



Tailoring the properties of palygorskite by various organic acids via a one-pot hydrothermal process: A comparative study for removal of toxic dyes



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ABSTRACT

Naturally abundant palygorskite (PAL) has been frequently used as an efficient, stable, low cost and environment-benign adsorbent to remove toxic pollutants for alleviating their harm to human health. However, the adsorption capacity of natural PAL is limited, which restricts its applications as an efficient adsorbent. As the aim to improve the adsorption capability of natural PAL and develop a high-efficient silicate adsorbent, the organic acids with different structures (i.e., acetic acid, glycolic acid, glycine, chloroacetic acid, benzoic acid, oxalic acid and citric acid) were employed to modify natural PAL via a simple one-step hydrothermal process. The effect of hydrothermal process in the presence of organic acids on the microscopic structure, physico-chemical features and adsorption properties of the PAL-derived adsorbent was studied comparatively using the dyes methylene blue (MB), methyl violet (MV) and malachite green (MG) as the model pollutants. It was found that the structural evolution of PAL and the introduction of functional groups positively contribute to improve the adsorption capacity. The PAL-derived adsorbents in the presence of chloroacetic acid (CAA-PAL) and citric acid (CA-PAL) show excellent adsorption capacity, which could almost completely remove the MB, MV and MG dyes from 200 mg/L of the solution, but the raw PAL can only remove 59% (for MB), 63% (for MV) and 88% (for MG). The intensified electrostatic attraction, hydrogen-bonding interaction and chemical association of $-\text{Si}-\text{O}^-$ groups with dyes, resulting from the hydrothermal evolution of PAL crystal, are primarily responsible for the enhancement of adsorption capacity.

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1. Introduction

Adsorption technique has been frequently used for the enrichment and removal of various pollutants owing to its simple, high-efficient, low-cost and flexible advantages in structure design of adsorbents (Kumar et al., 2013; Wang et al., 2013a; Kiransan et al., 2014; Barreca et al., 2014; Vakili et al., 2014; Kyzas et al., 2014; Zeng et al., 2015; Mthombeni et al., 2015). Generally, activated carbon (AC) is one of the most commonly used adsorbents for removing dyes or other pollutants (Saka et al., 2012; Islam et al., 2015). The larger surface area and multi-porous structure of AC make it easily attract various molecules or ions by the capillarity action of pores and the interface interaction between AC and adsorbates, but the contribution of physical adsorption to the adsorption capability is limited. Thus, the application of AC as an adsorbent was challenged by the development of many economic and efficient adsorbents due to the relatively higher cost and lower

adsorption capacity of AC. Hence, the design and development of low cost, high-efficient and eco-friendly adsorbents derived from earth-abundant natural resources, e.g., clay minerals become the subject of great interest (Zhou et al., 2013; Chakraborty and Nagarajan, 2015; Quali et al., 2015; Zhou et al., 2016). Much clay minerals such as kaolinite (Tabrez et al., 2012), sepiolite (Doğan et al., 2007), montmorillonite (Chen et al., 2014; Kiransan et al., 2014; Lu et al., 2014), montmorillonite-illite clay (Oztop et al., 2006), beidellites (Grundgeiger et al., 2015), halloysite (Matusik, 2014), vermiculite (Duman et al., 2015), and Akadama clay (Zhao et al., 2015) have received considerable attention as the materials of “greening 21st century material worlds” (Sinha Ray et al., 2005). By virtue of the excellent surface performance and eco-friendly advantages (Schoonheydt et al., 2011), clay minerals were recognized as one of the most promising adsorbent for the purification of wastewater.

Palygorskite (PAL, also called as attapulgite) is a natural Mg-rich silicate clay mineral with one-dimensional (1D) nanorod-like crystal morphology, rich pores and active surface groups (Bradley 1940; Drits et al., 1971; Galán, 1996). PAL is composed of 2:1 type ribbon-layer structure. The regular connection of the alternately arranged ribbon continuous Si_4O_{11}

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tetrahedron sheets and the discontinuous octahedral sheets through Si–O–Si bonds forms numerous channels with the size of 0.37 nm × 0.64 nm along the *c*-axis of rods (Bradley, 1940). The PAL rods are negatively charged due to the isomorphous substitution of trivalent cations for the divalent cations in the octahedral sheet (Galán and Carretero, 1999; Guggenheim et al., 2006; Chryssikos et al., 2009). So, PAL has greater specific surface area, better ion-exchange capacity and stronger surface polarity, and has been extensively used for the removal of dyes (Giustetto et al., 2011; Wang et al., 2015a; Zhang et al., 2015a), heavy metal ions (Zhou et al., 2015; Wang et al., 2015b) or other organic matters (Frini-Srasra et al., 2009; Li et al., 2011; Tian et al., 2015a). However, the adsorption capability of natural PAL is poor owing to the finite adsorption sites (i.e., active surface groups, pores, and surface charges). This was also confirmed by previous researches that the removal ratio of dyes by adsorption with raw PAL clay is only 44% and 59% (Zhang et al., 2015a). So, the modification of PAL by employing a simple but effective method is the only feasible way to enhance its adsorption properties and extend its application as a high-efficient adsorbent.

