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Insight into the impact of interaction between attapulgite and graphene oxide on the adsorption of U(VI)

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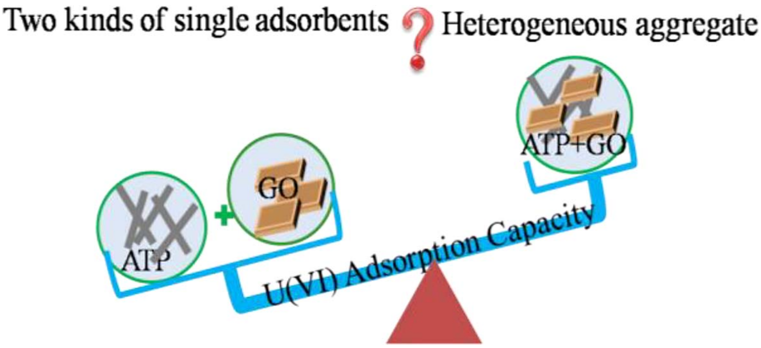
HIGHLIGHTS

- Interaction between GO and APT inhibited U(VI) adsorption onto GO.
- The adsorption of U(VI) onto APT and APT + GO were influenced by time, pH, and ionic strength.
- Surface complexation, ion exchange and electrostatic attraction were in the interaction process between GO, APT and U(VI).

GRAPHICAL ABSTRACT



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ABSTRACT

The broad production and extensive application of graphene oxide (GO) possibly raised concern over their potential environmental impacts. In this work, attapulgite (APT) as a typical fibrillar mineral was chosen to investigate the impact of interaction between APT and GO on the adsorption of U(VI). The adsorption capacity order was GO > APT + GO > APT, which achieved from adsorption isotherms, indicating adsorption capacity was related with interaction between APT and GO. Then systematical investigation on U(VI) adsorption at various environment factors (time, pH, and ionic strength) was employed on single adsorbent (APT) and heterogeneous aggregate (APT + GO). Adsorption kinetics displayed both U(VI) adsorption on APT and APT + GO were better fitted with pseudo-second-order kinetic model than the first-order kinetic model. The solution pH had a great influence on interaction between APT and GO. Ionic strength had more influence on U(VI) adsorption on APT than APT + GO, indicating outer-sphere surface complex was important on U(VI) adsorption on APT. The interaction mechanism between GO, APT and U(VI) was further investigated by spectroscopy and morphology analysis. This study provided new insights into the impact of interaction between minerals and GO on the adsorption of pollutant.

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1. Introduction

Large amounts of radioactive wastewater containing uranium have been released into the environment with the rapid development of nuclear energy [1–3]. It is necessary to remove U(VI) ions from contaminated wastewater to protect human beings and environment [4–8]. Attapulgite (APT), a hydrated magnesium aluminum silicate present in nature as febrile mineral, has been widely used as adsorbent in the removal of pollutant [9], due to its favorable physical and chemical properties such as moderate cation exchange capacity, rapid hydration rate, and excellent salt resistance [10]. Numerous researches indicated that the adsorption capacity of APT was largely affected by solution chemistry (e.g., ionic strength, pH, and natural organic matter) [9,11–13]. For example, Fan's work indicated that the adsorption of Eu (III) on APT was highly affected by the pH and ionic strength, and independent of temperature while the effect of fulvic acid/humic acid on Eu(III) adsorption differs with different pH [10]. Various environment factors including pH, contact time and initial concentration for methylene blue adsorption on APT were systematically investigated by Liu et al. [9]. These researches displayed that solution chemistry had a significant impact on the APT adsorption capacity.

Beside solution chemistry, co-existing colloid in real water environments is another vital factor that can affect the adsorption capacity of the adsorbents. Graphene oxide (GO) with the high surface areas possesses abundant oxygen containing functional groups, which lead to high adsorption capacity toward U(VI) from aqueous solutions. In fact, many studies have focused on using GO as an adsorbent to remove U (VI) from aqueous solutions, manifesting that GO would be very suitable materials for adsorption of U(VI) [4,14,15]. With the widespread application of GO and GO-based materials, GO will be released into the environment easily [16–18]. Interaction between GO and minerals is inevitable once they are released into water environments which is critical in determining the fate and transport of GO [19–21]. Indeed, over the past few years, great efforts have been devoted to investigating interactions between minerals and GO. Zhao et al. provided insights into the governing mechanism of GO-goethite heteroaggregation [22]. Zou et al systematically studied the coagulation of GO on Mg/Al layered double hydroxides using batch experiments and theoretical calculation to simulate the property of GO nanosheets in aquatic [23]. Chowdhury et al. investigated the interactions of GO with silica surfaces using a quartz crystal microbalance with dissipation monitoring [24]. These results provided constructive guidance to understand the interaction between GO and minerals.

