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Adsorption Effect of Cetyltrimethyl-ammonium Bromide Modified Fly Ash on Methyl Orange Waste Water

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Abstract. Fly ash is a solid waste from power plant, which will pollute the environment if not handled properly. The modification of fly ash as an adsorbent is an ideal method of resource utilization. In this paper, fly ash was firstly treated with cetyltrimethy-lammonium bromide (CTAB), and then further stabilized to obtain the final adsorbent product. The proper treating conditions are obtained: mass ratio of CTAB to fly ash 0.017, modification temperature 32°C, and time 1 h. The removal rate for methyl orange with the modified fly ash stabilized by drying at 100 °C is up to 93.2 %, which is higher than that calcined at 500 °C. The adsorption effect of the modified fly ash is much better than that of unmodified fly ash.

1.Introduction

Fly ash is a common solid industrial waste from coal-fired power plant. If not properly disposed, it will seriously pollute the environment and harm human and animals [1]. Fly ash contains more than 60 percent of SiO₂, Al₂O₃ and CaO, which is similar to natural zeolite. This makes it possible for fly ash as an adsorbent [2]. In 1975, Gagoli [3] et al. first used fly ash to remove heavy metals from industrial waste-water, and investigated the mechanisms. Generally, the adsorption effect cannot meet the actual needs. Several technologies have been developed these years to improve the adsorbing performance of fly ash by acid modification, alkali modification and metal modification.

Li Weiging [4] and Peng Ronghua [5] used sulfuric acid to modify the fly ash, which is used for waste-water treatment in paper industry. It was found that the combined use of sulfuric acid-modified fly ash and carbonate has remarkable effect. Yang Jing [6] and Duan Xuemei [7] also modified fly ash with sulfuric acid. They found that the adsorption of fly ash is excellent and in accordance with the formula of Langmuir adsorption isotherm. Wang jingyun [8] used calcium hydroxide to modify fly ash, and used for the decoloration and adsorption treatment of active red dye waste-water. After adding calcium hydroxide, the dosage of fly ash is greatly reduced, and the adsorption chromaticity is obviously improved. Liu Jiali [9] et al. adopted Ca(OH)₂ to adsorb oily waste water, and got positive results. Tian Yongqi [10] used the mixture of NaOH and NaHCO3 to modify fly ash to treat copper containing waste-water, and obtaining high removal rate. Bai Maojuan [11] used ferrous ions to modify fly ash and used for the treatment of phosphorus waste-water. The removal rate is over 90 %. Zhang Xin [12] et al. used two kinds of metal salt modifiers, FeSO₄ and FeCl₃, to modify fly ash, and obtained desired results. Xia Changbin [13] used metal cations Al³⁺ and Fe³⁺ to modify fly ash, which is used to treat the waste-water containing p-nitrophenol. The results showed that the adsorption property of the modified fly ash is obviously improved.

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The aim of this work is to develop a suitable process for fly ash modification for the purpose of methyl orange waste-water treatment. We adopt two-step method to modify fly ash in this paper. Firstly, fly ash is modified with CTAB, and secondly stabilized by drying at 100 $^{\circ}$ C and calcining at 500 $^{\circ}$ C respectively, to investigate the adsorption effect for methyl orange.

2. Experimental

2.1. Materials

CTAB, sodium hydroxide, hydrochloric acid, hydrogen peroxide, copper chloride and methyl orange are bought on the market. Fly ash is provided by Shijiazhuang Jingxing Construction Material Corp. Ltd. Table 1 shows the chemical composition of fly ash.

Table 1. Chemical composition of fly ash (%)								
SiO ₂	MgO	CaO	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	SO_3	Others	
49.82	0.66	5.96	33.90	4.40	1.24	2.05	1.97	

2.2. Sample preparation

Fly ash is washed and dried. CTAB solution (2.5g/L) is prepared beforehand as a modifier. The optimal conditions for the modified fly ash are determined by changing the amount of CTAB, reaction time and reaction temperature. The modified fly ash samples are further treated by drying (at 100 °C) and calcining (at 500 °C) respectively, to obtain stabilized finish.

2.3. Adsorption test

Take a certain amount of distilled water (Keep the total volume of the solution at 25 mL), add 5 mL (100 mg/L) methyl orange solution. Then, add stabilized fly ash sample. After the reaction finished, centrifuges, the clarification liquid is used for the measurement of absorbance.

