Journal of Hazardous Materials 321 (2017) 111–120

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Layered double hydroxide intercalated with aromatic acid anions for the efficient capture of aniline from aqueous solution

Shujun Yu[a,b], Xiangxue Wang[a,b], Zhongshan Chen[a], Jian Wang[a], Suhua Wang[a], Tasawar Hayat[c,d], Xiangke Wang[a,c,e,*]

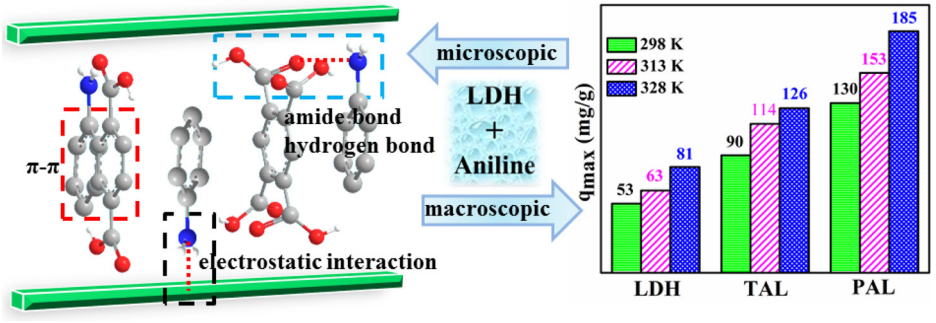
[a] School of Chemistry and Environment, North China Electric Power University, Beijing, 102206, PR China
[b] Key Lab of New Thin Film Solar Cells, Institute of Plasma Physics, Chinese Academy of Sciences, P.O. Box 1126, Hefei, 230031, Anhui, PR China
[c] NAAM Research Group, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia
[d] Department of Mathematics, Quaid–I–Azam University, Islamabad 44000, Pakistan
[e] Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, PR China

HIGHLIGHTS

- TAL and PAL are prepared via one-step hydrothermal method.
- TAL and PAL present high removal capacity for aniline from aqueous solutions.
- The interaction mechanisms are hydrogen bond and electrostatic interaction.

GRAPHICAL ABSTRACT

Higher affinity of aniline for PAL and TAL than LDH



ARTICLE INFO

Article history:
Received 4 June 2016
Received in revised form 19 August 2016
Accepted 4 September 2016
Available online 5 September 2016

Keywords:
Layered double hydroxides
Terephthalic acid
Pyromellitic acid
Aniline
Interaction mechanism

ABSTRACT

Aniline is toxic and hard to be degraded, and thereby causes the environmental pollution seriously. Herein, a practical and green hydrothermal method was applied to fabricate terephthalic acid and pyromellitic acid intercalated layered double hydroxides (LDH) (named as TAL and PAL) for aniline efficient removal. The sorption of aniline on LDH-based materials were investigated at different experimental conditions, and the results indicated that aniline sorption on LDH, TAL and PAL were strongly dependent on pH and independent of ionic strength. The maximum sorption capacities of aniline on TAL and PAL at pH 5.0 and 293 K were 90.4 and 130.0 mg/g, respectively, which were significantly higher than that of aniline on LDH (52.6 mg/g). Based on the BET, FTIR and XPS analysis, the higher sorption capacities of TAL and PAL were mainly due to high surface area and basal spacing as well as the abundant functional groups (e.g. $-COO^-$). The interactions of aniline with TAL and PAL were mainly dominated by hydrogen bonds and electrostatic interactions. Such a facile synthesis method, efficient removal performance and superior reusability indicated that the aromatic acid modified LDH materials had potential application for efficient treatment of organic pollutants in environmental pollution cleanup.

1. Introduction

Aniline, a kind of important organic chemicals, is widely found in effluents from dyestuff, pesticide, pharmaceutical, petrochemical

* Corresponding author at: School of Chemistry and Environment, North China Electric Power University, Beijing, 102206, PR China.
E-mail addresses: xkwang@ncepu.edu.cn, xkwang@ipp.ac.cn (X. Wang).

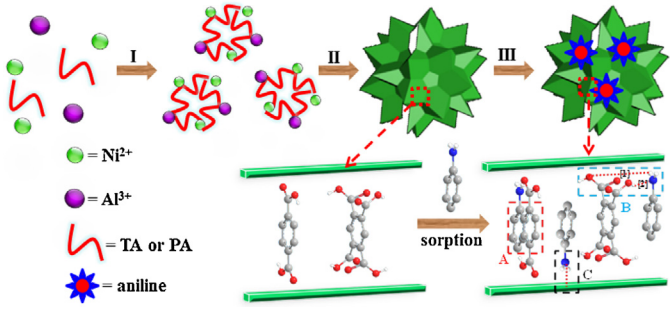
http://dx.doi.org/10.1016/j.jhazmat.2016.09.009
0304-3894/

and agrochemical industries, and more than 150 kinds of downstream products of aniline have been produced [1]. The amounts of aniline produced in US and China are over 457,000 and 80,000 t per year, respectively [2]. Aniline-containing wastewater has created serious environmental problems due to its high toxicity and environmental accumulation [3]. Considering its hazardous effects on human and wildlife, the maximum allowable limitation of aniline in natural water is very stringent in China (i.e., the effluent standard concentration is 1.0 mg/L in Chinese National Standard GB 8978-1996) and US (i.e., the water limitation is 0.262 mg/L in United States Environmental Protection Agency), and thereby the efficient removal of aniline has attracted growing attention [4,5].

