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Study of the Organic Soil Modified by Alkyl Quaternary Ammonium in Water Pollution Treatment

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Natural soil was modified by quaternary ammonium cationic surfactant octadecyl trimethyl ammonium chloride and characterized by Fourier transform infrared spectra and small angle X-ray diffraction. The results showed that the organic molecular chain had intercalated into the layers of natural soil layer lattice and arranged aslope by 50.2º. The adsorption capacity and the stability of octadecyl trimethyl ammonium chloride-modified and natural soil were compared by static and dynamic experiment respectively, which indicated that the COD_{Cr} of purified water was 18.11 mg L^{-1} and the COD_{Cr} removal efficiency was as high as 84.9 % by the modified soil as well as excellent stability. The experiment proved that octadecyl trimethyl ammonium chloride-modified soil exhibited good effect on wastewater purification and its application foreground was broad.

Key Words: Modified soils, Octadecyl trimethyl ammonium chloride, Water pollution treatment.

INTRODUCTION

Recently, the domestic and international scholars have always devoted themselves to the research of remediate contaminated environment using organoclays minerals. Quaternary ammonium salt was used for modification treatment of clay, with organic clay obtained and to increase its ability to remove pollutants from the wastewater[1-3]. In view of the actual requirement for the water quality improvement in east route of north-south water transfer project, constructed wetland wastewater treatment system has been used at present. But constructed wetland was easily affected by northern climate. During spring and summer, plants grow vigorously and biomass increase, which is good for wastewater purification. But, in the autumn and winter seasons, wetland plants will death cause secondary pollution to water body[4]. Thus, in order to improve the ability to remove pollutants and decrease COD_{Cr} values of wastewater, natural soils of constructed wetland were modified by long-carbochain quaternary ammonium salt.

In this article, natural soil was modified by octadecyl trimethyl ammonium chloride (OTAC) and characterized by FTIR, small angle X-ray diffraction. Based on the COD_{Cr} values of wastewater, the adsorption capacity and the stability of octadecyl trimethyl ammonium chlorid-modified and natural soil were compared by static and dynamic experiment respectively. The study may provide a basal parameter for the wastewater purification.

EXPERIMENTAL

The soil used in this work was collected from Jinxiang, Jining. Its chemical composition was found to be as follows: 66.76 % SiO_2, 3.77 % Fe_2O_3, 2.47 % Na_2O, 1.19 % CaO, 0.92 % MgO, 0.39 % C, 0.29 % OrgC, 0.037 % N. The COD_{Cr} value of wastewater used in the work was 120 mg L^{-1}.

All the reagents used were of analytical grade.

Preparation of modified-soil: The cation exchange capacity (CEC) was determined with NH_4Cl-NH_4OAc method[5]. The calculated cation exchange capacity of natural soil is 45 cmol(+) Kg^{-1}. Modified-soil was prepared by adding amounts of octadecyl trimethyl ammonium chloride surfactants equivalent to the cation exchange capacity.

Generally, the organically modified clay was prepared in aqueous solution by organic cation exchanged with inorganic cation in natural soil[6], expressed commonly for:

$$yM\text{-}C^x + xO \rightleftharpoons xO\text{-}C^y + yM$$

where, x is the valence of inorganic cation; y is the valence of organic cation; M is exchangeable metal cation in natural soil, O is organic cation, C is the position of ion exchange in clay. So, the synthesis of modified-soil was performed by the following procedure: a fixed amount of natural soils was first dispersed in deionized water, to which a desired amount of octadecyl trimethyl ammonium chloride was slowly added. The reaction mixtures were stirred for 2 h in 55 ºC. All products were washed until free chloride ions (tested by $AgNO_3$), dried at 60 ºC and grinded in an agate mortar. So octadecyl trimethyl ammonium chloride modified soil (1.0 CEC) was obtained.

Equipments and methods of characterization: Fourier transform infrared spectroscopy (FTIR) was carried out on a VERTEX-70 with a RT-DLATGS detector. The spectrum was recorded from 4000 to 400 cm^{-1} using KBr pellets. The structure of modified-soil was carried out using small angle X-ray diffractometer with CuK_{α}(λ = 1.542 Å) radiation.

