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Research paper

Hydroponic removal of organic contaminants from water by using ryegrass and organobentonites simultaneously

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ABSTRACT

Phytoremediation and adsorption are both important approaches for the removal of organic contaminants in water. In this study, cetyltrimethylammonium saturated bentonite as an effective adsorbent and ryegrass as a model plant, were used simultaneously to remove organic contaminants in a hydroponic system. Results showed that removal efficiency of phenol (100 mg/L) by organobentonite and ryegrass (OB + RY) reached 92.5% in 6 days, followed by ryegrass (RY, 88.5%) and organobentonite only (OB, 15.9%). The removal efficiency of aniline (100 mg/L) by organobentonite and ryegrass (OB + RY) reached 91.9% in 9 days, followed by ryegrass only (RY, 83.9%), and organobentonite only (OB, 63.0%). The combined remediation by organobentonites and the hydroponic ryegrass was an efficient and environmental friendly method for organic chemicals polluted wastewater.

1. Introduction

Phytoremediation was defined as the use of green plants to remove, contain or render harmless organic or inorganic environmental contaminants (Cunningham and Ow, 1996), which has gained increasing attention in recent decades as it is a cost-effective, noninvasive and complementary technology for engineering-based remediation methods (Doran, 2009; Gao et al., 2003; Pilon-Smits, 2006). Some aquatic organisms, such as algae and higher plants, were used to treat wastewater containing nitrogen, phosphorus, heavy metals, detergents, antibiotics and persistent organic compounds including polycyclic aromatic hydrocarbons (PAHs) (Chen et al., 2014; Tel-Or and Forni, 2011). However, the application of the phytoremediation still has certain limitations, especially for the tolerance limit of plants for relatively high concentration of organic contaminants (Li et al., 2015). How to make the plants survive in high concentration of organic contaminants in wastewater is the critical problem in phytoremediation.

Organobentonite was a typical adsorptive material for organic contaminants. It was synthesized by the intercalation of cationic surfactants into bentonite, and was more hydrophobic than bentonite (Jordan, 1949; Ruan et al, 2008; Zhu et al., 2009). Organobentonites could be used to effectively treat organic wastewater by taking up the contaminants to the hydrophobic phase in interlayer (Smith and Jaffe, 1991; Smith and Galan, 1995; Ruan et al., 2015). Organic modification of mineral clay using the monomer ethenyl acetate was performed, which greatly enhanced removal of lead in aqueous solution (Stojiljkovic et al., 2013). The application of organic modified bentonite in treatment of organic pollutants, heavy metal ion contaminants and the printing and dyeing waste water treatment were prospected (Chen et al., 2012). In this study, a new hypothesis is proposed that the sorption capability of organobentonites that could be applied to decrease the concentration of organic contaminants in order to help the plants to survive in wastewater, as well as to keep the concentration of organic contaminants in a certain range by the equilibrium of adsorption and desorption thus enhancing the efficiency of the total phytoremediation process.

Even though the positive effects of combining plants with microorganisms have been displayed in many other studies (Fan et al., 2014), there are few studies on combined remediation of organobentonites and Ryegrass. Bentonite, as a kind of natural clay, it is environmentally friendly. For our hypothesis, organobentonites will adsorb the chemicals in wastewater quickly at the beginning to reduce the concentration of chemicals so that the plant in water may not be harmed. Afterwards, plants can keep on uptake the organic contaminants in a suitable concentration range with the release of the adsorbed organic contaminants from organobentonites.

In this study, ryegrass was selected as the model plant (Zhang and Zhu, 2009; Zhu and Zhang, 2008),which is known for its high yield, rapid regrowth, and potential for remediation of heavy metal contaminated soils (Lambrechts et al. 2011; Lou et al. 2013). In this study, a typical organobentonite, cetyltrimethylammonium saturated bentonite

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(CTMAB-bentonite), was chosen as adsorbent. Aniline ($S_w = 34$ g/L, $\log K_{ow} = 0.9$) and phenol ($S_w = 83$ g/L, $\log K_{ow} = 1.46$) (Yaws, 1999) were selected as the model organic contaminants since they were two typical chemicals that normally exist in industrial wastewater.

2. Materials and methods

2.1. Materials

The raw material was a calcium bentonite from Inner-Mongolia, China, containing more than 95% of purity of montmorillonite. The total interlayer charge and cation exchange capacity (CEC) were 0.82 per formula unit and 108 cmol/kg, respectively. It was passed through a 100-mesh sieve after washing, dried and triturated for further use. Cetyltrimethylammonium bromide (CTMAB) was selected to prepare organobentonite. CTMAB, aniline and phenol are analytical pure.

Ryegrass (*Lolium multiflorum Lam*) was selected as the model plant in this study. The seeds were germinated on wet quartz sand for about 4 days, and seedlings were then transferred to black-covered glass beakers for further cultivation with half-strength Hoagland solution. After 3 weeks, symmetrical ryegrass seedlings were selected for further experimentation. All the experiments for the growth of ryegrass including the following toxicity and removal of organic compounds experiments were conducted in the phytotron.

