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Removal of methyl orange from aqueous solutions through adsorption by calcium aluminate hydrates

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Abstract

Methyl orange (MO) is a kind of anionic dye and widely used in industry. In this study, tricalcium aluminate hydrates (Ca-Al-LDHs) are used as an adsorbent to remove methyl orange (MO) from aqueous solutions. The resulting products were studied by X-ray diffraction (XRD), infrared spectroscopy (MIR), thermal analysis (TG-DTA) and scanning electron microscope (SEM). The XRD results indicated that the MO molecules were successfully intercalated into the tricalcium aluminate hydrates, with the basal spacing of Ca-Al-LDH expanding to 2.48 nm. The MIR spectrum for CaAl-MO-LDH shows obvious bands assigned to the N=N, N=H stretching vibrations and S=O, SO_3^- group respectively, which are considered as marks to assess MO^- ion intercalation into the interlayers of LDH. The overall morphology of CaAl-MO-LDH displayed a “honey-comb” like structure, with the adjacent layers expanded.

Keywords:

Methyl orange (MO), Tricalcium aluminate (C_3A), Hydrates, Intercalation, Adsorption

1. Introduction

Numerous textile or printing industries which mainly use dyes, release a large amount of highly colored effluents into the environment, probably containing more than 100,000 kinds of commercial dyes and over 7 million tons annually [1].The discharge of colored effluent even at very low concentrations can cause serious damage because these dyes prevent sunlight and oxygen penetration and then has a derogatory effect on photosynthetic activity in aquatic systems [2]. Moreover, some dyes degrade into compounds which have toxic, mutagenic or carcinogenic influences on living organisms [3]. In addition, dyes are stable to light, oxidation and biodegradable process because of their synthetic origin and complex chemical structure, which makes them exist for a very long time in the environment [4-6]. Therefore, it is imperative to improve a sustainable method for the removal of dyes from industrial effluents.

Various methods such as biological treatment, adsorption, chemical oxidation and coagulation have been used to remove dyes from colored wastewater [7, 8]. Among the methods, adsorption is considered as one of the most competitive methods because of its high adsorption properties, low cost, low energy requirements and simple operations [9].

Hydration of tricalcium aluminate (C_3A), which is an important component in cement, produces metastable compounds such as $4CaO{\cdot}Al_2O_3{\cdot}19H_2O(C_4AH_{19})$, $4CaO{\cdot}Al_2O_3{\cdot}13H_2O(C_4AH_{13})$ or $2CaO{\cdot}Al_2O_3{\cdot}8H_2O(C_2AH_8)$ [10], and they belong to the family of calcium aluminum layered double hydroxides (Ca-Al-LDHs). Their structures show $[Ca_2Al(OH)_6]^+$ main layers with OH^- anions and H_2O molecules in the interlayer region. Exchangeability of interlayer anions, good thermal stability and good mixed oxides homogeneity are important properties of LDHs [11, 12]. Recently, the removal of anion by C_3A through intercalation reaction has been reported in some references [13, 14]. However, there is little investigation on removal of dyes by C_3A.

In this study, the methyl orange (MO) as the representative of dye was chose and it was investigated that the adsorption behaviour of MO with C_3A by the X-ray diffraction (XRD), mid-infrared spectroscopy (MIR) and scanning electron microscope (SEM).

2. Experimental

2.1 Starting materials

Tricalcium aluminate（$3CaO{\cdot}Al_2O_3$，abbreviated as C_3A）, was synthesized through the solid state reaction. The mixture of $CaCO_3$ and $Al(OH)_3$ at a molar ratio of 3:2 was heated in quartz crucibles at 1350 ^{o}C (4h), followed by two intermediate grindings. Investigations by X-ray powder diffraction and a modified Franke test confirmed the resulting product to be pure tricalcium aluminate.

2.2. Synthesis of CaAl-MO-LDH by adsorption process

Based on the former bath experiments about OM adsorbed onto C_3A, the optimal synthesis process was chose as follow: 0.1 g was added to methyl orange aqueous solutions (20 mL) with concentrations of 0.2 M. The mixture was shaken at 150 rpm in a thermostatic bath shaker at 25 ^{o}C for 24 h. After stirring, the precipitate was aged at 60^{o}C for 24 h. Finally, the sample was washed with distilled water via filtration, and dried at 70^{o}C for 4-8 h. The resulting sample was named as CaAl-MO-LDH.

2.3. Characterization of materials

2.3.1. X-ray diffraction

The powder X-ray diffraction patterns for the solid sample were collected in a D/max RBX diffractometer with Cu Kα (40 kV, 100 mA) radiation at room temperature. CaAl-MO-LDH was scanned at a rate of 6 ^{o} min^{-1} in the range of 5–65 ^{o}.

2.3.2 Mid-infrared spectroscopy

Mid-infrared spectra were recorded using a Nicolet Nexus 370 Fourier transform infrared spectroscopy (FTIR) spectrometer with a smart endurance single bounce diamond ATR cell. Spectra were obtained from 4000 to 600 cm^{-1} by the co-addition of 64 scans with a resolution of 4 cm^{-1}. A mirror velocity of 0.6329 cm/s was used.