Static experiment: Many researches show that the time of equilibrium adsorption of pollutants by clays was 24 h[7]. So the time of equilibrium adsorption in this work was 24 h, the adsorption capacity in the different dosage of natural soils and modified soils were studied to determine the optimal dosage. On this basis, the effect of repeated times of natural soils and modified soils on adsorption of pollutants were studied.

Dynamic experiment: Glass column had been used in dynamic simulation experiment, with the length and diameter were 45, 5.0 cm respectively (Fig. 1). In present studies, the loading parameters of wastewater absorption layer (natural and modified soils) as follows: quantity of soils 85 g, thickness 3.5 cm. The packed column was stood for 7 days in certain humidity[8], which used in the treatment of the wastewater by applying 40 cm raw sewage, keeping stable pressure of water. The raw sewage was allowed to pass through by gravity flow and the effluent collected was analyzed. COD_{Cr} was chosen to assess the degree of purification of water in order to quick analysis.

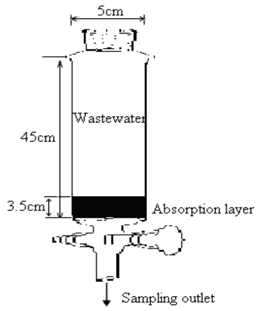

Fig. 1. Equipment of dynamic simulation experiment

RESULTS AND DISCUSSION

Modified-soils characterization: The FTIR spectra of natural and modified soils are presented in Fig. 2. The spectrum of natural soils shown a weak absorption peak at 3625 cm^{-1}, which indicated the less hydration degree on soil surface; a broad absorption peak at 1024 cm^{-1}, which was due to the Si-O-Si stretching vibration; the band at 785 cm^{-1} represents the characteristic frequency of quarz and the bands close-by 532 cm^{-1} may be the Si-O-Al, Si-O-Mg bending vibration[9,10].

The FTIR spectra of modified soils shown addition bands at 2931cm^{-1} and 2853 cm^{-1} due to the stretching and bending vibrations of $-CH_3$, $-CH_2-$, CH≡, which were the organic group of octadecyl trimethyl ammonium chlorid; the band at 1476 cm^{-1} represents the characteristic absorption peak of C-N. These data clearly confirm the existence of organic molecular chain in the crystal structure of soil[11]. And the addition band at 3430 cm^{-1}, which is due to the hydrogen bonded O-H stretching vibration, its deep cause was that absorbed water during the preparation of modified soil. In the view of the strength of absorption, absorption bands at 1024 cm^{-1}, 785 cm^{-1}, 532 cm^{-1} have greatly changed compared with natural soil, which indicated that the organic molecular chain of octadecyl trimethyl ammonium chloride had exchanged successfully with the inorganic cation of soil. But, the crystal structure of soil was not has an obvious change.

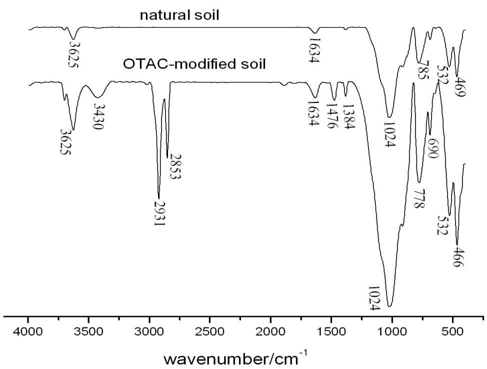

Fig. 2. FTIR patterns of soil

Fig. 3 showed that the diffraction patterns of natural and modified soils. In the small angle X-ray diffraction patterns of natural soil, the diffraction peak at 2θ = 0.5º, but in modified soil, the diffraction peak shifts to short degree direction. Based on the Bragg equation ($2d \sin\theta = n\lambda$), the layer space of modified soil (d_{001} = 3.295 nm) was bigger than that of natural soil (d_{001} = 2.982 nm). The results showed that octadecyl trimethyl ammonium chloride had inserted into the interlayers of soil and exchanged successfully with the inorganic cation of soil. It not only made the layer space enlarged but also the internal surface area increased, which can improved obviously its adsorbability.