Various methods including oxidation, sorption, biodegradation and photocatalysis have been used to eliminate aniline from the aqueous solutions [6–10]. Specifically, sorption is the most widely used technique to remove the organic pollutants from the polluted wastewater because of its simple operation, high efficiency, non-generation of harmful byproducts [11]. In the past few decades, carbon-based nanomaterials were widely developed to removal pollutants from wastewater [12–15]. However, the relatively expensive cost of carbon-based nanomaterials has obviously restricted their practical applications.

Layered double hydroxides (LDHs), with unique structural properties such as intercalation, topological transformation, and self-assembly with other functional materials and the formula of $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}]^{x-}\cdot mH_2O$ (where M^{II} and M^{III} are di- and trivalent metal cations, respectively, A^{n-} is the interlayer anion (or gallery anion), x is the molar ratio of $M^{III}/(M^{II}+M^{III})$, and m is the molar amount of co-intercalated water), have attracted increasing interest in environmental pollution cleanup [16,17]. Taking the advantage of the structural merits of LDHs, the active center structure (e.g., crystal facets, defects and electronic states) can be facilely manipulated for specific sorption processes with largely enhanced performances, and thereby have been widely applied as adsorbents for various inorganic pollutants (e.g., phosphate, arsenate, chromium and selenite) and organic pollutants (e.g., reactive red, methylene blue, methyl orange and congo red) [16,18–21]. Yan's group [18–20] successfully synthesized many kinds of LDH-based materials and used them for the removal of environmental pollutants. Recently, our group [17,22] prepared some novel LDH-based materials (e.g. LDH/graphene oxide and magnetic polydopamine-LDH) and applied them for the preconcentration of heavy metal ions and anionic dyes. However, few articles have addressed the study of LDH-based materials for amines-containing wastewater treatment, which can broaden the applicability of LDH for the cleanup of toxic pollutants in the environment.

Amines are widely used chemicals with considerable industrial/agronomic importance and environmental impacts, and many researches have demonstrated that hydrophobic interaction, π-π interactions and hydrogen bonds are the dominant interaction mechanisms [23,24]. Wang et al. [25] indicated that π-π and hydrophobic interactions between the benzene rings in aromatic compounds (phenanthrene, naphthalene and 1-naphthol) and multiwalled carbon nanotubes were the main dominated mechanism. An et al. [2] reported that the carboxyl groups of poly(methacrylic acid)/SiO_2 could form hydrogen bonds (O—H···N or N—H···O hydrogen bonds) with N atoms of aniline which acted as the acceptors. Wu et al. [26] observed that amide bonds (i.e., –CONH–) were formed between amino groups of anilines and carboxyl groups of multiwalled carbon nanotubes by amidation reactions. Such strategies should point to utilize benzene rings and carboxyl groups for efficient removal of aniline. Thus, a strategy of fabricating aromatic acid anions intercalated LDHs by utilizing layered anionic exchange ability of LDHs for the application of amines-containing wastewater treatment would be of significance.



Scheme 1. Schematic illustration of the approach used for the preparation of the materials (I: formation of Ni^{2+}/Al^{3+}-TA/PA complex; II: hydrothermal treatment; III: interaction with aniline) and the proposed mechanisms of aniline onto LDH, TAL and PAL (Color code by atom: gray carbon, red oxygen, blue nitrogen, white hydrogen. The three interactions are (A) π-π interaction, (B) hydrogen bond (Ref. [1]: N—H···O bond; Ref. [2]: O—H···N bond) and (C) electrostatic interaction). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Herein we presented that terephthalic acid (TA) and pyromellitic acid (PA) intercalated Ni-Al LDHs (named as TAL and PAL) were good aniline removal materials consistent with the hypothesis that hydrophobic interaction, π-π interactions and hydrogen bonds could efficiently remove amines. We expected the combination of aromatic acid anions with the LDH layers to be a powerful advantage producing material capable of possessing amine binding sites, to be used for efficiently aniline capture. This results indicated that aromatic acid anions intercalated LDHs could remove amines efficiently from wastewater in organic pollution cleanup.

2. Experimental

2.1. Materials

All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., China and used as received without further purification. The Ni-Al LDHs were synthesized according to previous articles [27]. Aromatic acid anions intercalated Ni-Al LDHs were synthesized by a simple hydrothermal method [27–30]. The protocol for the synthesis of the LDHs was illustrated in Scheme 1. In a typical procedure, TA (0.5 mM) or PA (0.5 mM), $Ni(NO_3)_2{\cdot}6H_2O$ (1.5 mM), $Al(NO_3)_3{\cdot}9H_2O$ (0.5 mM) and $CO(NH_2)_2$ (5 mM) were dissolved in 35 mL of distilled water and stirred to form a clear solution. The pH of the resulting solution was adjusted to 10.0 by adding 2 M NaOH. After stirring for 1 h, the aqueous solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave, which was sealed and maintained at 110 °C for 12 h, and then allowed to cool to room temperature naturally. The obtained precipitate was centrifuged (at 895*g* for 10 min) and rinsed with ultrapure water several times. The final products were dried at 40 °C overnight using a vacuum-drying method. The dried materials were ground using a mortar and pestle into fine powder.

2.2. Characterization

The morphology of the materials was observed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and transmission electron microscopy (TEM, JEM-1011, Japan). The elemental chemical states were measured by X-ray photoelectron spectroscopy (XPS), Fourier-transformed infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The XPS spectrum was recorded using an AXIS ULTRA DLD spectrometer with monochromatized Al Kα source operated at 200 W. FTIR spectrum was performed by a Bruker Tensor spectrophotometer in the range of 4000–400 cm^{-1}. The XRD pattern was recorded on a MAC Science Co. M18XHF diffractometer