Journal of Hazardous Materials 275 (2014) 63–71

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Application of cetyltrimethylammonium bromide bentonite–titanium dioxide photocatalysis technology for pretreatment of aging leachate

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HIGHLIGHTS

- An innovative approach of combining organobentonite and TiO_2 was applied to pretreat aging leachate.
- Composite organobentonite was characterized by FESEM/EDS and FTIRS.
- Removing of COD and NH_3-N relied on both adsorption and photocatalysis.
- Removal efficiency of simultaneous utilizing CTMAB2.5 and TiO_2 was better than them in succession.
- The technology showed superior removal rates of COD and NH_3-N, up to 89% and 61%, respectively.

ARTICLE INFO

Article history:
Received 21 October 2013
Received in revised form 18 March 2014
Accepted 22 April 2014
Available online 29 April 2014

Keywords:
Leachate
Organobentonite
Adsorption
TiO_2
Photocatalysis

ABSTRACT

Organobentonite–photocatalysis technology was applied to pretreat aging leachate containing refractory pollutants. The organobentonite was synthesized by organic modifier cetyltrimethylammonium bromide (CTMAB) and natural bentonite. In characterization experiments, we could confirm that organic functional groups of cetyltrimethylammonium ($CTMA^+$) cations were successfully loaded on the surface of bentonite. The combination of CTMAB2.5 adsorption and TiO_2 photocatalysis was superior to either running separately. Furthermore, removal efficiency of simultaneously utilizing CTMAB2.5 and TiO_2 was better than them in succession. The combination technology was feasible and was optimized by response surface methodology (RSM) with COD and NH_3-N removal rate as the target responses. The optimal operation conditions calculated from the regression equations were CTMAB2.5 dosage of 7.5 g/L, pH at 3.5, TiO_2 dosage of 1.63 g/L, and reaction time for 60.02 min, which maintained the removal of COD and NH_3-N at 82% and 37%, respectively.

1. Introduction

While sanitary landfill is regarded as an economical and environmental method to deal with solid wastes, the leachate containing many toxic contaminates from the landfills has great threat to groundwater and surrounding soil [1]. The leachate mainly derives from percolating rainwater, containing water of the wastes piles and the degradation of organic fraction [2]. Thus, characteristics of leachate predominantly depend on ingredients of solid garbage and the biological and chemical reaction processing in the landfill as well as the climate, hydrogeology, ages and landfill size [3–5]. In addition, the leachate has complex ingredients with high concentrations of organic compounds and ammonia, at the top strengths of 5000–20,000 mg/L and 3000–5000 mg/L, respectively [3,4]. If the leachate is not treated appropriately and discharged directly into groundwater, it will cause serious consequences such as hypoxia, eutrophication and deterioration of the water [2–4].

In recent years, biological techniques, with advantages of reliability, simplicity and low cost, can show reasonable performance when treating young leachate (landfill age <5 years). However, when treating aging leachate (landfill age ≥5 years), physico-chemical treatments can effectively remove refractory substances while biological techniques are not able to do this [6]. Furthermore, physico-chemical treatments are regarded as refining step after biological techniques due to stable quality of discharged water [7]. Additionally, advanced oxidation processes have been researched and applied widely during recent decades because of the ability

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http://dx.doi.org/10.1016/j.jhazmat.2014.04.050

of decomposing recalcitrant compounds in leachate [2,7]. Because of complex composition and characteristic of the leachate, individual treatment cannot meet environmental requirement and the combination of two or three treatments is more and more applied [8–11].

Adsorption as a kind of physico-chemical treatments is utilized widely. And the bentonite with special features can be regarded as adsorbent. Bentonite is mainly composed of montmorillonite whose structure is one aluminum oxide octahedral sheet in the center of two silicon–oxygen tetrahedral sheets [12]. The isomorphous substitutions of Al^{3+} for Si^{4+} in the tetrahedral sheet and Mg^{2+} or Zn^{2+} for Al^{3+} in the octahedral sheet can cause net negative charges on the surfaces [13]. Unbalance charges are offset by exchanged cations adsorbed on layer surfaces. However, those exchanged cations easily hydrate to form a thin water film. Adsorption of nonionic organic matters from effluent to bentonite is relatively weak due to preferential attraction of polar water molecules to polar mineral surface [14,15]. Moreover, low organic carbon content of bentonite limits nonionic organic compounds sorption by partition into bentonite [14].

Organobentonite is synthesized by natural bentonite and organic modifier. Organic cations are intercalated into the lattice structure of bentonite [16]. In comparison with bentonite, organobentonites have more surface active sited available for adsorption due to the surfaces of transition from hydrophilic to hydrophobic and sorptive phase formed [17–20]. The sorption of organobentonite is mainly influenced by the configuration and loading of organic modifier [12,18–20]. Zhu et al. [12] demonstrated that organobentonites with long alkyl chains of cation surfactants possessed higher removal relative to those with short alkyl chains. Ling et al. [20] treated leachate after pretreatment by struvite with organobentonite modified by di-octadecyl dimethyl ammonium chloride and COD removal was 90%.