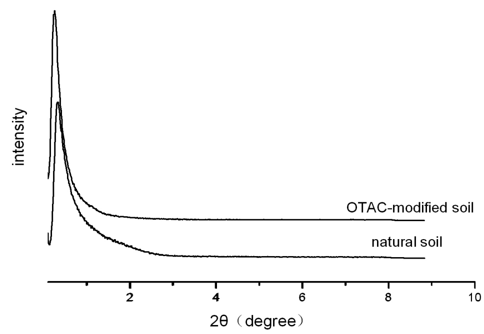

Fig. 3. Small angle X-ray diffraction patterns of soil

The chain length of octadecyl trimethyl ammonium chloride can be calculated as follows:

$$L = 1.27(n-1) + 2r_M + r_{C-N}(1+\sin\theta)$$

where, n is the number of long-chain carbon atoms of quaternary ammonium salt; r_M is van der Waals diameter of end methyl (0.3 nm); r_{C-N} is the bond length of C-N (0.147 nm); θ is the bond angle of C-N-C (108º)[11]. The chain length of octadecyl trimethyl ammonium chloride obtained by calculating, L was 3.04 nm. It was defined that the angle between organic molecular chain of octadecyl trimethyl ammonium chloride and layer of soil was ϕ; the thickness of single phyllosilicate was 0.96nm; ϕ was 50.2º can be calculated from the equation $d_{001} = L \sin\phi + 0.96$. The structure of modified soil was shown in Fig. 4, it indicated that octadecyl trimethyl ammonium chloride organic molecular chain had intercalated into the layers of natural soil layer lattice and arranged aslope by 50.2º.

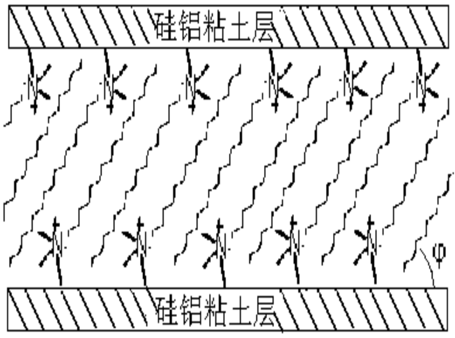

Fig. 4 Structure of the modified soil

To discuss further, the reasons of the layer space enlarged basically have the following characteristics: 1. The natural soil was ion exchanged with octadecyl trimethyl ammonium chloride, which decreased the Coulomb force; 2. After modification, the space between clay layer and interlayer of soil was occupied by octadecyl trimethyl ammonium chloride, which can led to lower van der Waals force; 3. The modifying agent was the alkyl chain with hydrophobic, take octadecyl trimethyl ammonium chloride for example, when ammonium ion on the top was exchanged with the inorganic cation of soil. The alkyl chain was follow-up subsequently. If the low modifying agent concentrations in soil interlayer, alkyl chain of octadecyl trimethyl ammonium chloride will parallel arrangement in it and with the modifier concentration increase. The alkyl chain will gradual transition a single layer to double and gradually arrange at certain angle. In general, the results of FTIR and small angle X-ray diffraction shown that the properties of modified soil have been improved and the layer space have been enlarged.

Effect of soils dosage: The effect of natural soils and modified soils dosage on the adsorption of pollutants was studied at different dosage of soils treatment with 25 mL wastewater (Fig. 5). Considering the dissolution of a few octadecyl trimethyl ammonium chloride in initial using of modified soils, which can increase the COD_{Cr} values of wastewater, the COD_{Cr} was chosen after wastewater treatment by the soils three times in the experiment. Fig. 5 showed that the removal efficiency of COD_{Cr} increased with the dosage of natural soils and modified soils. Of which, the removal rate of COD_{Cr} achieved maximum when the amount of soils was 0.5 g, afterwards, the variation tend of COD_{Cr} was not increased markedly.

