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ScienceDirect
Journal of Hazardous Materials 147 (2007) 133–138
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

The performance and application of fly ash modified by PDMDAAC

X.Y. Cao [a,b], Q.Y. Yue [b,*], L.Y. Song [a], M. Li [a], Y.C. Zhao [a]

[a] School of Environmental Science and Engineering, Tongji University, Shanghai 200092, China
[b] School of Environmental Science and Engineering, Shandong University, Shandong 250100, China

Received 9 October 2006; received in revised form 19 December 2006; accepted 19 December 2006
Available online 30 December 2006

Abstract

Fly ash modification by polydimethydiallylammonium chloride (PDMDAAC) in laboratory scale was explored in this work and the adsorption performance of modified fly ash and its application in dyeing wastewater treatment were also studied.

The key factors (concentration and temperature) for PDMDAAC to affect the adsorption properties of fly ash (FA) were revealed using the orthogonal test with four factors. The results indicated that the adsorption magnitude of fly ash to PDMDAAC increased due to its favorable specific surface causing the change of the surface charge nature. Hence, adsorption performance of modified fly ash on organic molecules and its ion exchange capacity are strengthened. The maximum color removal efficiency was obtained as 88.2% by modified fly ash with 2.0 g/100 mL dosage in dyeing wastewater, which is much higher than 12.5% color removal efficiency by raw fly ash with the same dosage. And, the used modified fly ash could be used for cement production as additive agent. The intensity of cement produced with 15% the modified fly ash in weight reached the Chinese Cement Standard (GB/T17671-1999), blazing a promising novel way in fly ash utilization.

Keywords: Fly ash; Modification; Orthogonal array; Adsorption mechanism; Performance; Efficiency

1. Introduction

Fly ash is mainly produced during the electricity generation of coal-consuming power plants [1]. Although the disposal of fly ash using landfilling is routinely practiced, increasing disposal costs and serious environmental concern over the leaching of latent toxic substance from the ash to soil, surface water and groundwater [2–4] are making the utilization of fly ash a more attractive alternative compared with direct disposal (landfilling).

In china, the amount of fly ash has increased continuously as the chief method for electricity generation plant is and will be coal-consuming in the near future. Statistics has shown that it will reach 200 million tons in 2010, approximately occupying 1.33 million square meter land [4]. At present, the fly ash reuse ratios can reach 100% in Japan [5], however, a relative low ratio 41.7% is in China [6], so new ways should be explored to improve the reuse ratio.

The mean chemical components of fly ash are SiO_2 (50.6%), Al_2O_3 (27.1%), Fe_2O_3 (7.1%), CaO (2.8%), MgO (1.2%) in China [7]. At the same time, zeolite is mainly consists of SiO_2, so the fly ash reuse is available. Much research has been done for the improvement of the absorption capacity of fly ash, such as the chemical modification of it into zeolite-like crystalline materials [8–10] or other surface modification method [6,11].

Due to favorable pozzolanic properties, fly ash is a commercially valuable additive for the production of blended cements and concrete mixtures. Besides, another large quantity of fly ash is used for raw materials in chemical industry and soil amender in agriculture, respectively. With the in-depth knowledge of chemical and physical performance of fly ash, its application in wastewater treatment, e.g., dyeing wastewater, has acquired increasing attention.

Dyeing wastewater is mainly derived from the dye manufacturing and textile finishing. Generally, dyes can be grouped into three categories: anionic (direct, acid, and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes) [12]. Dyeing wastewater is hard to biodegrade due to the presence of heat and light stable dyes. The conventional methods used in sewage treatment, such as secondary wastewater treatment system does not work [13]. Comparing with traditional wastewater treatment methods, adsorption had been proved to be efficient in removal for the difficult biodegradation pollutants. Various inexpensive

* Corresponding author. Tel.: +86 531 86753159.
E-mail address: qyyue@sdu.edu.cn (Q.Y. Yue).

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doi:10.1016/j.jhazmat.2006.12.056

and readily available adsorbents have been used for the removal of dyes in the wastewater, such as natural clay [14,15], boiler bottom ash [16], wood chips [17], peat [18], and bagasse fly ash [19].