In view of the widespread co-existing colloids in natural aquatic systems, the interaction between minerals and GO can easily occur and it would impact on adsorption capacity of GO [16,19,25]. Besides, it is expected that the interactions of GO with minerals would alter its mobility, bioavailability, toxicity, and subsequently environmental risks. Hence, it is not only important to understand the interaction mechanisms but also the fate of GO in natural environments to investigate of interaction between metal ion and GO in the presence of minerals colloidal systematically. Ren et al. established the relationship between GO and the co-adsorption of Cd(II) and phosphate [25]. Results revealed that these interactions subsequently affect the GO colloidal behavior. Yu et al. demonstrated the individual and mutual removal mechanism of GO and Cu(II) on titanium dioxide. However, these studies did not focus on how the interaction between minerals and GO affect on its adsorption capacity [16]. Actually, interactions between minerals and GO are highly likely to occur simultaneously when GO as an adsorbent for removal pollution. Up to date, little study has been focused on the effect of interaction between GO and APT on the adsorption of uranium.

In this study, we have explored the influence of interaction between APT and GO on the adsorption of U(VI) under different environment conditions (pH, ionic strength and time). The experimental equilibrium was analyzed using Langmuir and Freundlich models, and the adsorption kinetic was investigated by three kinetics models. The mechanism of the interaction between U(VI), GO and APT was identified by spectroscopy and morphology analysis.

2. Materials and methods

2.1. Materials and chemicals

APT was purchased from Kaidi Co. (Gansu, China) and first calcined at 180 °C for 5 h to remove organic compounds. Then, the sample was dispersed into 1 M HCl solution and stirred for 48 h to release more surface hydroxyl groups. The as-prepared APT was thoroughly washed with distilled water with up to pH 6.0. Finally, the wet solid was dried at 110 °C for 24 h [26].

GO was prepared by the modified Hummers method [27] from the natural flake graphite (average particle diameter of 38–44 μm, 99.95% purity, Qingdao Tianhe Graphite Co. Ltd., China) using concentrated H_2SO_4 and $KMnO_4$ to oxidize the graphite layer. The oxidized graphite layers were exfoliated under ultrasonication. 30% H_2O_2 was added in the suspension to eliminate the excess MnO_4^-. The desired products were obtained by rinsing with plenty of deionized water. The purification of GO was performed in a dialysis tube (500 Da, molecular weight cutoff) for about 24 h. The hydrodynamic diameter (D_h) of GO was about 430 nm (Fig. S1).

All chemicals were analytical grade, and all solutions were prepared using Milli-Q water. The U(VI) stock solution (60 mg/L) was prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ in 0.01 M HNO_3 solution.

2.2. Characterization of GO and APT

The zeta potential and D_h of the samples were measured at 25 °C using a Zetasizer Nanosizer ZS instrument (Malvern Instrument Co.). The scanning electron microscope (SEM) images were recorded on a field-emission SEM (FEI Quanta 200 FEG SEM). X-ray photoelectron spectra (XPS) were collected on an X-ray photoelectron spectrometer (ESCALAB250Xi, Thermo Scientific). A Shimadzu UV-2550 spectrophotometer was used to obtain ultraviolet–visible (UV–vis) absorption spectra of GO. The spectrophotometer (V-1600 Mapada, Shanghai) was used to detect U(VI) concentration. Fourier transform infrared (FT-IR) spectroscopy was performed, with spectra acquired at 8 cm^{-1} resolution under N_2 purge. The concentration of dissolved Mg in the APT suspensions as a function of the pH value was determined using inductively coupled plasma (ICP-6300, Thermo Fisher Scientific).

2.3. Batch experiments

The attachment experiments for GO onto APT were performed in 10 mL glass screw-cap tubes at 25 °C. 10 mL tube already contained APT (1.0 g/L) suspension, deionized water and GO suspension. The mixtures were shaken for 24 h and got heterogeneous aggregate (APT + GO). Then APT was separated from water after centrifugation (3000 rpm, 10 min). After centrifugation, 4.0 mL of supernatant was carefully moved to another vial and GO concentrations in the supernatants (C_e) were determined using UV–vis spectrophotometer. The standard curves for GO were plotted and depicted in Fig. S2.

For the adsorption of U(VI) experiments, negligible amount of solutions with 0.1–1.0 M HCl or NaOH were added into polyethylene centrifuge tubes (10 mL) to adjust pH values. The tubes were shaken on an oscillator for 24 h to reach adsorption equilibrium. The adsorption of U(VI) (10 mg/L) on APT (1.0 g/L) in the presence of various amounts of GO (13.3, 26.6 and 39.9 mg/L) from pH 2 to 10 were investigated at 298 K. The adsorption isotherms of U(VI) on single adsorbent (APT or GO), APT (1.0 g/L) and GO (26.6 mg/L) suspensions were obtained with various initial U(VI) concentrations under aqueous solution pH value of 5.0. The influence of addition sequences on the co-adsorption behavior of U(VI) on GO and APT were studied at pH 5.0. The addition