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Advanced treatment of stabilized landfill leachate after biochemical process with hydrocalumite chloride (Ca/Al–Cl LDH)

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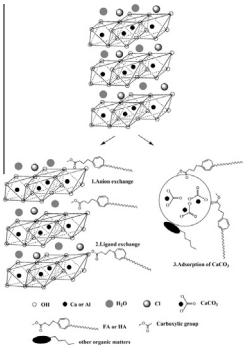
HIGHLIGHTS

- Ca/Al–Cl LDH can efficiently remove the organic matters in stabilized landfill leachate.
- The formation of Ca/Al–LDH have a greater beneficial to remove organics than the other reagents.
- The removal of fulvic acid-like compounds by Ca/Al–LDH was much better than humic acid-like ones.
- Ca/Al–LDH had a selectivity for the removal of compounds with more carboxylic groups.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the effectiveness of Ca/Al–Cl LDH for the treatment of stabilized landfill leachate. Experiments were performed including different dosage of Ca/Al–Cl LDH and comparison with different reagents, such as $CaCl_2$ and $AlCl_3$. As a result, Ca/Al–Cl LDH efficiently removed organic matters in stabilized landfill leachate with the maximum removal (59.41% COD, 62.06% DOC and 70.56% UV_{254}) at the dose of 30 g/L. According to UV_{254} and EEM, it is remarkable that the formation of Ca/Al–LDH has a greater beneficial to organic removal than other reagents, especially for fulvic acid-like and humic acid-like compounds. Moreover, the removal of fulvic acid-like compounds was much better than humic acid-like compounds. The previous compounds had more carboxylic groups, thus had a better removal selectivity.

1. Introduction

Landfill leachate was produced from sanitary landfills because of rain percolation, degradation of wastes and so on. Biological method is not suitable for the treatment of stabilized leachate such as old leachate and leachate treated by microorganism due to the bio-refractory organic matter. These refractory organics mainly includes humic substances (Zhang et al., 2013; Zhao et al., 2013), phenols (Kalmykova et al., 2013), polycyclic aromatic hydrocarbons (PAHs) (Kalmykova et al., 2013), phthalic acid esters (PAEs) (Gao et al., 2013). By contrast, these refractory organics in leachate could be effectively disposed by a variety of physicochemical processes, such as coagulation–flocculation, adsorption, chemical oxidation, nanofiltration, microfiltration and reverse osmosis.

Coagulation–flocculation is a relatively simple method which has successfully disposed of old landfill leachate (Amokrane et al., 1997). Aluminum coagulants efficiently removed humic acid (Yang et al.,

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2013), PAEs (Zhang and Wang, 2009) and carboxyl containing organic matter (Xiaoxiao et al., 2012). In addition, removal of hydrophobic fraction was much more effective than transphilic and hydrophilic fraction by aluminium formate (Mikola et al., 2013). On the other hand, calcium coagulants enhanced the removals of both hydrophobic and hydrophilic fractions of humic acid with smaller molecular sizes (Duan et al., 2012). However, this method only resulted in moderate removal of COD (or DOC), together with producing excessive sludge. As an advanced oxidation method, Fenton reagent efficiently degraded phenols (Zazo et al., 2005) and trichloroethylene (Teel et al., 2001). But chemical oxidation could produce many by-products that were more poisonous than original organics (Swietlik et al., 2004). Over the last few years, adsorption was regarded as one of the most efficient and promising method in wastewater treatment (Daifullah et al., 2004). Various adsorbents have been employed in stabilized landfill leachate treatment, such as activated carbon and zeolite. Activated carbon showed a preferential adsorption of fulvic-like organic matter (Singh et al., 2012) and selectivity for phthalates (Freitas et al., 2004). Moreover, inorganic clays were also widely used.

Layered double hydroxides (LDHs) are also called anionic clays, represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}]\cdot mH_2O$, in which $M^{2+} = Ca^{2+}$, Mg^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+} and $M^{3+} = Al^{3+}$, Fe^{3+}, Cr^{3+}; A^{n-} is an anion, such as CO_3^{2-}, SO_4^{2-}, NO_3^-, Cl^-, OH^- and even an organic anion (Das et al., 2004). LDHs have attracted considerable attention for their potential use as adsorbents and ion exchangers. As adsorbents, LDHs have been used for oxyanion ($Cr_2O_7^{2-}$, PO_4^{3-} and NO_3^-, etc.) removal. LDHs were also used to treat humic substances, dyes and herbicides by surface adsorption, ligand exchange reactions with surface groups and intercalation (Zhang et al., 2012a). There is an interesting group of LDHs consisting of calcium ions as the divalent metal in layer sheets. One of the most special features of Ca-containing LDHs is that calcium will be released into solution during adsorption (Zhang et al., 2012b). Our group have reported that phosphate was removed by forming hydroxyapatite (HAP) with released Ca^{2+} from Ca/Al LDH (Qian et al., 2012), and zinc was removed by Ca/Al–Cl LDH through self-dissolution and re-precipitation of Zn/Al LDHs (Liu et al., 2011). Our previous work has also shown that sodium dodecyl sulfate (SDS) intercalated Ca/Al LDHs had enhanced sorption of nitrobenzene and naphthalene from water compared with inorganic Ca/Al–Cl LDH, and the adsorption capacity was related to the polar of contaminants (Ruan et al., 2011).