Raw fly ash often showed low efficiency in dyeing wastewater treatment with the same negative charge causing the repulsion action during the adsorption process. But the surface modification of fly ash was paid more attention to improve the specific surface area and surface roughness [20–23], and little information concerns the change of surface charges of fly ash. As a result, the improvement of the adsorption magnitude of fly ash should be focused on the change of surface charge for the reduction of the sludge produced during the process of dyeing wastewater treatment.

PDMDAAC is a widely-acceptable cationic poly-flocculent for its good performance such as high density of positive charge, better dissolubility, cost effectiveness, and non-toxicity [24,25]. In this article, PDMDAAC was employed as one modification agent for the increase of fly ash adsorption magnitude, expecting to improve the effects of fly ash on the dyeing wastewater treatment.

2. Materials and methods

2.1. Properties of raw fly ash

Fly ash was collected with the completion of a second order dust removal from a coal-consuming power plant in Shandong province, China, and the basic chemical ingredients of this fly ash was shown Table 1.

2.2. Modification agent and dyeing wastewater

The basic chemical properties of PDMDAAC were 40% solid content and 1.0 viscosity coefficient.

The dyeing wastewater with smalt and odor (pH 6.4) was obtained from a dyeing plant without biological treatment.

2.3. Modification of fly ash

A 50 g dried fly ash and 100 mL PDMDAAC were mixed in a 500 mL flask, and then the mixture was agitated using an electromagnetic stirrer. The whole process was designed with orthogonal method, and the corresponding influence factors were temperature (20, 30, 40 and 50 °C), time (1.0, 1.5, 2.0 and 2.5 h), PDMDAAC concentration (5, 10, 15 and 20 g/L) and pH (2, 6, 10 and 12).

The reaction product was filtrated using a vacuum couch, washed twice and then dried at 85 °C for 1 h. The dried product was ground and sieved using a 0.125 mm mesh sieve.

Table 1
Chemical ingredients of fly ash

Component	Content (%)
SiO_2	57.54
Al_2O_3	24.38
Fe_2O_3	7.12
CaO	6.00
MgO	1.60
SO_3	1.04
Others	1.32

2.4. Analysis of adsorption magnitude

A 0.5 g modified fly ash was burned at 400 °C for 2 h using a muffle (400 °C is enough for PDMDAAC entirely burned out, while the raw fly ash was stable), and then the adsorption magnitude a (mg/g) of the modified fly ash was determined using the weight reduction:

$$a = \frac{m_a - m_b}{m_a} \times 1000$$

where m_a is the weight of modified fly ash before burning (g); m_b is the weight of modified fly ash after burning (g).

2.5. Decoloring of dyeing wastewater

In a 250 mL flask, modified fly ash was put into 100 mL dyeing wastewater, agitated for 80 min [26] and then placed for 10 min. The decoloring ratios of the supernatants thus separated were detected at 320 nm with spectrophotometer (UV-754) using distilled water as blank.

2.6. Cement intension test

The experiment for the shaping of cement model was conducted with the ambient temperature of 20 ± 2 °C and relative humidity not less than 50%. The used modified fly ash, ground cement grog and gypsum were mixed with a ratio of 15:80:5. The rupture strength and compressive strength of the model thus produced were tested with both 3- and 28-day steam curing, respectively, at 20 ± 1 °C and relative humidity higher than 90% (Chinese Cement Standard).

3. Results and discussions

3.1. Adsorption performance of fly ash

The orthogonal test with four factors and four levels is designed to analyze the adsorption performance of PDMDAAC on fly ash (Table 2). And the $L_{16}(4^5)$ table was designed to detect the effects of different factors on the adsorption of PDMDAAC

Table 2
Factors and levels

No.	Temperature (°C)	Time (h)	PDMDAAC concentration (g/L)	pH
1	20	1	5	2
2	30	1.5	10	6
3	40	2	15	10
4	50	2.5	20	12

Table 3
Effects of different factors on the adsorption of PDMDAAC

No.	Temperature (A)	Adsorption time (B)	Concentration (C)	pH (D)	Adsorption magnitude (mg/g)
1	1	2	3	2	0.48
2	3	4	1	2	0.56
3	2	4	3	3	0.56
4	4	2	1	3	0.58
5	1	3	1	4	0.32
6	3	1	3	4	0.62
7	2	1	1	1	0.36
8	4	3	3	1	0.62
9	1	1	4	3	0.58
10	3	3	2	3	0.54
11	2	3	4	2	0.62
12	4	1	2	2	0.60
13	1	4	2	1	0.50
14	3	2	4	1	0.66
15	2	2	2	4	0.48
16	4	4	4	4	0.72
T_1	1.88	2.16	1.82	2.14	$\sum\eta = 8.8$
T_2	2.02	2.20	2.12	2.26	
T_3	2.38	2.10	2.28	2.26	
T_4	2.52	2.34	2.58	2.14	
Range (*R*)	0.64	0.24	0.76	0.12	–

Note: $R = T_{max} - T_{min}$, *T*: sum of each level.