Photocatalysis may be termed as photoinduced reaction accelerated by the presence of catalyst [21]. After semiconductor oxides are exposed in photon irradiation, charge separations are formed because of electrons from valence band promoting to conduction band [21–23]. Hence, holes are generated in valence band and electron–hole pairs are produced. Photocatalytic reaction mainly depends on the oxidation of holes. The holes can directly oxidize organic matters, or indirectly oxidize OH^- and H_2O on the surface of catalysts to form hydroxyl radicals ($OH^\bullet$). $OH^\bullet$ can powerfully oxidize organic matters [21–24]. TiO_2, a wide band-gap (3.2 eV) semiconductor, corresponds to radiation in the near-UV range [21,24]. Compared to immobilized TiO_2, suspended TiO_2 can obtain better efficiency because TiO_2 in the state of suspension can freely contact with UV irradiation [25]. Meeroff et al. [25] and Poblete et al. [22] treated the leachate with TiO_2 photocatalysis and the optimal COD removal were up to 71% and 57%, respectively.

Obviously, the leachate treatment by organobentonite adsorption alone and TiO_2 photocatalysis alone was researched but the performance was not superior to combination efficiency. Kurniawan et al. [8] verified that analogous combination of GAC adsorption and ozone oxidation had higher removal efficiency of 86% COD and 92% NH_3-N compared to ozonation alone with 35% COD and 50% NH_3-N.

The main objectives of this paper were two aspects. First, we needed to develop a kind of organobentonite with greater adsorption than natural bentonite. The second goal was to investigate the possibility of pretreating aging leachate with combining organobentonite and photocatalysis and to find optimal operation by response surface methodology. Currently, there is relatively little published information on dealing with aging leachate by organobentonite–photocatalysis technology.

Table 1
Properties of raw leachate.

Constituent	Range	Average	Units
COD	6400–7800	7000	mg/L
BOD_5	685–810	750	mg/L
Ammonia	1660–1770	1700	mg/L
SS	79–94	87	mg/L
Color	300–400	350	PCU
pH	7.8–8.3	8.1	

2. Materials and methods

2.1. Materials

Natural bentonite was chemical grade and from Sihaowei Chemical Co., Ltd., Shanghai. TiO_2 and CTMAB were analytical grade and supplied by Damao Chemical Reagent Factory, Tianjin.

The used leachate was taken from Heimifeng Landfill located in Changsha, China. This plant covers about 174 ha surface, which has been in operation since 2003, and treats more than 3000 tons solid waste daily. The properties of leachate were shown in Table 1.

2.2. Preparation of CTMAB-bentonite

In this study, CTMAB was chosen as organic modifier. $CTMA^+$ can create an organic partition medium through the conglomeration of their flexible and long alkyl chains [12,15].

CTMAB-bentonite was prepared as follows. First, 20 ml HCl and 30 ml H_2SO_4 were added into 750 ml distilled water. Then 100 g natural bentonite was added into the mixture liquor. Thirdly, mixture solution was stirred by magnetic stirrer (ZNCL-S) at the speed of 700 r/min for 3 h at room temperature. Fourthly, 0.6 g polyaluminium chloride (PAC), 0.05 g polyacrylamide (PAM), which were conductive to agglomerate and conglutinate organic modifier and bentonite, and a little CTMAB were added into suspension obtained from the third step. The solution was stirred by magnetic stirrer at the speed of 700 r/min for 5 h at 60 °C. After that, the solution was filtered by stainless steel pressure filter (SHXB-Z-2L). The precipitate was washed until that no silver bromide in the filtrate was generated detected by $AgNO_3$. The precipitate was put in the oven (101A-2) to dry for 4 h at 90 °C and activate for 1 h at 110 °C. Eventually, dried material was grinded into fine power and CTMAB-bentonite was obtained. Optimal additive CTMAB dosage was determined by actual experiments operated under the same condition of 60 min reaction time, 1.5 g/L CTMAB-bentonite dosage and without pH adjustment.

2.3. Characterization of organobentonite

Organobentonite was characterized by Environmental scanning electron microscope (ESEM)/Energy dispersive spectrometer (EDS) (Quanta 200 FEG, FEI, US) and Fourier transform-infrared spectrometer (FTIRS) (FTIR-8400S, IRprestige-21). ESEM was in low vacuum mode at an acceleration potential of 20 kV. Moreover, microanalysis of CTMAB2.5 was carried out with EDS equipped on the Quanta 200. The samples were blended with dry KBr in the agate mortar and were finely powdered to press the KBr pellets. The FTIR spectra in the range of 4000–400 cm^{-1} were reduced at an optical resolution of 2 cm^{-1}.

BET surface area and organic carbon content were measured by specific surface area and pore volume adsorption analyzer (OMNISORP100CX, Coulter, USA) and total organic carbon analyzer (TOC-V CPH, Shimadzu). Particle size and zeta potential was determined by Zetasizer (Nano-ZS90, Malvern, England).