Preparation and Characterization of Loess/Polyacrylamide Composites

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Abstract. Using a kind of rich soil in the world, loess soil (LS), as natural silicate minerals materials, a novel low-cost inorganic / synthetic polymer composite, loess/polyacrylamide composite (LS/PAM), was prepared by in-situ polymerization of acrylamide. The obtained LS/PAM composite was characterized by infrared spectra (IR), thermogravimetric analysis (TG) and scanning electron microscope (SEM). The results indicate that polyacrylamide (PAM) was uniformly composited with loess particles successfully.

1. Introduction
Loess soil (LS), a typical loose and porous silicate minerals with easily vadose [1,2], is a kind of rich soil in the world, and major deposits are observed in the USA, Argentina, China and some countries in Asia and Europe. In China, the Loess Plateau cover almost all the northwestern region and part of northeast region. Thus, it has prospective in industrialization. In past decades, the geologic origin, distribution, composition, and properties of Loess have been investigated by geologists, pedologists and environmental scientists [3]. Loess have high pH values, carbonate content, porosity and permeability, and low organic matter content. Its main compositions are silica, aluminosilicate, CaCO3, iron oxide particles, and carbonaceous particles. And main clay minerals in the natural loess are illite, kaolinite, chlorite, and montmorillonite [4]. The chemical composition of loess soil is mainly SiO2, followed by Al2O3, CaO, and a small amount of Fe2O3, MgO, K2O, Na2O, TiO2, and MnO. It was found that loess could be used to remove pollutant from aqueous solution [5,6], but its adsorption capacity was not higher in comparison with other natural or synthetic polymer adsorbents [7]. Nevertheless, we found that polymer modification is effective methods for improving its adsorption capability. For instance, loess based poly(acrylic acid-2-hydroxyethyl methacrylate) complex and loess based polymethylacrylic acid-g-chitosan complex were synthesized successfully and applied to remove contaminant in wastre water [8,9]. In this paper, a loess soil composited synthetic polymer, loess/ polyacrylamide composite (LS/PAM), was prepared by in-situ polymerization, and characterzied by IR, TG and SEM.

2. Experimental

2.1. Materials
Loess soil (LS) was obtained free from the local hill located in Longnan of China. It was collected at 50 cm - 100 cm below the surface. Acrylamide (AM) and ammonium persulfate (APS) were supplied
2.2. Preparation of LS/PAM

Firstly, the raw material of loess powders was ground and sieved with 100 meshes, which afforded the powders of loess soil (LS).

Secondly, loess/polyacrylamide composite (LS/PAM), was prepared by in-situ polymerization of acrylamide: 12 g of loess soil (LS) was dispersed uniformly in 30 mL of distilled water with stirring for 30 min at room temperature. Then, 4 g of acrylamide (AM), 0.03 g of N,N-methylene-bis acrylamide (MBA) were added and stirred for 30 min at room temperature. The mixture was heated to 45 °C under stirring. After adding 0.05 g of ammonium persulfate (APS), the temperature was raised to 75 °C and the mixture was stirred for 60 min under continuous stirring, which afforded a gel-like solid. In order to remove unreacted monomers, the gel-like solid was washed by H2O, and EtOH, respectively. Finally, the product was cut into small pieces and vacuum dried at 50 °C for 10 hrs, which afforded loess/polyacrylamide composite (LS/PAM).

2.3. Characterization

Following equipment was used to characterize the obtained particles, including FT-IR (DIGILAB-FTS-3000 spectrophotometer), thermogravimetric (TG) and differential thermal analysis (DTA) (PerkinElmer, Pyris Diamond), and scanning electron microscope (SEM) (ULTRA Plus, at 5 kV, Germany). FT-IR spectra were recorded between 4000 and 400 cm\(^{-1}\) through the KBr method with a FTS - 3000 spectrophotometer. The morphology of loess particles was observed using a SEM microscope.