Until recently, there was little work dealing with the treatment of practical organic wastewater by LDHs. Let alone the superiority removal of different type of refractory organic matters. In this report, Ca/Al–Cl LDH was utilized to treat stabilized landfill leachate after biochemical process. The treatment efficiency was determined and discussed in terms of COD, DOC and UV_{254}. The target was to investigate the type of organics removed by LDH according to 3D-excitation emission matrix (EEM) and gas chromatography–mass spectrometer (GC–MS) analysis.

2. Methods

2.1. Materials

Stabilized landfill leachate used in this work was supplied by Laogang Municipal Landfill in Shanghai, China. Waste age of the landfill was over 10 years and the leachate had been treated by lagoon. Characters of the leachate are listed in Table S1. The leachate was collected in 20 L plastic barrels, transported to the laboratory and stored at 4 °C.

All the chemicals used in this study were analytical grade, including $CaCl_2$, $AlCl_3\cdot6H_2O$, NaOH, CH_2Cl_2, $K_2Cr_2O_7$ and $(NH_4)_2SO_4\cdot FeSO_4\cdot6H_2O$. All the aqueous solutions were prepared using double-distilled water.

2.2. Preparation of Ca/Al-Cl LDH materials and treatment experiments

Ca/Al–Cl LDH was prepared by co-precipitation method as follows. Add 5.55 g $CaCl_2$ and 6.04 g $AlCl_3\cdot6H_2O$ to the beaker contained 50 mL of distilled water. The solution above was dumped to 100 mL of 1.5 mol/L NaOH solution. The mixture was purged with N_2 on magnetic stirrer for an hour, stirred for another 23 h in the sealed condition, and then filtered. The residue was washed with double-distilled water three times, then dried at 105 °C for 24 h and ground to 100 mesh. All the samples were stored in a vacuum desiccator for further use.

Treatment experiments were performed in a constant temperature water bath oscillator at the room temperature of 25 °C. 100 mL of landfill leachate was taken in a series of 250 mL plastic bottles. Then these bottles were separated into two batches: (a) different amount of Ca/Al–Cl LDH was added into the leachate; (b) $CaCl_2$ and $AlCl_3$ equal to 10 g/L dosage of Ca/Al–Cl LDH were added as comparisons. Leachate in batch b was treated with $CaCl_2$, $AlCl_3$, $CaCl_2$ and $AlCl_3$ at different pH. They are labeled as $CaCl_2$, $AlCl_3$, Ca + Al-1 and Ca + Al-2. During the process, pH of $CaCl_2$, $AlCl_3$ and Ca + Al-1 should be adjusted to the same as the leachate with 10 g/L dosage of Ca/Al-Cl LDH. But the pH of Ca + Al-2 should be adjusted to 12. The bottles were shaken for 24 h in the oscillator. After that, the samples were filtered and dried to be measured. All the samples are prepared in duplicate.

2.3. Characterization

2.3.1. X-ray diffraction (XRD)

Solid samples were analyzed by powder X-ray diffraction (XRD) with a DX2700 X-ray diffractometer (Haoyuan, China). The operation conditions were as follows: 40 kV, 40 mA, and Cu Kα (=0.15418 nm) radiation. Ca/Al–Cl LDH was scanned at a rate of 6° per minute in the range of 2θ from 5° to 80°.

2.3.2. 3D-excitation emission matrix fluorescence spectroscopy (EEM)

EEM Fluorescence spectra of stabilized landfill leachate samples were measured using a fluorescence spectrophotometer (F97Pro, Lengguang Tech, China). The samples were collected in a 1 cm quartz cell. The EEM spectra were generated by scanning excitation fluorescence from 200 to 600 nm at 5 nm steps and the emission wavelength from 250 to 650 nm at 5 nm steps. The spectra were operated at a scan rate of 6000 nm per minute. Before 3D-EEM analysis, stabilized landfill leachate samples were filtered through membranes with pore size of 0.45 μm, and diluted 5 times. The spectrum of deionized water was recorded as blank. The raw EEMs were processed in MATLAB.

COD was measured by closed reflux, titrimetric method. DOC and TN was tested by multi N/C 2100 instrument (Analytik Jena AG). The ultraviolet absorbance at 254 nm (UV_{254}) was measured with an ultraviolet and visible spectrophotometer (4802UV/VIS, Unico, China). Samples should be filtrated through membranes with 0.45 micron. The concentration of anion and metal ion was detected by ion chromatography and ICP (Inductively Coupled Plasma Emission Spectrometer), respectively.

3. Results and discussion

3.1. Characteristic of solid phase produced in the leachate

The XRD patterns of solid phase after treatments are shown in Fig. S1. XRD of the synthesized Ca/Al–Cl LDH was in excellent