To natural soil, the pollutants in wastewater were adsorbed by distribution[12]. Because of many exchangeable metal cation in natural soil, which formed a layer of water film on the soil surface by hydration, the pollutants of wastewater were very difficult to adsorb on the surface of soil[13]. So it was considered that the mechanism of removing pollutants by natural soil was the result of distribution. For modified soil, however, the mechanism of adsorbing pollutants was also the result of distribution[14]. This is because abundance of organic quaternary ammonium salt cations in modified soil, which formed a huge organic phase by mutual interaction. Therefore, based on the principle of the dissolution in the similar material structure, which can improve the distribution of pollutants on the modified soil. In view of the efficiency of COD_{Cr} removal from sewage, the modified soil was superior to the natural soil and the removal rate of COD_{Cr} was up to 81.6 %.

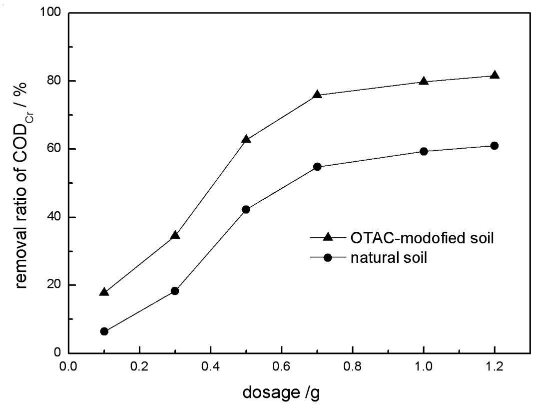

Fig. 5. Effect of soils dosage on removal rate of COD_{Cr}; Wastewater volumn: 25 mL

Cycling test of soils: The stability of modified soil involves the removal efficiency of pollutants and the potential effect on the environment, which mainly contained two aspects: One was the stability of modified soil and the other was the degradation of organic cation in modified soil. But, the organic cation in modified soil was hardly biodegradable, which had good biochemical stability[15]. Accordingly, the experiment basically was to be aimed at former to study. The effect of cycling times of natural soils and modified soils on the adsorption of pollutants was shown in Fig. 6. The COD_{Cr} removal of wastewater was negative in the initial stage. The reason was that octadecyl trimethyl ammonium chloride not only exchange with inorganic ions in natural soil but also attach to its surface during the preparation of modified soil, the trace attached octadecyl trimethyl ammonium chloride was easily dissolved in water, causing increase of COD_{Cr}. The result showed the COD_{Cr} removal of wastewater increased with cycling times increasing by the absorption of pollutants on modified soil and approached the equilibrium adsorption gradually. Through analysis the cycling times of modified soil, it can be used repeatedly to remove the pollutants of sewage.

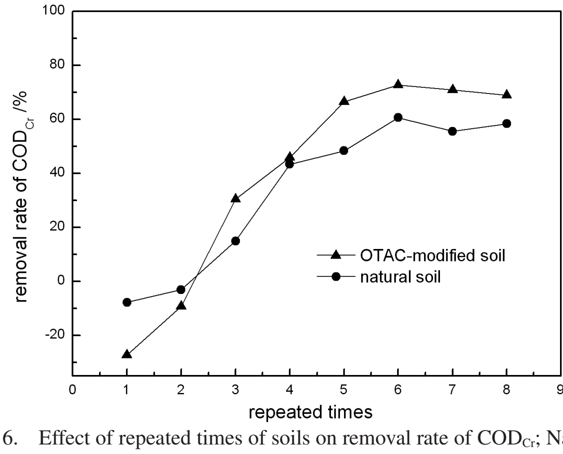

Fig. 6. Effect of repeated times of soils on removal rate of COD_{Cr}; Natural soils: 0.5 g; modified soils: 0.5 g; wastewater volumn: 25 mL

The reason of COD_{Cr} removal in the initial natural soil was that the impurities on soil was dissolved in water, then, with the increasing of cycling times, the distribution of pollutants on natural soil can cause the COD_{Cr} of wastewater decreased. A comparison of the continuous change of COD_{Cr} between the different soils, which showed that modified soil had better removal efficiency for pollutants and its performance was stable.

Analysis of dynamic simulation experiment: The X-axis (W/S) in Fig. 7 represents the ratio of water yield to the quantity of adsorption layer, the results showed that the COD_{Cr} of sewage increased firstly and approached to stable finally. In the initial stages, the reason of COD_{Cr} removal negetived was that octadecyl trimethyl ammonium chloride in modified soil and the impurities on natural soil were dissolved in water, respectively.