3. Results and discussion

As we know, polyacrylamide (PAM) are a relatively cheap and widely commercially relevant cationic polymer utilized mainly for water treatment due to its high efficiency and rapid dissolution, which show eminent application prospect in sewage treatment [10], such as adsorbent [11], green flocculent [12,13], or catalyst [14]. One of the largest uses for polyacrylamide is to flocculate solids in a liquid. This process applies to water treatment, and processes like paper making and screen printing. Polyacrylamide can be supplied in a powder or liquid form, with the liquid form being subcategorized as solution and emulsion polymer. Polyacrylamide can adsorb solid particles suspending in polluted water to make particles aggregate and form precipitates. Therefore, it can accelerate the settlement of the particles in the suspension, and obviously speed up solution clarification and the effect of filtration [15]. Being compositied with natural polymers [16] or synthetic inorganic materials and mineral materials [17], its activity or selectivity could be improved [18]. For example, Amino functionalized polyacrylamide was grafted on magnetite nanoparticles via surface -initiated atom transfer radical polymerization (ATRP) [19]. Liu et al [20] reported that Al(OH)\(_2\)- polyacrylamide chemically modified with dithiocarbanates was synthesized using formaldehyde, diethylenetriamine, carbon disulfide, and sodium hydroxide for rapid and efficient removal of Cu\(^{2+}\) and Pb\(^{2+}\). Ramirez-Muniz et al [21] had prepared goethite- PAM composite by immobilizing goethite (iron oxides) on the PAM hydrogel, and PAM hydrogel was prepared vie in-situ free radical polymerization using MBA as crosslinking agent. They also found that the immobilization of goethite on the PAM hydrogel reduces the specific surface area of the composite, compared with the powder goethite, which slightly affects the arsenic adsorption capacity. Wang et al reported the synthesis of polyacrylamide intercalated molybdenum disulfide composites (PAM/MoS\(_2\)) by a simple hydrothermal method for the efficient elimination of Cr(VI) from aqueous solutions [22]. They found that Cr(VI) ions were firstly adsorbed onto the surfaces of the composites by electrostatic attraction, and then entered into the interlayer and combined with amide group at the interlamination of the composites. Saad et al [23] reported that the ordered mesoporous silica (MCM-41) could be grafted with polyacrylamide(PAM) through in situ
radical photopolymerization process. The obtained composite was then employed for the uptake of Hg(II) from aqueous solutions, and its maximum adsorption capacity got to 177 mg/g at condition of 25 °C and pH 5.2.

Functional materials could be prepared by modifying or compositing PAM. However, most of costs were high. Therefore, one of developing direction is prepare an efficient and inexpensive functional polymer materials. Loess soil, a yellow soil with the uniform particle size and the porosity of the porous, is a green natural material of richness. In China, the Loess Plateau covers almost all the northwestern region and parts of others. Although its adsorption activity was investigated [24], there are few reports about loess composites. In the present study, in order to get a novel polymer adsorbent with low-cost, a loess soil compositing polymer, loess/polyacrylamide composite (LS/PAM), was prepared by in-situ polymerization, and characterized by IR, TG and TEM.

**FT-IR spectra:** Loess/polyacrylamide composite (LS/PAM) and its materials (LS) were characterized by FT-IR spectra, and results are showed in Figure 1. In the spectrum of LS, a broad absorption peak at 1037 cm\(^{-1}\) is assigned the Si-O-Si stretching vibrations. And the sharp peak at 797 cm\(^{-1}\) corresponds to the quartz [25]. In the spectrum of LS/PAM, some characteristic peaks of LS are remained near 1037 cm\(^{-1}\) and 797 cm\(^{-1}\). And some characteristic peaks of polyacrylamide appears too. The peak at 1685 cm\(^{-1}\) is attributed to the stretching vibration of -C=O, and peaks at 1645 cm\(^{-1}\), 3184 cm\(^{-1}\) is corresponding to the deformation vibration and characteristic absorption peak of -NH\(_2\) [26]. The results suggest that polyacrylamide was composited with loess successfully.

**TG analysis:** Loess/polyacrylamide composite (LS/PAM) and its materials (LS) were characterized by thermogravimetric (TG) and differential thermal analysis (DTA), and results are showed in Figure 2. In TG curve of LS/PAM, the physically adsorbed water was quickly escaped below 100 °C. The interlayer water and bound water were lost slowly above 100 °C, and 5% weight was lost totally. In TG curve of LS/PAM, there are two stages of mass loss. The initial 5% of weight was lost below 100 °C, which is attributed to the escape of physically adsorbed water. The second weight loss in 250 ~ 350 °C was related to the decomposition of carboxyl group; and the last weight loss is associated with the breakage of polymer chain. DTA showed two well-differentiated exothermic peaks at 300 ~ 350 °C, which coincided with the pyrolysis of the organic matter.

**SEM images:** The micromorphology of loess/polyacrylamide composite (LS/ PAM) and its materials (LS) were characterized by SEM (Figure 3). Loess soil look like to be united by small particles. In SEM image of LS/PAM, the surface of LS particles are covered and linked by polymer film of PAM. It indicates that loess was composited with polyacrylamide uniformly.
Based on above characterization, it concludes that polyacrylamide was composited with loess successfully. In another side, the polyacrylamide molecular chain contains a large amount of amide groups, which have good water solubility, excellent flocculation performance and adsorption properties. It can be form hydrogen bonds with many substances use affinity or adsorption. Therefore, it show eminent application prospect in sewage treatment.

The adsorption behaviors of LS/PAM were investigated with removing lead ions in aqueous solutions. The results showed that the removal rate of lead ions was more than 98 % under optimal conditions. That means a novel low-cost loess based polymer composites adsorbents was successfully prepared.

4. Conclusions
Loess soil (LS), a kind of rich soil in the world, was used as materials, acrylamide as functional monomer, a novel low-cost inorganic minerals/polymer composite, loess/polyacrylamide composite (LS/PAM), was prepared by in-situ polymerization. And it was characterized by infrared spectra,
thermogravimetric analysis and scanning electron microscope. It indicates polyacrylamide was uniformly composited with loess successfully, which afforded a novel low-cost loess-based polymer composites adsorbents.

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