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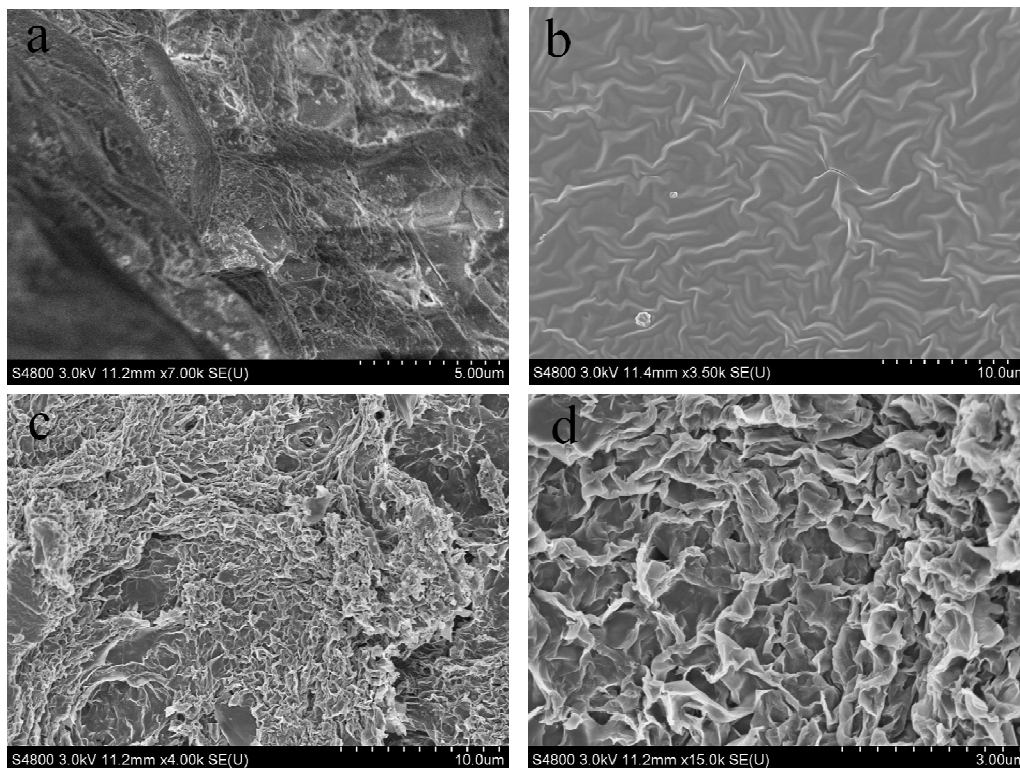
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GO firmly planted on the surface of quartz sand, will not fall off and have secondary pollution. Through a series of experiments show that the GO coated sand (GOS) granules has a strong adsorption performance for organic matter and heavy metal ions.



SEM micrographs of NS (a), KHS (b) and GOS (c)(d).

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PAPER

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Graphene oxide coated quartz sand as a high performance adsorption material in the application of water treatment

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In order to increase the water treatment performance, the quartz sand filter medium was improved by surface modification using 3-aminopropyltriethoxy silane coupling agent (KH550), then GO was grafted to the surface of sand through the chemical reaction between the functional groups. The interfacial interactions between quartz sand surface and GO were studied. Fourier-transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) analyses showed that the GO binds strongly to quartz sand surface. Scanning electronic microscopy (SEM) observation showed that a thin GO layer was formed on the surface of modified quartz sand. The modified sand was used as sorbent for the removal of turbidity, organic matter, Cd(II) and Pb(II) ions from large volumes of aqueous solutions. The results indicate that the GO play an important role in improving the water treatment performance of quartz sand filter.