(Table 3). Furthermore, the fly ash modification adsorption magnitudes reflecting the decoloring results were also listed.

It was found that the PDMDAAC concentration and temperature with 0.76 and 0.64 constant *R*, respectively, were the key factors affecting the PDMDAAC adsorption on fly ash (Table 3).

PDMDAAC is cationic surface-active agent which incorporates with negative charges existing on the surface of fly ash fast, and with the increasing of the PDMDAAC concentration, the interaction process is increasing relatively. The increasing temperature makes the Brownian motion of ions increasing corresponding to take the interaction process enhanced.

pH did not affect this reaction with range 2.0–12.0. As mentioned above, the cation–anion reaction is very fast, and the relative short time can assure the reaction complete absolutely, and the extra time will be not needed. These adsorption time and pH showed subordinate factors on this reaction, which can be proved from their low 0.24 and 0.12 constant *R*, respectively (Table 3).

3.1.1. Influence of PDMDAAC concentration

The adsorption isotherm of PDMDAAC on fly ash fits to the classical LS adsorption isotherm [27] (Fig. 1). The maximum adsorption magnitude of PDMDAAC on fly ash is 1.40 mg/g.

The adsorption isotherm can be divided into two stages. At the initial stage of adsorption, several PDMDAAC molecules were slowly adsorbed onto the fly ash surface through electrostatic attraction, so the adsorption curve ascends with slow slope in Fig. 1 from 5 to 25 g/L of PDMDAAC concentration. At the second stage with PDMDAAC concentration of 35 g/L, the dissolved PDMDAAC ions reacted with PDMDAAC adsorbed on the surface of fly ash through hydrophobic interaction because surface micelles were formed using the prior adsorbed PDMDAAC ions as the active center causing the quick increase of adsorption magnitude, so the adsorption magnitude increases sharply.

3.1.2. Influence of temperature

It was seen that the adsorption magnitude of PDMDAAC on fly ash increased with the temperature range of 20–70 °C (the PDMDAAC concentration is 20 g/L), and decreased from 70 °C (Fig. 2). This phenomenon occurred due to the interaction between the electrostatic attraction and Van der Waals force existing during the whole adsorption.

The increase of temperature can improve the molecule energy so that the PDMDAAC molecules can overcome the space resistance and enhance their diffusion rate in the solution, and

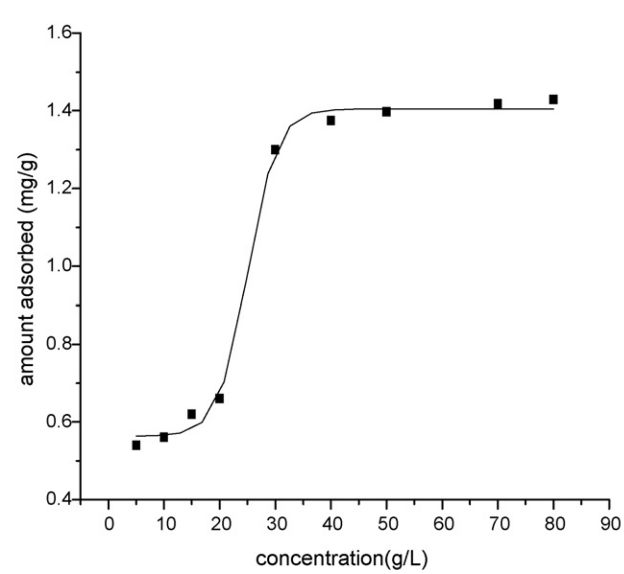

Fig. 1. Adsorption isotherm of PDMDAAC on FA.