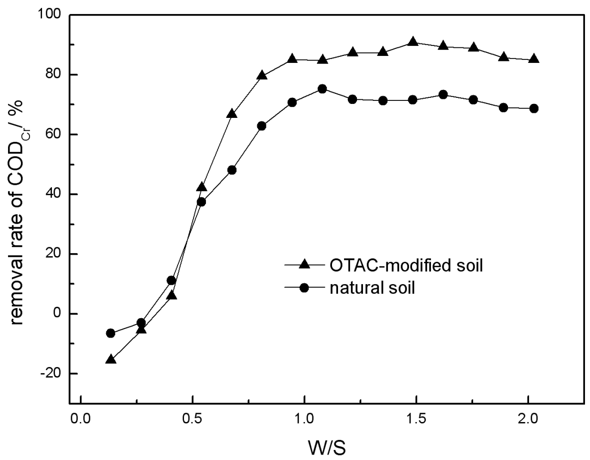

Fig. 7. Continuous series of curves of dynamic experiment; Natural soils absorption layer: 85 g; modified soils absorption layer: 85 g; the length of wastewater: 40 cm

The results indicated that the modified soil had good effect on removal of pollutants, the COD_{Cr} of wastewater decreased from 120 mg L^{-1} to 18.11 mg L^{-1} and finally the removal efficiency reached to 84.9 %. Because of the interval between soils layers and the internal surface area were expanded evidently after organic modification and the property of surface variated from hydrophile to hydrophobic, which made it adsorbed the pollutions easily by distribution and exterior adsorption. This is more powerful description of the effect of sewage purification by modified soil.

To natural soil, the pollutants in wastewater were mainly adsorbed by distribution, in addition, ion exchange, physical and biological functions were all play a certain role along with the increase of natural soil in dynamic experiment[7]. The pollutants were blocked, filtrated firstly, then distributed on the surface of soil layers while exchanged with inorganic ions in soils and degraded by microorganism at appropriate conditions to obtain a good effect on removal of pollutants. The COD_{Cr} of wastewater only decreased to 30.2 mg L^{-1} compared with modified soils. The results indicated that these functions of natural soils were much less than the chemical adsorption of modified soils. So modified soil has its own distinguishing features and advantages in wastewater purification.

Previous study had shown that organic quaternary ammonium salt cation once was adsorbed onto the soil surface, its own inherent bactericidal performance would disappear[16]. And the bacterial did not die even a litter residual of quaternary ammonium salt. Thus, natural soils of constructed wetland were modified by octadecyl trimethyl ammonium chloride had no harmful effects on the plants and degradation bacteria. So, constructed wetland modified by octadecyl trimethyl ammonium chloride was feasible and promisingly amicable technique to environment in wastewater treatment.

Conclusion

In this study, octadecyl trimethyl ammonium chloride was used as modifying agent to prepare modified soil (1.0CEC) successfully and characterized by Fourier transform infrared (FTIR) spectra, small-angle X-ray diffraction (SAXRD), the results showed that octadecyl trimethyl ammonium chloride organic molecular chain had intercalated into the layers of natural soil layer lattice and arranged aslope by 50.2º.

Through static experiment, the most appropriate dosage of natural soil and modified soil were decided, the results showed that the COD_{Cr} removal efficiency was up to 81.6 %, which is higher than that of natural soil, when the dosage of soil was 0.5 g (25 mL sewage). Meanwhile, the modified soil can be used in circulation to remove the pollutants of sewage and good performance stability. The continuous series of curves was obtained by dynamic experiment, which indicated that the COD_{Cr} of purified water was 18.11 mg L^{-1}, the COD_{Cr} removal efficiency was as high as 84.9 % by the modified soil as well as excellent stability. From above conclusions, octadecyl trimethyl ammonium chloride-modified soil exhibited good effect on wastewater purification plus with lower cost of octadecyl trimethyl ammonium chlorid, which will have a promising future in wastewater treatment and can be widely used in constructed wetland.

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