1. Introduction

Pollution of the freshwater systems by the industrial and agricultural waste has become one of the key environmental problems.¹ Among all water contaminations, organic matter and heavy metals ions can cause severe health problems in humanity and animal beings.² For example, excessive Pb²⁺ could lead to a wide range of health problems, such as nausea, convulsions, coma, renal failure, cancer, and negative effects on metabolism and intelligence.^{3,4} Excessive Cd²⁺ could also cause a range of diseases, including hemochromatosis, gastrointestinal catarrh, cramps in the calves, skin dermatitis, brass chills⁵ and Wilson disease.⁶ Many methods or technologies such as chemical precipitation, membrane processes, ion exchange, electrolysis, adsorption processes have been developed to remove the contaminations from wastewater.^{7–11} However, each method has been found to be limited by cost, complexity, efficiency as well as by secondary waste.² Among these technologies, adsorptive removal of organic matter and heavy metals is widely applied because this method is easy to handle, relatively low cost, and effective at low concentration.¹² Especially, the developments of nanoscience and biological science for organic matter and heavy metal removal have received remarkable attention due to their special features.¹³

Following the discoveries of fullerene and carbon nanotubes (CNTs) in earlier decades, the emergence of graphene with its combination of extraordinary physical properties has opened up an exciting new field in the science and technology of two-dimensional (2D) nanomaterials.¹⁴ Graphene's unique structural elements, including being a single two-dimensional and extensively conjugated, endow it with advantageous thermal

conductivity,¹⁵ unique electric¹⁶ and mechanical properties,¹⁷ excellent mobility of charge carriers.¹⁸ Research has revealed that graphene has exhibited better adsorption behavior for heavy metal ions and fluoride than nanotubes.^{19–20} Unlike carbon nanotubes, which require special oxidation processes to introduce hydrophilic groups to improve metal ion sorption, the preparation of graphene oxide (GO) nanosheets from graphite using Hummers method introduces many oxygen-containing functional groups such as -COOH, -C=O, and -OH, on the surfaces of GO nanosheets. These functional groups are essential for the high sorption of heavy metal ions.

Natural quartz sand (NS) is widely used for processes of the magnitude of municipal water supplies to small domestic water filters, particularly as packed bed filters. History, affordability and the granular nature of sand that forms filter beds have popularized sand-filtration (SF). Indeed, early Indian and Greek writings dating back 6000 years refer to sand and gravel-filtration as means to securing clean water and currently are a water purification process endorsed by the World Health Organization. Of the two broad classifications of SF, fine-SF has higher retention of pathogens, organic matter, and heavy metal ions but has low throughput. Although the production rates are higher for the more popular coarse-SF, the absence of functionality and nanostructures limit pathogen, organics and heavy metal ions retention.^{21–23}

In Zhao's study,²⁴ few-layered GO nanosheets were synthesized from graphite using the modified Hummers method, and were used as sorbents for the removal of Cd(II) and Co(II) ions from large volumes of aqueous solutions. The results

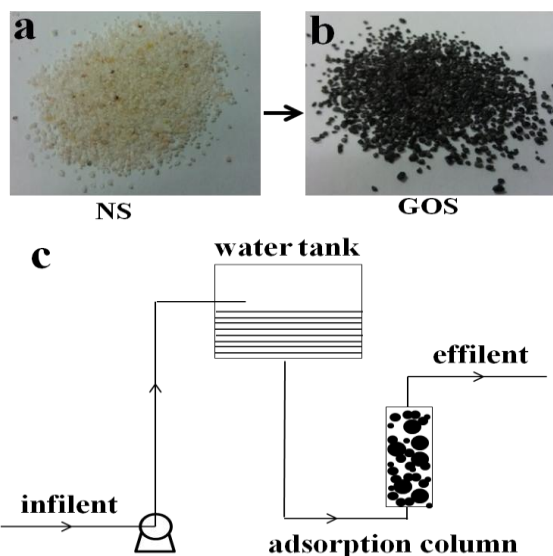


Fig. 1 Photographs of NS (a) and GOS (b). Schematic diagram of the experimental set-up (c).

indicated that abundant oxygen-containing functional groups on the surfaces of GO nanosheets played an important role on Cd(II) and Co(II) sorption. Gao²⁵ demonstrated a simple technique for conversion of regular filtration sand into “core-shell” GO coated sand (GO-sand) granules by assembling water dispersible graphite oxide on sand grains. The results showed that the nanostructured GO-coated sand retains at least 5 fold higher concentrations of heavy metal and organic dye than pure sand. In this study, assembly process essentially consists of physical mixing of the water dispersible GO colloids with sand, followed by a mild heat treatment that causes the nanosheets to adhere to each other over the sand surface, likely through van der Waals interaction. Due to the combination of graphene and sand is simply the physical effect, so in the process of water treatment, graphene is easy to fall off the sand cause secondary pollution.