The removal rate of methyl orange is calculated as following.

$$R = (1 - \frac{A}{A_0}) \times 100\%$$
 (1)

Where A_0 and A are the absorbance before and after the reaction. R is the removal rate of modified fly ash sample for methyl orange.

3. Results and discussion

3.1. Effect of mass ratio of CTAB to fly ash and stabilization process

Table 2 shows the effect of dosage of CTAB on the adsorption performance of modified fly ash stabilized by drying at 100 $^{\circ}$ C and calcining at 500 $^{\circ}$ C. The modification temperature and time are fixed at 30 $^{\circ}$ C and 1h.

Mass ratio	Temperature/°C	R/%			
0.0092	100	66.2			
0.0083	550	10.9			
0.0125	100	76.8			
0.0123	550	8.6			
0.017	100	85.4			
0.017	550	11.4			
0.025	100	89.2			
0.023	550	11.9			
0.022	100	90.0			
0.033	550	12.3			

Table 2. Effect of mass ratio of CTAB to fly ash(in different stabilization method)

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The results show that with the increase of the mass ratio of CTAB to fly ash, the removal rate for methyl orange gradually increases. The adsorption effect of CTAB modified fly ash is much better than that of unmodified fly ash. The removal rate for methyl orange with the modified fly ash stabilized by drying at 100 $^{\circ}$ C is higher than that calcined at 550 $^{\circ}$ C. Considering the cost-effectiveness, the optimal mass ratio of CTAB to fly ash is 0.017, and the removal rate for methyl orange reaches 85.4 %.

3.2. Effect of modification temperature

Table 3 shows the effect of modification temperature on the adsorption performance of modified fly ash stabilized by drying at 100 $^{\circ}$ C and calcining at 500 $^{\circ}$ C. In the experiments, the mass ratio of CTAB to fly ash is 0.017, the modification time is 1h.

		<u> </u>
Reaction temperature/°C	Temperature/°C	R/%
22	100	88.0
	550	11.8
22	100	92.1
52	550	12.6
42	100	91.0
42	550	10.2
52	100	83.5
32	550	9.6

Table 3. Effect of modification temperature on the removal rate for methyl orange

The results show that the removal rate for methyl orange with the modified fly ash dried at 100 $^{\circ}$ C, is higher than that calcined at 550 $^{\circ}$ C. At higher temperature, a large number of voids in the samples were sintered. The optimal modification temperature is 32 $^{\circ}$ C, at which, the removal rate for methyl orange is up to 92.1%.

3.3. Effect of modification time

Figure 1 shows the effect of modification time on the adsorption performance of modified fly ash stabilized by drying at 100 $^{\circ}$ C. In the experiment, the modification temperature is 32 $^{\circ}$ C, the mass ratio of CTAB to fly ash is 0.017.



Figure 1. Effect of modification time on the adsorption for methyl orange

IOP Conf. Series: Materials Science and Engineering 409 (2018) 012006 doi:10.1088/1757-899X/409/1/012006

It is shown that the removal rate of methyl orange increases first and then decreases with the increase in modification time. The optimal modification time is 1 h and the maximum removal rate reaches 93.2%. The good adsorption effect of modified fly ash is mainly due to the application of modified particles on the surface of fly ash, which increases the specific surface area of fly ash and enhances the adsorption capacity of methyl orange. Besides, the modified fly ash changes from hydrophilic to oleophilic, and the hydration of CTAB is less than that of inorganic cation, which reduces the resistance of modified fly ash to methyl orange, thus improving the adsorption capacity for methyl orange.

4. Conclusions

- Two-step method to modify fly ash is developed, in which fly ash is firstly modified with CTAB, and secondly stabilized by drying at 100 °C and calcining at 500 °C respectively. The adsorption effect of CTAB modified fly ash is much better than that of unmodified fly ash.
- The optimized modification conditions are obtained: mass ratio of CTAB to fly ash 0.017, modification temperature 32 °C, and time 1 h. Compared to calcining at 500 °C, the modified fly ash stabilized by drying at 100 °C shows higher adsorption rate for methyl orange.
- The good adsorption effect of modified fly ash is mainly due to the application of modified particles on the surface of fly ash, which increases the specific surface area and reduces the resistance of modified fly ash to methyl orange, improving the adsorption capacity for methyl orange.

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