2.2. Preparation and characterization of organobentonite

Five grams of the original calcium bentonite was dispersed in 200 mL water, and then a given amount of $CTMA^+$ was added to satisfy its 100% CEC. The suspension was stirred at 50 °C for 2 h and aged at 60 °C for 10 h, then filtrated. The filtration residue was washed with distilled water for five times, then oven-dried at 80 °C and ground through 100-mesh. The product is denoted as organobentonite. Organic carbon contents of bentonite and organobentonite were analyzed by an organic carbon analyzer (Shimadzu TOC). X-ray diffraction (XRD) patterns were recorded from 2° to 10° (2θ) by a Rigaku D/max-2550 diffractometer with Cu Kα radiation at a relative humidity of 60–70% and at 25 °C. Basal spacings (d_{001}) were determined according to the peaks in XRD patterns (Fig. 1).

2.3. Toxicity of aniline and phenol to ryegrass

Ryegrass was planted hydroponically in nutrient solution with a series of aniline and phenol concentrations. 500 mL conical flasks were used as container in this part of the experiment. 500 mL nutrient solution with aniline or phenol was filled into the flasks. The flasks were disinfected at 105 °C to eliminate the microorganism. Each flask contained 15 strains of symmetrical ryegrass seedlings of similar growth situation (8–10 g per stain). The sponge was used for sealing each flask to avoid the volatilization of the organic compounds and keeping the green portion of ryegrass outside for the photosynthesis. The concentration ranges of aniline and phenol were 2–400 mg/L and 100–700 mg/L, respectively. The growth of plants was observed for two weeks to identify the critical concentration that plants can survive in aniline/phenol solution. Concentrations of artificial aniline/phenol wastewater in further study were chosen according to this experiment.

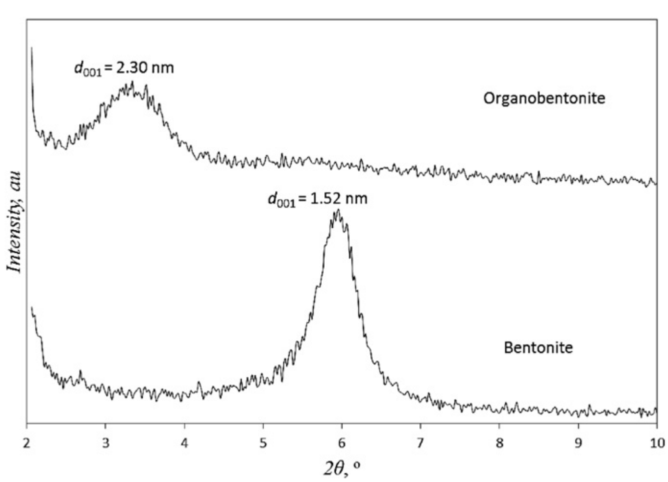

Fig. 1. X-ray diffraction (XRD) patterns of organobentonite and bentonite.

2.4. Removal of aniline and phenol in water

Artificial wastewater containing aniline and phenol in water was used in this study. 500 mL conical flasks were used as container in this part of the experiment. 500 mL nutrient solution with aniline or phenol was filled into the flasks. The initial concentration of aniline and phenol in water was 100 mg/L according to the toxicity experiment described in 2.3 as to keep the normal growth of ryegrass. Four series of treatments were prepared as follows: (a) control (without organobentonites or ryegrass); (b) organobentonite only; (c) ryegrass only and (d) organobentonites and ryegrass. Each flask was sealed by a sponge. The weight of organobentonite in each treatment is 2.0 g. Each flask contained 15 strains of symmetrical ryegrass seedlings of similar growth situation (8–10 g per stain) for the treatment with ryegrass. Concentration of aniline and phenol in water were monitored at different time.

2.5. Determination of aniline and phenol

Water samples were collected and centrifuged for 20 min at 3000 rpm to remove possible particles. Aniline and phenol in suspension were determined by ultraviolet spectrophotometer with the wavelength of 230 nm and 270 nm.

3. Results and discussion

3.1. Structural characteristics of organobentonite

The organic carbon contents (f_{oc}) and basal spacings (d_{001}) of organobentonite and bentonite are presented in Table 1. After saturated with $CTMA^+$, the respective f_{oc} values of CTMA–bentonite is 19.7%, approximately satisfied with 100% CEC. The d_{001} values of CTMA–bentonite (2.30 nm) is larger than Ca–bentonite (1.52 nm), indicating that $CTMA^+$ cations are intercalated into the interlayer. All these results manifest that CTMA+ cations are packed as a micelle-like structure in the interlayer of bentonite, and the organic phase formed by the alkyl tail of $CTMA^+$ may act as the efficient sorption domain for organic contaminants (Mishael et al., 2002; Polubesova et al., 2005; Zhu and Chen, 2009; Ruan et al., 2015).

3.2. Toxicity of phenol and aniline to ryegrass

The growth of ryegrass in the nutrient solution containing phenol and aniline was observed. Preliminary experiments were conducted prior to test the tolerance limit of ryegrass for the concentration of

Table 1
The structural characteristics of organobentonite and bentonite in air-dry state.

Sample	Organic carbon content (f_{oc}), %	CEC occupied by $CTMA^{+}$ [b)], %	Basal spacing (d_{001}), nm
Bentonite	–[a)]	–	1.52
Organobentonite	19.7	106	2.30

a) The f_{oc} value for Ca–bentonite is less than 0.04%. b) The percentage of CEC occupied by $CTMA^+$ was calculated by converting f_{oc} to the adsorbed-amount of $CTMA^+$ (cmol/kg) and then divided by the CEC value of Ca–bentonite.