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Full Length Article

Fabrication and adsorption properties of hybrid fly ash composites

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ABSTRACT

In order to realize the utilization of fly ash (FA) as industrial solid waste better, high-efficient inorganic/organic hybrid composite adsorbents derived from ($Ca(OH)_2/Na_2FeO_4$) modified FA (MF) was fabricated. The hydrophilic cationic polymer (P(DMDAAC-co-AAM) or hydrophobic modifier (KH-570) were used. The prepared composites were characterized by X-ray fluorescence spectroscopy, energy dispersive spectroscopy, scanning electron microscopy, Brunauer-Emmett-Teller, Fourier transform infrared spectroscopy, thermogravimetry, and contact angle test. The adsorption of cationic composites MF/P(DMDAAC-co-AAM) towards Orange II in wastewater was investigated. The results show that: adsorption amount of 24.8 mg/g with 2000 mg/L of composites, 50 mg/L Orange II, original pH (6–8), at 40 min and room temperature, was obtained. Meanwhile, oil adsorption ratio Q(g/g) of hydrophobic composites MF/KH-570 was also evaluated. The maximum *Q* of 17.2 g/g to kerosene was obtained at 40 min. The isotherm and kinetics of these two adsorption processes were also studied. The results showed that the fabricated MF composites modified with hydrophilic or hydrophobic group can be used to adsorb dye in wastewater or oil effectively.

1. Introduction

As an industrial solid waste and most common silicate material, the principle components of fly ash (FA) consisted of silica, alumina, ferrous oxide, calcium oxide and various of carbon, so many active sites exhibit on its surface [1].

Reusing FA as adsorbents in removal of different kinds of pollutants in wastewater has aroused broad attention. For its hollow sphere and activated surface area, FA has been used to the removal of heavy metals, dyes from water, as a non-conventional suitable efficient sorbent [2]. But adsorption capacity of raw FA is limited for large closed holes. All kinds of traditional modified fly ash, such as acid/FA [3], alkali/FA [4] and mixed modified FA have been widely used to the adsorption of pollution from wastewater. However, these modifications cannot make it fully activated, which limit the application. Moreover, the disposal of alkaline or acidic wastewater presents an additional difficulty in practical application.

To improve the adsorption properties of FA and the resource utilization as solid waste, most of surface modification techniques have been investigated [5,6]. Yang etc. [7] has studied the surface modification of purified FA and its application in polymer, the result showed that the treated FA can be filled well in polymer as filler. Karakasi and Moutsatsou have discussed the sorption of three types of oil (heating oil, light cycle oil and Iranian light crude oil) on two high calcium FAs (HCFA). and the results showed that the addition of HCFA to an oil spill form a semi-solid oil-HCFA phase, allowing the quite total removal of oil from the water surface [8]. However, these single modifications by a monomer or polymer mainly focused on increasing the specific surface area and roughness to improve adsorption capacity.

Extensive use of the industrial material in various parts of the world always generate harmful pollutants, such as coloured effluents, which containing various dyes and pigments, large amounts of these dyes from textile industries often are very toxic even at a very low concentration when they are discharged to natural water bodies [9]. Azo dyes are important synthetic colorants that represent the largest class of dyes generally characterized by the presence of one or more azo bonds (—N=N—) [10].

In addition, one of the most visible and important source of marine pollutions is the oil pollution caused oil spills and chemical leakage. And approximately tens of thousands of tones of oil are spilled annually worldwide in the past [11]. Oil pollution is harmful to both environment and biology immediately and chronically.

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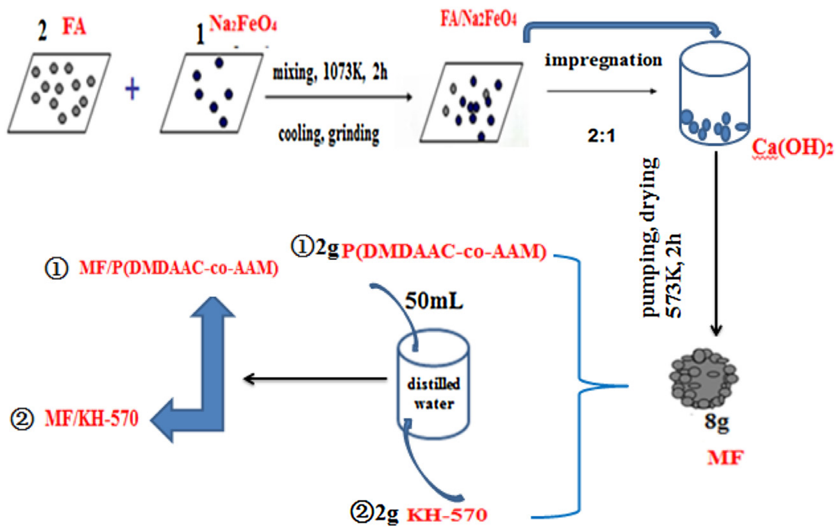

Scheme 1. Flow diagram of the composite adsorbents preparation.