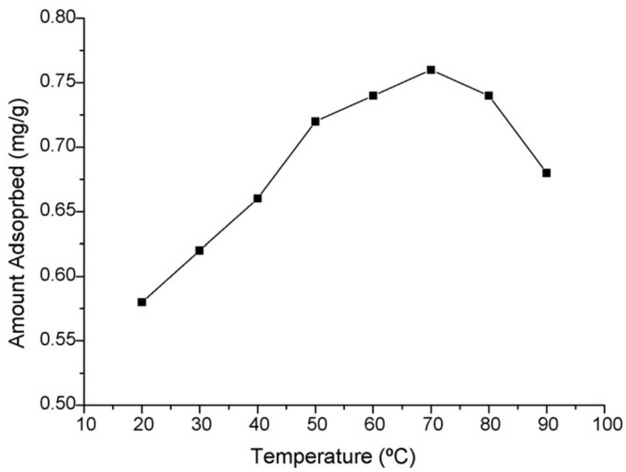

Fig. 2. Effect of temperature on PDMDAAC adsorption.

the adsorption magnitude increased. The maximum adsorption was established when the temperature reached 70 °C when the desorption rate is equal to the adsorption rate. After adsorption equilibrium above 70 °C, the desorption rate is faster than adsorption rate causing the decease of adsorption magnitude [28].

3.1.3. Zeta potential

The zeta potential was determined to explore the pollutant removal mechanism of modified fly ash in wastewater treatment.

The impact of temperature on surface charge of fly ash modified by PDMDAAC concentration of 40% was presented in Fig. 3. The positive charge on surface increased with temperature less than 70 °C, and decreased when the temperature was over 70 °C. This trend is similar with the effects of temperature on PDMDAAC adsorption (Fig. 2).

The zeta potential of modified fly ash ascended with the increase of the adsorbed PDMDAAC (Fig. 4). Moreover, the adsorption balance was established at an adsorption magnitude of 1.40 mg/g when the zeta potential achieved 20 mV, and at the same time, the surface positive charge also achieved balance.

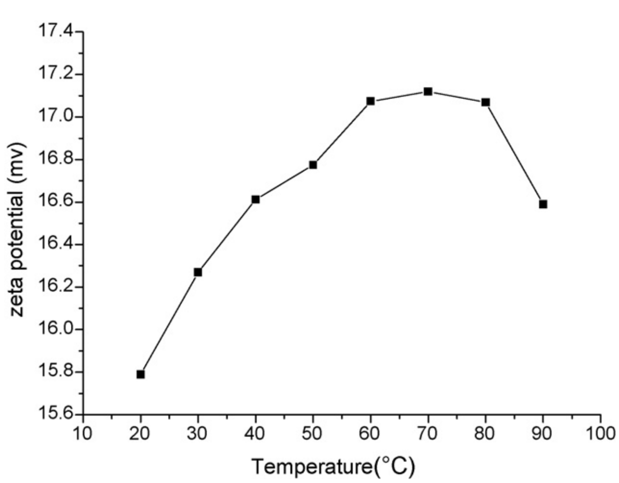

Fig. 3. Effects of temperature on surface charge.

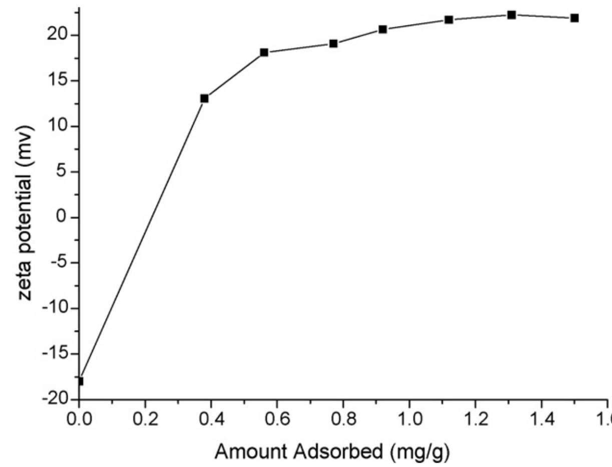

Fig. 4. Effects of adsorption capacity on surface charge.

