log K - n \log C_e \quad (4)$$

where n is the Freundlich constant, K is the adsorption coefficient, q_e is the weight adsorbed per unit weight of adsorbent, and C_e is the equilibrium oil concentration in the water. The values of K and $1/n$ were calculated from the intercept and slope of linear curve presented in Figure 5.

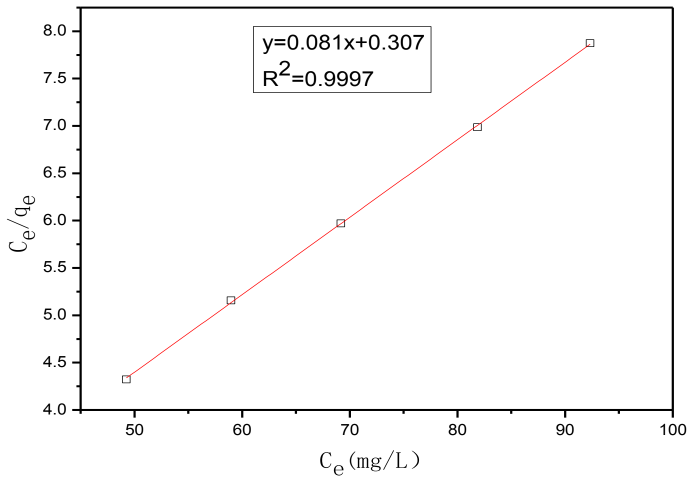

Figure 4. Langmuir models for oil removal rate.

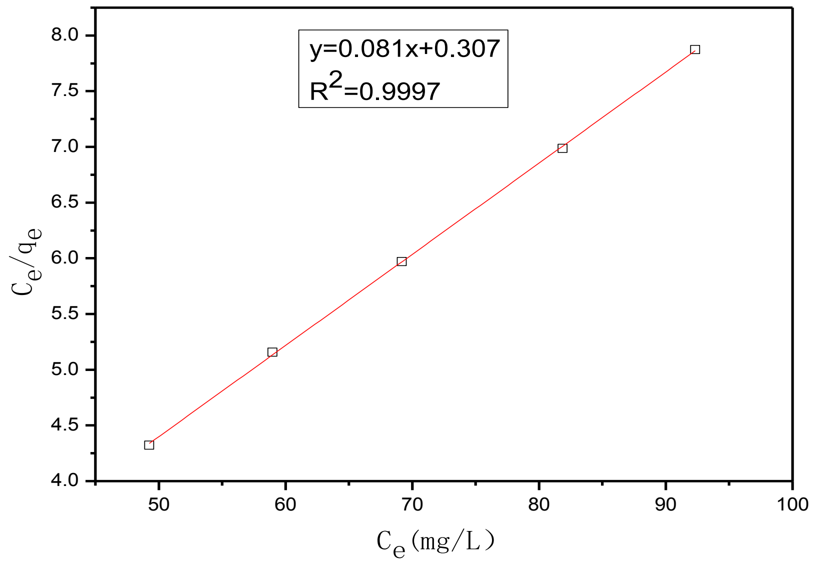

Figure 5. Freundlich models for oil removal rate.

The constants related to the aforementioned isotherm models were calculated (Table 3), and the results indicated that the data obtained throughout the experiments were well fitted to Langmuir isotherm model, with a correlation coefficient of 0.99. Moreover, the adsorption capacity of macroporous resin for the removal of oil was determined to be 11.727 mg/g; which represents an improved capacity compared with the capacities of other well-known adsorbents.

Table 3. Isotherm constants for oil adsorption

Langmuir			Freundlich		
Q_m	b	R^2	K	n	R^2
0.264	12.345	0.999	8.561	-0.051	0.933

4. Conclusion

The present study shows that macroporous resin is an effective adsorbent for the removal of oil from desulphurization wastewater. The adsorption capacity of the macroporous resin was 12.35 mg/g and the equilibrium adsorption time was about 3 h. The results of dynamic adsorption experiments showed that with the increase of flow rate, the adsorption time was reduced and the penetration time was shortened. Isotherm model studies indicated that the Langmuir isotherm model fits the equilibrium data very well for the macroporous resin adsorption system. In conclusion, the investigations indicated that macroporous resin is effective for oil adsorption due to its special adsorption characteristics. The results of this study are useful for the design of treatment process for the removal of oil in the desulphurization wastewater.

Reference

[1] Tang, X.J., Li, T., Yu, H. and Zhu, Y.M. 2014 *Ocean Eng.* **76** 98
[2] Li Tie, Yu Hang, Li Ye-ye, Liu Quan, Chen Chen, Guo Lin and Zhu Yi-min 2015 Int J *Environ. & Poll.* **53** 1
[3] Xiao-ru Cheng and Ying-wen xue 2002 *Environ. Sci. & Tech.* **3** 38
[4] Oguz E, Keskinler B and Celik Z 2005 *Dyes Pigments* **64** 01
[5] Zheng-qing Yang, Li-Xia Yang, Yi-ning Hou and An Wang 2006 *Environ. Sci. & Man.* **31** 119
[6] Yang Bai 2003 *Sci-Tech Information Development & Economy* **13** 113
[7] Chang-ying Guo, Peng-cheng Zhao and Jing Xiao 2010 *Environ. Sci. & Man.* **3** 96
[8] M. Ghaedi, S. Heidarpour, S.N. Kokhdan, R. Sahraie, A. Daneshfar and B. Brazesh 2012 *Powder Technol.* **228** 18.
[9] S. Chatterjee, S. Chatterjee, B.P. Chatterjee and A.K. Guha 2007 *Colloids Surfaces A* **299** 146
[10] D. Mohan, K.P. Singh, G. Singh and K. Kumar 2002 Indus. Eng. Chem. Res. **41** 3688
[11] Y.E. Benkli, M.F. Can, M. Turan and M.S. Celik 2005 Water Res. **39** 487.