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Ammonia enhanced electrokinetics coupled with bamboo charcoal adsorption for remediation of fluorine-contaminated kaolin clay

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ABSTRACT

The remediation of fluorine-contaminated kaolin using ammonia enhanced electrokinetics coupled with bamboo charcoal adsorption was assessed. Six electrokinetic experiments were conducted in self-made electrokinetic apparatus with deionized water as catholyte. Ammonia with concentration of 0, 0.01 and 0.1 mol/L was used as anolyte, and the voltage gradient was set at 1.0 and 1.5 V/cm. Bamboo charcoal was loaded in the central part of the electrolytic cell as adsorbent to adsorb various forms of fluorine pollutants migrating here. The effects of different ammonia concentration and voltage gradient on the removal of soil fluorine were analyzed. Ammonia enhanced electrokinetic not only increased electric current, but also changed the pH values of catholyte, anolyte and soil which made different fluorine speciation exist in soil such as anions F^-, HF_2^- and cations $(AlF)^{2+}$, AlF_2^+. The removal of fluorine increased significantly with the concentration of the ammonia, which indicated that ammonia could facilitate soil fluorine to transform into dissolved form effectively and desorption of soil fluorine was a key limiting factor for fluorine-contaminated soil by electrokinetics. F^-, HF_2^-, and $(AlF)^{2+}$, AlF_2^+ in soil solution had opposite charges and moved in reverse direction under the function of electrokinetics, which caused fluorine pollutants to move to the central section of the electrolytic cell, where they were adsorbed exactly by the bamboo charcoal loaded there. The maximum adsorption capacity of fluorine by bamboo charcoal was 3.17 mg/g and the removal rate of soil fluorine reached 75.70%. The integration of ammonia enhanced electrokinetics with bamboo charcoal adsorption as a hybrid method was most effective for the remediation of fluorine-contaminated soil.

1. Introduction

Since 1970s, fluorine has been generally confirmed as an environmental pollution element. In recent years the fast development of China's modern industry has caused increasingly serious fluorine pollution. The 2014 statistical bulletin on the development of health and family planning in China showed that 1219 counties have endemic fluorosis areas. 32.682 million people are dental fluorosis patients and 3.153 million fluorosis patients [1]. The fluorine in human body comes mainly from drinking water and foods. In most areas the soil fluorine is the major source for the fluorine in ground water, drinking water and food [2,3]. So it has become an urgent realistic problem to study how to reduce the fluorine content in soil and to remediate fluorine-contaminated soil.

At present many techniques can be used to remediate fluorine-contaminated soil, such as chemical stabilization technology, soil washing technology, electrokinetic remediation and so on [4–6]. Among these techniques, electrokinetic remediation has drawn people's close attention because it is very suitable for the removal of pollutants in low permeability clay soils [7–9]. The studies on the remediation of fluorine-contaminated soil by electrokinetics show that the removal efficiency of soil fluorine is rather low in cases where there is no enhancement, especially at the later stage of remediation process. Therefore, researchers used various enhancement methods, such as using sodium hydroxide solution as anodic electrolyte in order to augment soil fluorine desorption and increase electroosmosis flow, using strong alkaline solution to saturate fluorine soil so as to induce electrode electrolysis reaction and improve soil electrical conductivity, using pulsed electric field–ion exchange membrane to control concentration polarization and prevent ion entering soil so as to increase remediation electric current and electroosmosis flow, etc [6,10–13]. These methods increased the removal efficiency of soil fluorine, however

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Table 1
Kaolin chemical and physical properties.

Particle composition			pH	Porosity	Cation exchange capacity	Electrical conductivity	Permeability coefficient
Sand	Slit	Clay					
0	15.3%	84.7%	6.41	57%	41 mmol/kg	243.0 μS/cm	9.4×10^{-8} cm/s

the soil pH increased obviously after remediation, for example, the original soil pH was 4.96, after remediation the whole soil pH was over 12 [12]; in another study the original soil pH was 8.91, after remediation the soil pH was between 11.0 ~ 12.3 [6]. Moreover, the pH difference between anode soil and cathode soil increased obviously, for example, the initial pH of original soil was 8.17 or 7.862, after remediation the pH near anode soil reduced to 3 while that near cathode increased to 11 [11,13]. As a result, the soil properties were changed significantly, which further affected the soil fertility, plant growth and quality.