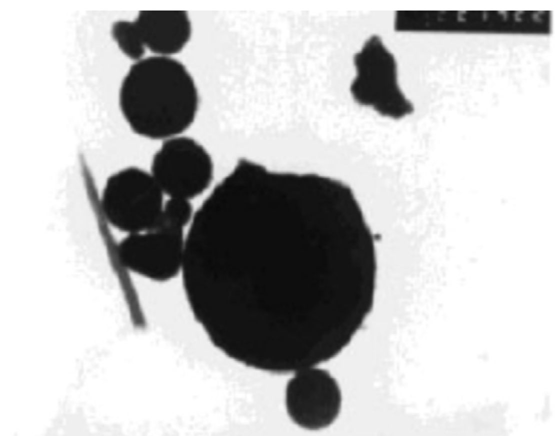

Fig. 5. TEM photo of raw FA.

3.2. The morphology of the modified fly ash

The surface of modified fly ash was more uneven in comparison with raw fly ash (Fig. 5) for the adsorption of PDMDAAC (Fig. 6). The adsorbed PDMDAAC changed the surface nature of fly ash and increased its positive surface charges, but a little more specific surface area was increased. Furthermore, some PDMDAAC molecules were absorbed into the holes of raw fly

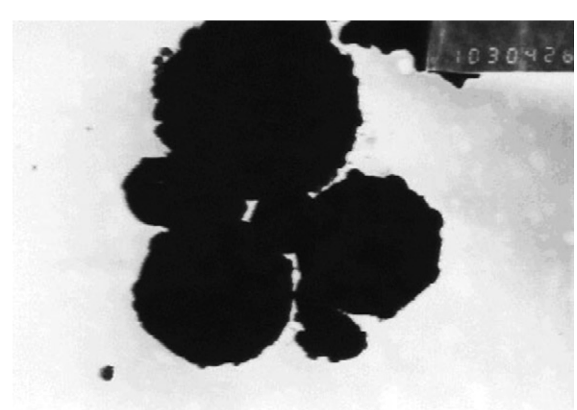

Fig. 6. TEM photo of modified FA.

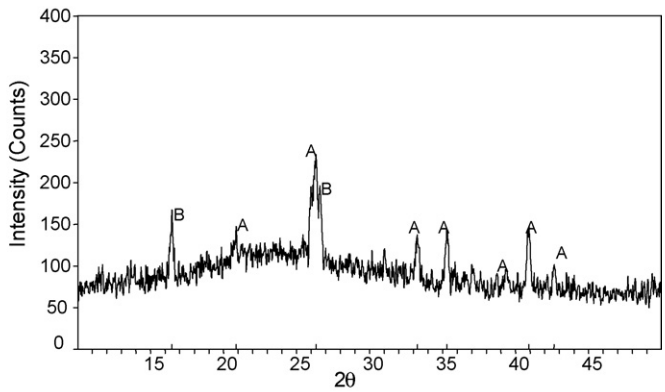

Fig. 7. XRD pattern of raw fly ash.

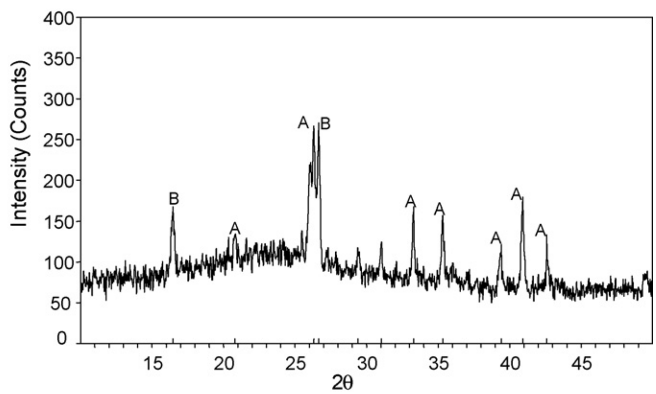

Fig. 8. XRD pattern of modified fly ash. A: quartz, B: mullite.

ash, which also increased the positive charges and consequently improved its adsorption to organic molecules and ion exchange capacity.

3.3. XRD patterns of raw fly ash and modified fly ash

It is seen that there is no significant difference for both XRD (Figs. 7 and 8) profiles suggesting no phase transformation occurred during the course of modification. The major phases for both are quartz and mullite. The results show that the modification by PDMDAAC will not induce phase changes.

