



Research paper

Direct acid activation of kaolinite and its effects on the adsorption of methylene blue

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ABSTRACT

Coal-bearing kaolinite was directly treated with concentrated sulfuric acid to improve its surface properties and adsorption ability. Acid treatment was carried out at various temperatures (i.e., room temperature – 250 °C), by varying time of treatment from 0 to 120 min. The samples were characterized by X-ray diffraction analysis, elemental analyses, thermogravimetric analysis, N₂ adsorption-desorption analysis, high-resolution transmission electron microscopy, and Fourier transformed infrared spectroscopy. The activation of kaolinite strongly depended on the acid treatment including treatment temperature and time. Acid treatment at room temperature did not cause significant alterations either in the chemical composition or in the structure of the kaolinite. On the other hand, treatment at increased temperature led to the removal of Al³⁺ ions and thus increased the porosity of the material. The surface area and the pore volume of original kaolinite could be greatly changed as a function of treatment temperature and time of treatment, and they increased from 13.6 to 257.8 m² g⁻¹ and from 0.045 to 0.25 cm³ g⁻¹, respectively, when the kaolinite was treated at 200 °C for 30 min. The adsorption ability of acid-activated kaolinite (AAK) was investigated using methylene blue (MB) as a typical pollutant. For this, the effects of contact time, pH, initial MB concentration and temperature were studied in batch mode. Gibb's free energy (ΔG^0), entropy (ΔS^0) and enthalpy (ΔH^0) changes for MB adsorption were calculated. Owing to its high surface area, the AAK showed higher removal efficiency for MB than for original kaolinite, with a maximum adsorption capacity of 101.5 mg g⁻¹.

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1. Introduction

Kaolinite (Al₂Si₂O₅(OH)₄), being abundant in nature, is widely used in ceramics, paper, rubber, plastic, cosmetics, and catalysts (Bhattacharyya and Gupta, 2008; Cheng et al., 2012). It has also attracted much attention from an environmental perspective as a promising low cost adsorbent (Duarte-Silva et al., 2014; Koteja and Matusik, 2015; Unuabonah et al., 2013). However, it has been extensively demonstrated that the adsorption capacity of natural kaolinite is considerably lower than those of commonly used adsorbents (e.g., activated carbon), due to its inactive nature and low specific surface area (Vimonses et al., 2009; Yavuz and Saka, 2013). Therefore, improvements in the adsorption properties of kaolinite are necessary for it to be suitable for practical use. In last decades, various activation methods such as milling, heat treatments, mechanochemical activation, plasma treatment, and chemical treatments have been developed for improving the reactivity of kaolinite (Belver et al., 2002; Makó et al., 2006; Michot

et al., 2008; Temujin et al., 2001a, 2001b; Yavuz and Saka, 2013). The heat treatment at high temperature can lead to the complete destruction of crystal structure of kaolinite, but it does not significantly increase the surface area of resulting solid. The main advantage of plasma treatment is that it can effectively improve the surface properties of solid in a short time without damaging the bulk structure. Therefore, this method can be used to modify the material surface and is widely used for improving the reactivity of adsorbents. Especially, cold plasma techniques have recently attracted much attention owing to its high efficiency, simple operation, energy saving, and non-pollution (Yavuz and Saka, 2013; Sahin et al., 2015). Chemical treatments, which usually include acid and alkaline treatments, have been proven to be the most useful methods for activating kaolinite. Chemical activation of kaolinite under acid and alkaline conditions was systematically studied by Belver et al. (2002). According to their studies, alkaline treatment mainly lead to the formation of K – F zeolite and does not significantly change the Al₂O₃ content in kaolinite. For this reason, the alkaline-treated kaolinite usually showed a very low surface area. In contrast, acid treatments are reported to be favorable for activating kaolinite, which mainly cause the removal of Al³⁺ ions and thus alter the chemical composition of

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Table 1
Textural properties of RK and AAK.

Sample	A.C.S. ^a (nm)	S _{BET} ^b (m ² g ⁻¹)	V _s ^c (cm ³ g ⁻¹)	A.P.D. ^d (nm)
PK	33	13.6	0.045	54.2
AAK-RT-30	32	28.0	0.061	36.3
AAK-150-30	36	37.5	0.066	25.6
AAK-180-30	37	133.2	0.12	11.5
AAK-200-30	34	257.8	0.25	7.8
AAK-220-30	–	179.6	0.21	12.7
AAK-250-30	–	70.3	0.18	21.1
AAK-200-0	37	145.9	0.14	11.7
AAK-200-15	35	238.0	0.21	7.9
AAK-200-60	30	189.0	0.20	8.7
AAK-200-120	28	182.6	0.24	8.2

^a A.C.S.: average crystallite size;

^b S_{BET}: BET surface area;

^c V_s: specific pore volume at P/P₀ = 0.97;

^d A.P.D.: average pore diameter.

kaolinite, leading to the formation of a porous solid. Through such an acid activation process, the specific surface area and pore volume of kaolinite can be greatly increased, depending on the nature of acid and the treatment conditions. Owing to its high reactivity and large loading capacity, the resulting acid-activated kaolinite (AAK) is not only promising as an adsorbent or catalyst, but also is competitive in different industrial applications (Nascimento et al., 2011; Wang et al., 2010). In fact, as has been extensively demonstrated in the past, the adsorption capacity of kaolinite can be significantly improved after acid activation. For example, in the case of adsorption of heavy metals and dyes, acid activation enhanced adsorption capacity of kaolinite by ~9.8%, ~20.2%, ~8.0%, 16.7%, and 42.9%, for Cu(II), Cd(II), Pb(II), Ni(II), and methylene blue, respectively (Bhattacharyya and Gupta, 2008; Bhattacharyya and Gupta, 2011; El Mouzdahir et al., 2010).