So far, many physical and chemical methods have been employed to modify PAL in order to improve its adsorption properties. The physical methods (Liu et al., 2012; Wang et al., 2015c) may enhance the adsorption capacity of PAL through dispersing the crystal bundles and uncovering more surface groups. The chemical methods e.g., acid treatment (Frini-Srasra et al., 2010), heat treatment (Su et al., 2012), organification modification (Zhang et al., 2010) and organic–inorganic hybrids (Kiransan et al., 2014; Barreca et al., 2014), may partially break the Si–O–M bonds to form more Si–O[−] groups on the surface of PAL (as the cavity sites for adsorption), alter the surface charges and improve the surface activity. It was also demonstrated that the breakage of inert Si–O–Si (or M) bonds as active Si–O[−] groups and the introduction of organic functional groups (i.e., –COOH) may form more cavity for holding adsorbates to enhance the adsorption properties.

Among numerous modification methods, hydrothermal process has been widely concerned as an effective method to modify the structure of PAL at the aim to enhance the adsorption properties of clay minerals (Sun et al., 2012; Wu et al., 2014; Zhang et al., 2015b; Zhang et al., 2015c). As is expected, the hydrothermal modification of PAL could evidently increase the adsorption capacity for heavy metal ions (Wang et al., 2015b; Wang and Wang, 2016) and dyes (Zhang et al., 2015b; Tian et al., 2015b) due to the corporate contribution of structure evolution and functional groups to adsorption capacity (Zhang et al., 2015c). Comparatively, the structure evolution fails to be achieved by the traditional modification methods. These researches suggest a new approach to design adsorbent derived from PAL clay by combining the organic molecules containing functional groups and the hydrothermal process. In this process, the type and structure of organic molecules may be key to affect the structure and properties of the as-prepared adsorbent; however,

there is little research concerns this effect despite these are worth to be intensively studied in both academic and industrial areas.

Hence, as a continuation of our systematic research work, several different organic acids (acetic acid, glycolic acid, glycine, chloroacetic acid, benzoic acid, oxalic acid and citric acid) were used as “donors” of functional groups to modify PAL through a one-step hydrothermal process. The effect of organic acids on the structure, physico-chemical features and adsorption properties of PAL was intensively studied by combining TEM, XRD, FTIR, TGA characterizations and batch adsorption experiments. The contribution of different kinds of organic acids to the adsorption properties was emphatically evaluated and compared using cationic dyes MB, MV and MG as the model pollutants. The detail research route was illustrated in Scheme 1.

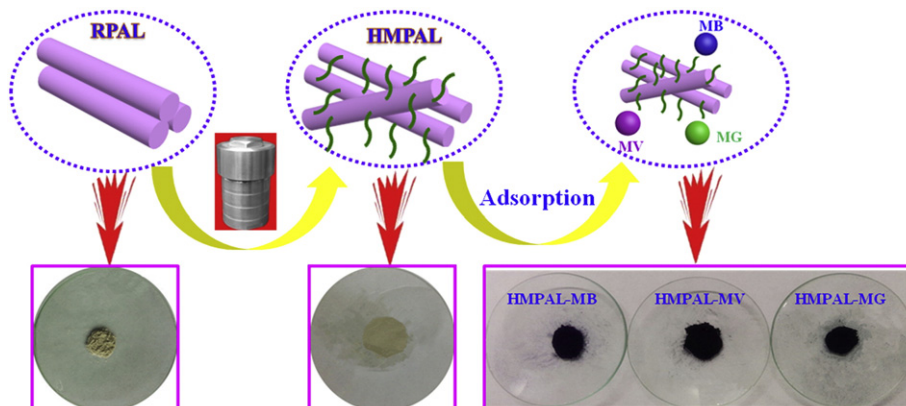
2. Experimental

2.1. Materials

Natural PAL was from Huangnishan Mine located at Xuyi County of Jiangsu Province in China and was provided by Huida Mineral Sci-Technology Co. Ltd. (Jiangsu, China). The chemical composition of the PAL clay (the raw material for the experiment) is SiO₂ 52.37%, Al₂O₃ 11.67%, MgO 6.92%, Fe₂O₃ 7.91%, CaO 1.91%, K₂O 1.49% and Na₂O 0.27%, as determined by a MiniPal 4 X-ray fluorescence spectrometer (PANalytical Co., Netherland). Acetic acid (C₂H₄O₂, AA), glycolic acid (C₂H₄O₃, GA), glycine (C₂H₅O₂N, GY), chloroacetic acid (C₂H₃O₂Cl, CAA), benzoic acid (C₇H₆O₂, BA), oxalic acid (C₂H₂O₄, OA) and citric acid (C₆H₈O₇, CA) are all of analytical grade, and are purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The structural formulas of these carboxylic acids are shown in Fig. 1. Methylene Blue (MB, C₁₆H₁₈N₃SCl, Indicator Grade), Malachite Green (MG, C₂₃H₂₅ClN₂, Indicator Grade) and Methyl Violet (MV, C₂₅H₃₀N₃Cl, Indicator grade) were purchased from Alfa Aesar A Johnson Matthey Company and used without further purification. All other reagents are of analytical grade and all solution is prepared with deionized water.

2.2. Hydrothermal modification of PAL with different organic acids

Natural PAL clay was pretreated using 5% of HCl solution for 4 h at the solid/liquid ratio of 1/10 to remove the carbonates. The resultant aqueous dispersion was passed through a 300-mesh sieve to remove the large grains of impurities like quartz and dolomite, and then the filtrate was centrifuged at 5000 r/min for 20 min to separate the solid from the dispersion. The solid product was fully washed with deionized water until the pH value of the supernate is about 7, and then was oven-dried at 105 °C for 4 h to a constant mass. Finally, the dried product was smashed and passed through a 200-mesh screen for further use.



Scheme 1. Schematic illustration for the hydrothermal modification of PAL and adsorption removal of dyes.

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