Table 1
The chemical composition of all FA samples.

Samples	Weight(%)							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	TiO_2	SrO
FA	50.95	36.10	3.91	2.94	2.23	0.70	1.06	0.09
MF	29.61	22.10	11.53	33.17	1.45	0.00	0.94	0.07
MF/P(DMDAAC-co-AAM)	34.16	24.63	10.13	26.60	1.67	0.56	0.84	0.07
MF/KH-570	37.47	20.44	9.05	30.38	0.00	0.59	0.85	0.09

Many different treatment techniques such as biological treatment, coagulation, oxidation, and adsorption have been used in the removal of coloured dyes [12–14]. And some oil spill cleanup techniques have been developed, such as the use of booms and skimmers, the oil pumping [15], the use of chemical agents, such as sorbents [16]. However, it has been reported that adsorption is one of the effective methods with the advantages of high treatment efficiency and no harmful by-product to treated water including dyes and oil [17]. Nowadays, there are more and more lots of non-conventional, low cost adsorbents such as activated carbon [18], clay including bentonite and kaolinite [19,20] and so on, have been used for removal dyes and oil. However, these adsorption materials all have high costs and problems in regeneration [21]. And the adsorption capacity of these adsorbents is also limited.

In our previous paper [22], Na_2FeO_4 and $Ca(OH)_2$ mixed modified FA ($Na_2FeO_4/Ca(OH)_2$/FA, MF) was fabricated with better mechanical strength, higher porosity and higher efficient in dye removal. Here MF from FA was further modified by the hydrophilic cationic polymer, dimethyl diallyl ammonium chloride-co-acrylamide (P(DMDAAC-co-AAM)) or hydrophobic γ-methyl propenyl acyloxy propyl trimethoxy silane (KH-570), to construct two types of hybrid composites with hydrophily or hydrophobicity, respectively, which then were used as adsorbents for dye removal from wastewater or oil adsorption. The surface of MF can be regulated by hydrophilic/hydrophobic groups instead of single modification to active surface fully, which can make full use of FA and realize resource utilization. Moreover, the adsorption behaviors for Orange II (O-II) (removal efficiency, R%) in wastewater by MF/P(DMDAAC-co-AAM) composite and kerosene (oil adsorption ratio, Q(g/g)) by MF/KH-570 were studied. The effects of various experimental parameters such as pH, concentration, contact time, and adsorbent dosage on the adsorption properties were evaluated. The hydrophobicity of MF/KH-570 was studied by contact angle test. In addition, the adsorption thermodynamics and kinetics of the composites were also investigated. Here, the purpose is to construct high-efficient adsorbents by modified MF with hydrophilic or hydrophobic group, the modification of MF or FA with two different organic polymer or group has rarely been reported, and it would further expand the utilization of solid waste FA.

2. Experimental

2.1. Materials and regents

The raw FA, was collected from the electro-filters from a power plant in Shaanxi Province. Dimethyl diallyl ammonium chloride (DMDAAC, analytical grade, and acrylamide (AAM, analytical grade were, purchased from Shanghai Chemical Co., China. γ-methyl propenyl acyloxy propyl trimethoxy silane (KH-570) was provided by Chengdu Chenguang Silane Co., Ltd, China. Other reagents were analytical grade and used without any further purification. Distilled water was used throughout.

O-II as a typical anionic dye, was chosen as the substrate in the hydrophilic adsorption test. Benzene, methylbenzene, kerosene, abies oil, and olive oil were chosen as the substrates in oil adsorption experiment.

2.2. Synthesis of composite adsorbents

$FA/Ca(OH)_2/Na_2FeO_4$(MF) was prepared as the previous paper reported [22]. 4 g organic hydrophilic (P(DMDAAC-co-AAM) (DMDAAC:AAM = 1:1) or hydrophobic modifier (KH-570) was dispersed into 25 mL distilled water with stirring evenly using SZCL-3A stirrer, 1 g MF was then introduced into the suspension at 343 K for 2 h. After the sample cooling, separated, and the precipitate was washed with distilled water 2–3 times, then dried at 373 K for