4. Application of the modified fly ash

4.1. Dyeing wastewater treatment

The decoloring results of dyeing wastewater treated by modified fly ash (1.28 mg/g of PDMDAAC loading) and raw fly ash were shown in Figs. 9 and 10. With the modified fly ash dosage

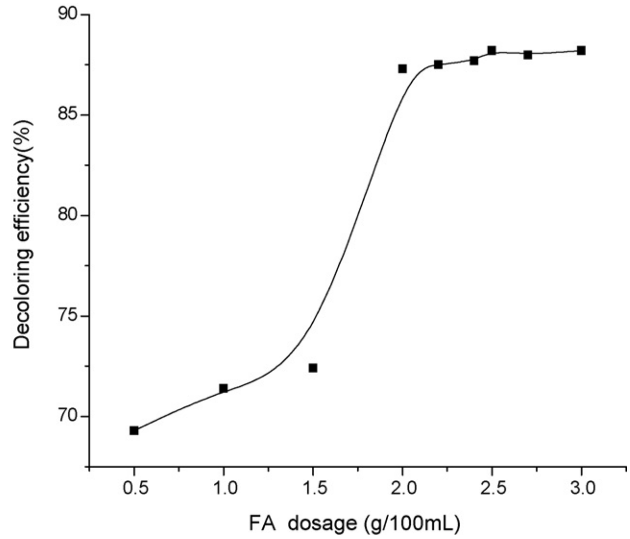

Fig. 9. Effect of modified FA dosage on decoloration.

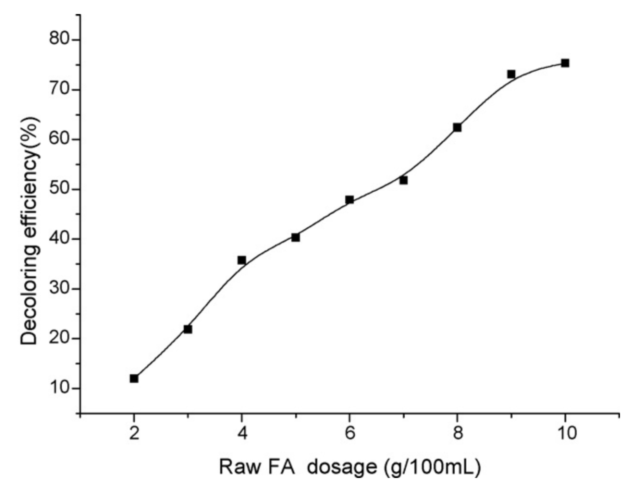

Fig. 10. Effect of raw FA dosage on decoloration.

increased, the color removal efficiency increased relatively, and when the dosage is 2.0 g/100 mL in dyeing wastewater, the maximum color removal efficiency was obtained as 88.2%. Comparing with raw fly ash, when its dosage is 2.0 g/100 mL, only 12.5% color removal efficiency could be reached, and even the dosage is 10 g/100 mL, the corresponding color removal efficiency was 76%.

4.2. Utilization of used modified fly ash

The cement performance (durability and workability) was improved with the blending of proper amount of used modified

Table 4
Cement strengths

Items	Rupture strength (MPa)		Compressive strength (MPa)	
Time (day)	3	28	3	28
Raw fly ash	3.8	6.5	18.3	39.9
Used modified fly ash	3.4	5.9	16.6	36.7
National criterion	2.5	5.5	11.0	32.5

fly ash, as the alkaline substance generated during the hydraulic reaction of cement can be a trigger for fly ash to form hydraulicity matter. The rupture strength and compressive strength of the cement with the blending of used modified fly ash were 3.4, 5.9 and 16.6, 36.7 MPa, respectively (Table 4), satisfying Chinese Cement standard [29,30]. However, with the decrease of chemical activity during the wastewater treatment, the cement strengths decreased.

5. Conclusions

This work focused on the ion modification in fly ash rather than rough specific surface area modification to improve the fly ash reuse in wastewater treatment.

Both raw fly ash and wastewater pollutants had negative charges, which caused low pollutants removal efficiency from wastewater. After modification by PDMDAAC, the fly ash surface charge was changed from negative to positive which is adverse to the negative charges of pollutants in wastewater, and the pollutants removal efficiency is improved greatly.

The surface of modified fly ash was covered by PDMDAAC, and the covering extent change with the adsorption magnitude so modified fly ash can treat dyeing wastewater more effectively due to the coordination effect between fly ash and the absorbed PDMDAAC. And the used modified fly ash can also be used as cement blending material, and its rupture strength and compressive strength at 3 and 28 days satisfied Chinese Cement Standard.

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