On the other hand, the principle of electrokinetic remediation relies on the application of a direct electric voltage to the contaminated soil between a couple of electrodes (cathode and anode). The direct electric field mobilizes charged species, which causes ions and water to move toward electrodes through the contaminated soil. The two primary transportation mechanisms in electrokinetics are called electromigration (the movement of ionic species in the electric field through soil toward an electrode with the opposite charge) and electroosmosis (the net flux of water towards one of the electrodes, which in most cases is the cathode, induced by the electric field through the porous structure of soil) [7,14–16]. However, fluorine can exist in soil solution in different forms, such as anion F^-, HF_2^-, $H_2F_3^-$ and cation $(AlF)^{2+}$, $(AlF_2)^+$ and so on [12,17,18], thus the different forms of fluorine with opposite charge have opposite moving direction under the function of electromigration and electroosmotic flow. As a result, the residual fluorine in soil concentrates on the center of the soil body after electrokinetic remediation, which further reduces the soil fluorine removal efficiency.

In view of these two points, the present study adopted ammonia that is a liquid nitrogen fertilizer for agriculture to make weak alkaline solution and used it as anodic electrolyte to enhance electrokinetic technology, aiming at improving soil electrical conductivity and remediation electric current, enhancing the desorption of fluorine in soil and the removal efficiency of soil fluorine, meanwhile, minimizing the rising range of the soil pH after remediation and the pH difference between anode soil and cathode soil as much as possible. At the same time new biomass material—bamboo charcoal was loaded in the central part of the electrolytic cell between the soil bodies to adsorb the fluorine moving here. The purpose was to investigate the remediation effect on fluorine-contaminated kaolin by ammonia enhanced electrokinetics coupled with bamboo charcoal adsorption under different applied voltage gradients in various anodic electrolyte concentrations as well as to analyze the variation of electric current intensity, potential distribution of soil, electrolyte pH with time during remediation process and the influence on soil pH after remediation, so as to provide technological support for optimizing the remediation of fluorine-contaminated clay soil by electrokinetics.

2. Materials and Methods

2.1. Kaolin and bamboo charcoal

Kaolin is a kind of clay with low permeability and has been employed by many researchers in feasibility studies of electrokinetic extraction to clean up heavy metal and organic contaminants from clay materials [19,20]. The chemical and physical properties of the commercial kaolin purchased from Guangdong Maoming kaolin industry Co., Ltd. are listed in Table 1.

Bamboo charcoal is a new biomass material and has features of special pore that is made up by onion-like fullerenes and expanded carbon nanotubes as well as a large number of surface oxygen groups, etc [21,22]. Such special structures endow it with good adsorption property. In addition bamboo charcoal has electric conductivity. Therefore the present study put bamboo charcoal in the central part of the electrolytic cell and used it as adsorbent for fluorine pollutants moving here. The bamboo charcoal used in the study was powdered carbon and purchased from Shenlonggu Carbon Industry Co., Ltd. of Suichang County. The nature of bamboo charcoal is shown in Table 2.

2.2. Experimental apparatus and methodology

A schematic of the experimental setup is shown in Fig. 1. The electrolytic cell was a rectangular translucent Plexiglas box (22 cm length × 8 cm width × 6 cm height) and was divided into five compartments by perforated Plexiglas plate, nylon mesh (100 mesh number), and microporous filter membrane. The central compartment was loaded with bamboo charcoal. The other two compartments on both sides were loaded with fluorine-contaminated kaolin. The rest two at the ends were electrode chambers. The left one served as cathode chamber and the right anode chamber. Each electrode chamber was connected to an additional reservoir that stored electrolyte through silicone tubes. A four channel peristaltic pump (BT00-300T + DG-4, Baoding Longer Precision Pump Co., Ltd. China) and two valves were utilized to circulate electrolyte and control the liquid level of the electrode chambers. The working electrode was made of high purity graphite sheet in this study. The electrodes were then connected to a DC power supply (GPC-6030D, Good Will Instrument Co., China) that provided constant potential difference across the soil column. Inert needle electrodes (platinum wire, 0.5 mm in diameter and 5 cm in length) were inserted into the kaolin and bamboo charcoal through eleven pores on the cover plate. A digital multimeter (F-15B, Fluke, USA) was utilized to measure the electric current passing through the soil and the electric potential distribution along the soil specimen.

500.0 mL NaF solution with a concentration of 1000 mg/L and 500.0 g air dried kaolin were mixed and stirred well. 800.0 g wet

Table 2
Nature of bamboo charcoal.

Moisture content	Ash content	Volatile matter	Fixed carbon	pH	Particle size	Resistivity	Density
8.4%	4.2%	9.3%	86.5%	9.2	300 mesh	0.77 Ω·cm	1.159 g/cm