2.3.2 Thermal analysis

Thermal analysis (TG-DTA) was examined by NET-ZSCH Simultaneous TG-DTA/DSC Apparatus STA 449C/4/G Jupiter-QMS 403C Aeolos at a heating rate of 10 ^{o}C /min within 40-1000 ^{o}C in pure N_2 atmosphere. Samples of 10-15 mg were used in each measurement with sintered α-Al_2O_3 as the reference.

2.3.3 Scanning electron microscope

The morphology of samples was obtained using a scanning electron microscope (SEM), Hitachi S-4800. Samples were coated with a thin layer of evaporated gold, and the SEM images were obtained using a secondary electron detector. The electric tension was 30 kV, and the working distance was 7 mm.

3. Results and discussion

3.1 XRD analysis

X-ray diffraction patterns of the CaAl-MO-LDH, C_3A, as well as the hydrate of C_3A (C_4AH_{19}) which was chosen from related reference [15] are shown in Fig. 1. For the XRD pattern of CaAl-MO-LDH, new sets of basal diffraction reflections (002), (004), (006) are observed at 3.56 ^{o}, 7.26 ^{o}, 13.01 ^{o}, which display well multiple relationship, indicating well-formed crystalline double layered structures. Moreover, related to the C_4AH_{19}, these basal peaks of CaAl-MO-LDH shifted to low 2θ angle, with the interlayer distance (*d* value) expanding to 2.48 nm，which is obviously larger than that of C_4AH_{19} (1.25nm), it is strongly evidenced that MO^- was successfully intercalated to C_4AH_{19}. In general, the arrangement of intercalated anions can be concluded from the *d* value of the LDHs. It was reported that the dimension of the long axis of the MO molecule is 1.31 nm [16], and the thickness of one LDHs sheet is about 0.48 nm [17], so it is easily calculated that the basal spacing of monolayer model and bilayer model is 1.79 nm and 3.10 nm respectively. In fact, the *d*-value of CaAl-MO-LDH is between the values mentioned, so the MO molecules are intercalated into LDHs with an interpenetrating bilayer model. Meanwhile, several peaks of the byproduct katoite ($Ca_3Al_2(OH)_{12}$, abbreviated as C_3AH_6, marked with k) were displayed in the XRD pattern of CaAl-MO-LDH, it was demonstrated that part of the metastable compound C_4AH_{19} converted to cubic katoite phase C_3AH_6, which is the thermodynamically stable hydration product of C_3A, but it had little effect on the results. In addition, no peak of C_3A is observed in the reaction products, it is deduced that the reaction finished completely between C_3A and MO.

3.2 FT-IR spectra

The FT-IR spectra of C_3A and CaAl-MO-LDH are presented in Fig. 2. As to C_3A, the bands centered upon the 900-500 cm^{-1} spectral region are attributed to the calcium oxide (Ca-O) and aluminium oxide (Al-O) lattice vibrations, and almost no band is observed at other wavenumbers. Compared with C_3A, many new bands are discovered in the FT-IR spectra of CaAl-MO-LDH. The broad band around 3430 cm^{-1} represented the stretching vibration of -OH groups and interlayered water. Meanwhile, the bands of C-H antisymmetric stretches, C-H aromatic out-of-plane bending vibration and C-H aromatic in-plane bend are observed at 2921 cm^{-1}, 848 cm^{-1} and 1006 cm^{-1}, respectively, which were in positions similar to the published results [18, 19]. What’s more, the N=N stretching bands emerge at 1606 and 1436 cm^{-1}, the N=H bending vibration is observed at 1518 cm^{-1}, and the significant bands of S=O and $-SO^{3-}$ group are found at 1120 and 1035 cm^{-1}. It is necessary to point out that the bands related to the calcium oxide (Ca-O) and aluminium oxide (Al-O) lattice vibrations shift to lower wave numbers, which is in harmony with other reports referred to intercalated materials into the LDHs [20, 21], indicating that MO^- ion was successfully intercalated into the hydrate of C_3A.

3.3 Thermal analysis

The TG-DTA curves of C_3A and CaAl-MO-LDH are shown in Fig. 3. Compared with the curve of C_3A (Fig. 3 a), three major mass loss stages of 9.16% around 93 ^oC, 5.47% between 93^oC and 342^oC, and 51.23% after 342^oC are observed in the TG-DTA curve of CaAl-MO-LDH, which correspond to the loss of adsorbed and lattice water molecules, dehydroxylation of the layer and the decomposition of MO, respectively. In the DTA curve of CaAl-MO-LDH, the endothermic peaks at 85^oC and 108^oC are due to the dehydration of water, while the exothermic peak at 388^oC is caused by decomposition of MO [22, 23]. For CaAl-MO-LDH, the temperature of dehydration is lower than that of C_3A, which indicating the changes of structure, and this phenomenon could due to that MO molecules successfully intercalated into interlayer of C_4AH_{19}, so that the hydrophobic nature of interlayer surface was increased, and the interlayered water adsorbing power was reduced.