However, it has been reported that the activation of natural kaolinite by acid treatment is difficult because of the inactive properties of this material; and, a heat treatment of kaolinite is considered to be necessary before acid treatments (Altiokka et al., 2010; Lenarda et al., 2007). Therefore, the calcination of kaolinite at temperatures between 600 and 800 °C is usually carried out prior to acid treatment. During the calcination process, kaolinite is transformed into metakaolinite (MK), accompanied with the loss of structural water and the destruction of the crystalline structure. MK, which has the chemical formula Al₂Si₂O₇, has been found to be more reactive to acid attack than parent kaolinite. For this reason, most of the studies concerned on acid activation of kaolinite reported up to now are limited to the activation of MK. It was reported that amorphized kaolinite obtained by grinding also has a high reactivity to acid and it becomes soluble in sulfuric acid (Makó et al., 2006; Temuujin et al., 2001a, 2001b). Despite the reports described above, a study on direct sulfuric acid treatments of natural kaolinite, with a detailed characterization of the obtained AAK, is rarely found in the literature.

In the present work, the behavior of kaolinite under direct concentrated sulfuric acid treatments and the removal ability of the resulting AAK for methylene blue (MB) were studied to explore a new possible route to the activation of kaolinite. For this, a coal-bearing kaolinite, which is found in abundance in the Inner Mongolia area of northern China, is used as target. This type of kaolinite is known to be low grade, since it contains impurities such as C, Fe, and organic compounds in high concentrations; and, most of it is currently discarded as waste. Therefore, another objective of this work is to probe the possibility of utilization of coal-bearing kaolinite for wastewater treatment. As mentioned earlier, traditional acid activation method include calcination and acid treatment processes; however, the present study showed that kaolinite can be effectively activated by a single process of sulfuric acid treatment. Moreover, up to now, no studies have been reported on

the direct activation of coal-bearing kaolinite using concentrated sulfuric acid. Therefore, this paper is the first study on such a research subject.

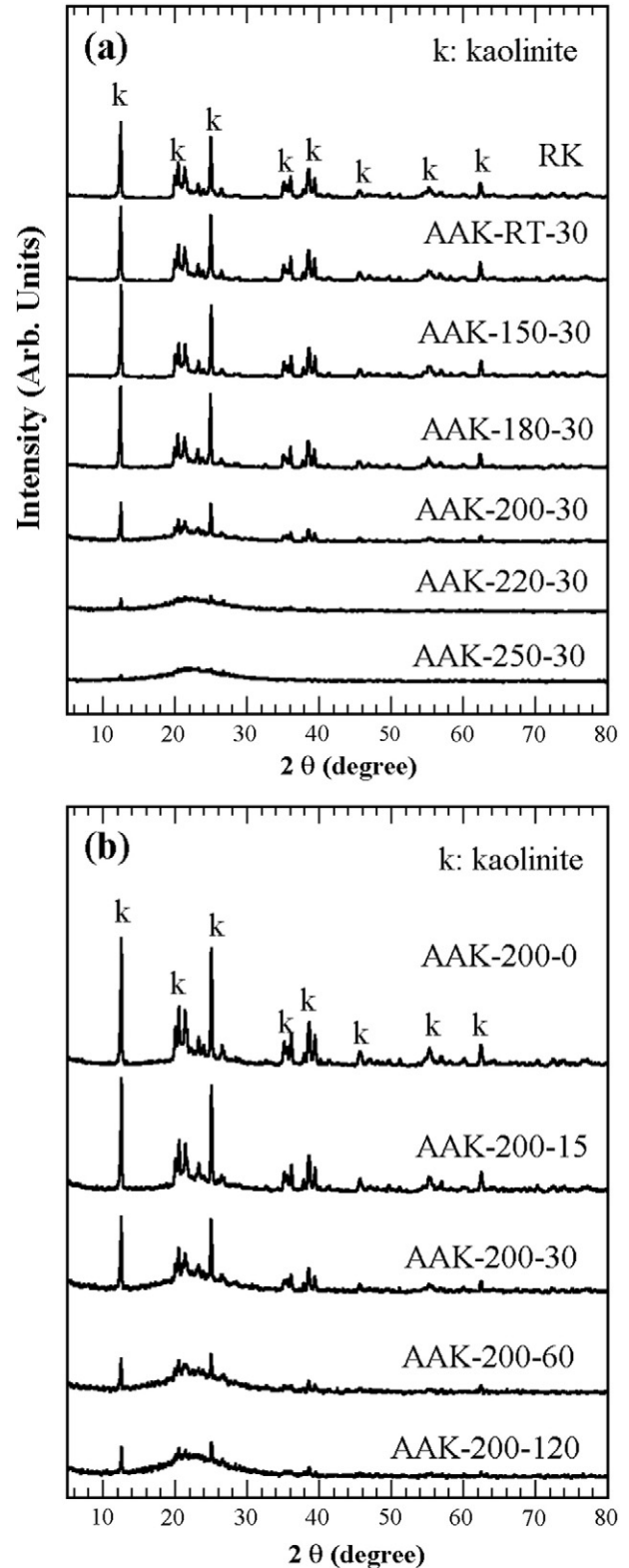


Fig. 1. XRD patterns of RK and samples prepared by acid treatment at different temperatures for 30 min (a) and of those prepared by acid treatment at 200 °C for different time (b).

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