In order to solve the problem mentioned above, the surface modification of natural quartz sand was made by using 3-aminopropyltriethoxy silane coupling agent (KH550), then the surface functional groups of quartz sand reacted with modified GO, the color has gone from white to black (Fig. 1). So GO firmly planted on the surface of quartz sand, will not fall off and have secondary pollution. Through a series of experiments show that the GO coated sand (GOS) granules has a strong adsorption performance for organic matter and heavy metal ions.

2. Experimental

2.1 Materials

Graphite powder (20 mm), concentrated H₂SO₄, SOCl₂, KMnO₄, N,N-dimethylformamide (DMF), pyridine, 3-aminopropyltriethoxy silane coupling agent (KH550) and natural quartz sand were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2 Synthesis of acyl chloride-functionalized GO (GO-Cl)

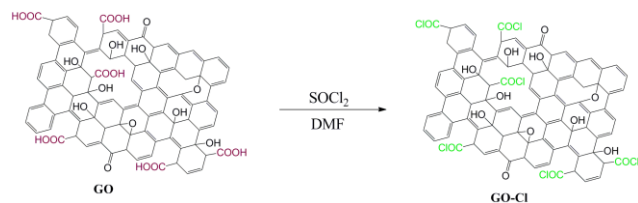


Fig. 2 Synthesis route of GO-Cl.

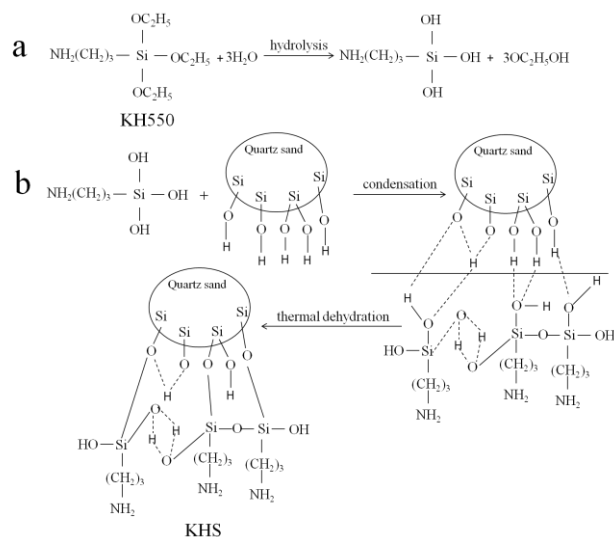


Fig. 3 The action mechanism of KH550 on the surface of quartz sand.

GO was fabricated from graphite powder (GP) by oxidation with KMnO₄ in concentrated H₂SO₄, followed by hydrolysis, washing and centrifugation, according to the modified Hummers' method.^{26,27} This procedure has been confirmed by AFM to yield GO sheets with majority of monolayer dispersed structures.

GO-Cl was prepared by reacting GO with SOCl₂.²⁸ As shown in Fig. 2, 50 mg GO was first sonicated in 20 mL of anhydrous DMF to form a homogeneous suspension, to which 50 mL SOCl₂ was added dropwise at 0 °C. GO-Cl was prepared by stirring at 0 °C for 2 h, and keeping stirring for 36 h at 70 °C. The obtained GO-Cl was collected by filtration through a PTFE membrane.

2.3 Preparation of quartz sand filter

The quartz sand filter with size fractions of 0.55 to 0.83 mm was obtained by dry-sieving through stainless steel sieves. The filter medium was boiled in deionized water for 30 min followed by washing several times with deionized water until the washed water no longer seemed turbid. Before being used, the cleaned filter medium was dried at 110 °C for 12 h. This procedure substantially eliminates the effect of any impurity on the filter medium surface.