3.4 SEM

The SEM micrograph of C_3A and CaAl-MO-LDH were shown in Fig.4. Compared with C_3A, CaAl-MO-LDH showed obvious changes in morphology. It revealed that the morphology of CaAl-MO-LDH is retained similar as other LDHs [24] , with sharp particle edges and similar particle sizes. The overall morphology of CaAl-MO-LDH displays a “honey-comb” like structure, with the thickness about few hundred nanometers and the lateral dimension around 2μm(Fig. 4b). In contrast, the morphology of C_3A demonstrated a non-rule structure, and the edge was not as sharp as that of CaAl-MO-LDH.

Generally, high molecular weight organic anions, such as methyl orange anion, are able to intercalate to the interlayer of LDHs, and as a result the original guest anions were replaced. Based on the results discussed previously, a reaction process between C_3A and methyl orange is proposed and was shown in Fig. 5. During the hydration of C_3A, the layered phases C_4AH_{19} which belongs to the family of calcium aluminum layered double hydroxides (CaAl–LDHs) are initially formed as metastable compounds, and then the hydroxyl ions were replaced by the methyl orange anion and formed CaAl-MO-LDH .

4. Conclusions

The present study investigated the adsorption of MO from aqueous solutions by using an adsorbent of tricalcium aluminate. The interlayer distance (*d* value) of the resulting product expanded to 2.48 nm, and the arrangement of MO^- ion showed an interpenetrating bilayer model. Moreover, the bands assigned to the N=N, N=H stretching vibrations and S=O, SO^{3-} group were displayed in the MIR spectrum of the resulting sample, and a “honey-comb” like structure was displayed in the overall morphology. Combining the results measured from XRD, MIR, TG-DTA and SEM analysis，it was concluded that MO^- ion was successfully intercalated into the interlayer spacing of tricalcium aluminate hydrates and formed CaAl-MO-LDH.

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References

[1] Y. Huo, Z. Xie, X. Wang, H. Li, M. Hoang, R.A. Caruso, Dyes Pigm. 98 (2013) 106.

[2] T. Kou, Y. Wang, C. Zhang, J. Sun, Z. Zhang, Chem. Eng. J. (2013) 76.

[3] [3] Z. M. Ni, S.J. Xia, L.G. Wang, F.F. Xing, G.X. Pang, J. Colloid Interface Sci. 316 (2007) 284.

[4] V Murali Ong, Soon-An Ho, Li-Ngee, Bioresour. Technol. 143(2013) 104.

[5] A.A. Jalil, S. Triwahyono, S.H. Adam, N.D. Rahim, M.A.A. Aziz, N.H.H. Hairom, N.A.M. Razali, M.A.Z. Abidin, M.K.A. Mohamadiah, J. Hazard. Mater. 181 (2010) 755.

[6] J. Plank, D. Zhimin, H. Keller, F.v. Hössle, W. Seidl, Cem. Concr. Res. 40 (2010) 45.

[7] G. Crini. Bioresour. Technol. 97(2006) 1061.

[8] J. Wang, X. Ren, X. Feng, S. Liu, D. Sun, J. Colloid Interface Sci. 318 (2008) 337.

[9] I.M. Ahmed, M.S. Gasser, Appl. Clay. Sci. 259 (2012) 650.

[10] F.R. Costa, A. Leuteritz, U. Wagenknecht, M. Auf der Landwehr, D. Jehnichen, L. Haeussler, G. Heinrich, Appl. Clay. Sci. 44 (2009) 7.

[11] Y. Wong, H Cooper, K. Zhang, J. Colloid Interface Sci. 369 (2012) 453.

[12] P. Zhang, G.R. Qian, H.S. Shi, J. Colloid Interface Sci. 365 (2012) 110.

[13] Johann Plank, Z.M. Dai, Helena Keller, Friedrich v. Hössle, Wolfgang Seidl, Cement and Concrete Research 40 (2010) 45.

[14] P. Zhang, T.Q. Wang, G.R. Qian, Ray L. Frost, Spectrochim. Acta, Part A 125 (2014) 195.

[15] B. Yu, H. Bian, J. Plank, J. Phys. Chem. Solids 71 (2010) 468.

[16] J. Wang, X.M. Ren, X.S. Feng, J. Colloid Interface Sci. 318 (2008) 337.

[17] IM Ahmed, MS Gasser, Appl. Surf. Sci. 259 (2012) 650.

[18] L Gaini, M Lakraimi, E Sebbar, J. Hazard. Mater.161 (2009) 627.

[19] J. He, X.B. Yang, Mater. Chem. Phys. 77(2003) 270.

[20] FR Costa, A Leuterltz, U Wagenknecht, Appl. Clay. Sci. 38 (2008) 153.

[21] S Lonkar, B Kutlu, A Leuteritz, Appl. Clay Sci. 71 (2013) 8.

[22] D.M. Chen, J. Chen, X.L. Luan, H.P. Jing, Z.G. Xia, Chem. Eng. J. 171 (2011) 1150.

[23] B.Yu, H. Bian, J. Physics. Chem. Solids 11 (2009) 4.

[24] FR Costa, M Goad Abdel, U Wagenknecht, Appl. Clay Sci. 44 (2009) 7.