2.4 Preparation of KH550-coated sand (KHS)

Synthesis route of KHS is show in Fig. 3. Firstly, 15% KH550 was added to alcohol-water solution to hydrolyze it sufficiently. The volume proportion of alcohol and water was 2:1. Secondly, the prepared quartz sand was added into above solution. The

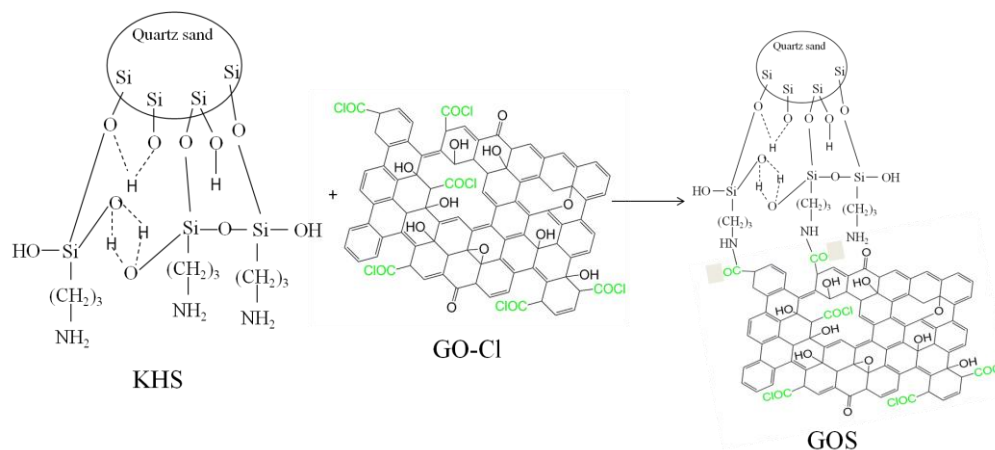


Fig. 4 Schematic illustration of the fabrication of GOS nanocomposite coatings

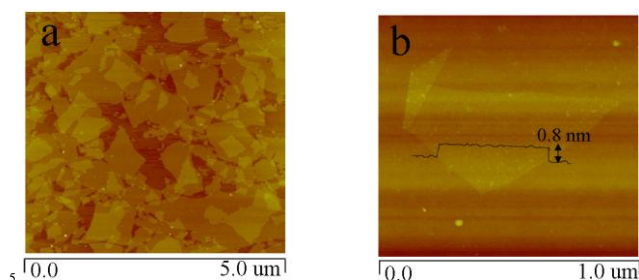


Fig. 5 AFM height image of GO on silicon wafer deposited from aqueous solution.

system was stirred and heated up to 70 °C using a water bath for 15 min followed by dried for 2.5 h at 110 °C. Thirdly, the reaction product was immersed in deionized water for 24 h and washed several times with deionized water to eliminate the influence of physical adsorption. Lastly, the surface modified filter was obtained by dried at 110 °C for 12 h.

2.5 Preparation of GOS

KHS was mixed with GO-Cl in pyridine, then stirring at 0 °C for 12 h. The coated sand was washed with distilled water until the runoff was clear, dried at 60 °C, and stored in capped bottles.

2.6 Column test on NS and GOS.

A mini-pilot-scale equipment was constructed and used in this study (Fig. 1c). For the column tests, the adsorption column (5.2 mm diameter *310 mm long) was filled with NS (Fig. 1a) or GOS (Fig. 1b), and the feed solution was flowed through the column at controlled flow rate, the eluted solution was continuous collected every 1 hour and the flow rate is 1 mL/min.

2.7 Characterization

Atomic force microscope (AFM) observation of GO sheets was recorded using a Veeco Digital Instrument Multimode V scanning probe microscope, in which samples prepared by spin-coating sample solutions onto freshly exfoliated silicon substrates. Fourier-transform infrared (FT-IR) spectra were recorded on a ProStar LC240 (Varian, USA). Scanning electron microscopy

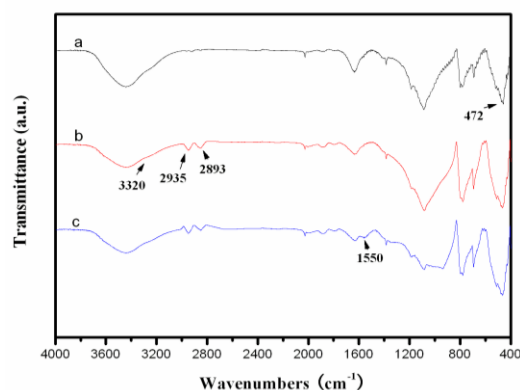


Fig. 6 FTIR spectra of NS(a), KHS(b) and GOS(c).

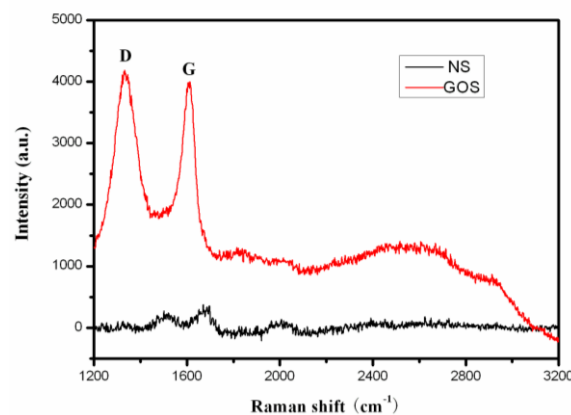


Fig. 7 Raman spectra of NS and GOS.

(SEM) images were taken on a Hitachi S-47000 field-emission SEM system. Thermal gravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 6 TGA instrument at a heating rate of 20°C min⁻¹ under nitrogen flow. Raman spectra were collected on a Jobin-Yvon Raman spectroscopy equipped with a 514 nm laser source (HR800, france). The turbidity was measured with a turbidimeter Hanna model HI93703. Dissolved

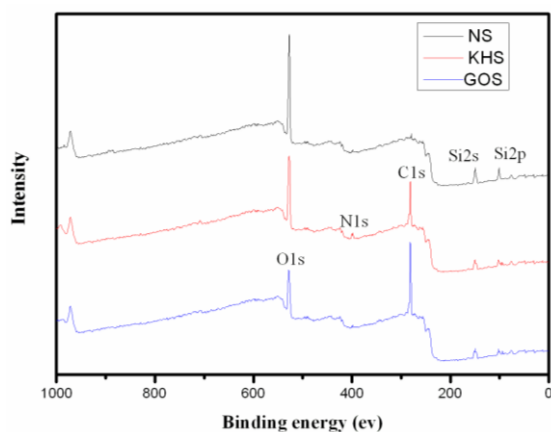


Fig. 8 XPS spectra of NS, KHS and GOS.

Table 1 Results of elemental analysis by X-ray photoelectron spectroscopy on the modified and unmodified quartz sand filter.

Element	NS	KHS	GOS
Si(%)	29.25	20.56	12.36
O(%)	70.75	47.76	35.21
C(%)	-	31.68	52.43
N(%)	-	0.22	0.14

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organic carbon (DOC) was measured with TOC analyzer (TOC-VCPH, Shimadzu, Japan). UV_{254} was measured with spectrometer (UV754, CANY, China). The concentrations of Cd^{2+} and Pb^{2+} were determined by ICP-MS.

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3. Results and discussion

3.1 Synthesis and characterization of GO and GOS.

The concentration of carboxylic acid groups in the GO was estimated by acid-base titration. Before titration, the GO were stirred in water for 2 days under argon and collected via filtration to remove acid residue. In a typical titration experiment, pretreated GO (80 mg) were stirred in 50.00 mL of 0.05 M aqueous NaOH solution under argon for 48 h. The mixture was filtered through a 1.2 μm pore-size membrane and washed with deionized water until the filtrate was neutral. The combined filtrate and washings were titrated with 34.50 mL of 0.05 M aqueous HCl solution to reach the neutral point (pH= 7.00), as monitored by a pH meter, and thus the content of acidic sites in the GO is calculated to be 0.78 mmol. The carbon content of the GO is estimated to be 6.67 mmol by assuming that the GO is solely composed of carbon, and thus the molar ratio of the acidic sites in the GO sample is 11.6%.

In our experiments, GO-Cl was firstly synthesized from GO (Fig.2), because the acyl chloride on the surface of GO are highly reactive. It is easy to react with modified sand, so GO can binds strongly to the surface of quartz sand (Fig.4). The molecular formula of KH550 modifier and its chemical changes during hydrolysis are shown in Fig. 3a. During hydrolysis of the silane, the $SiOC_2H_5$ group will transform into Si-OH. We hypothesize that the surface modification mechanism is carried on the mode

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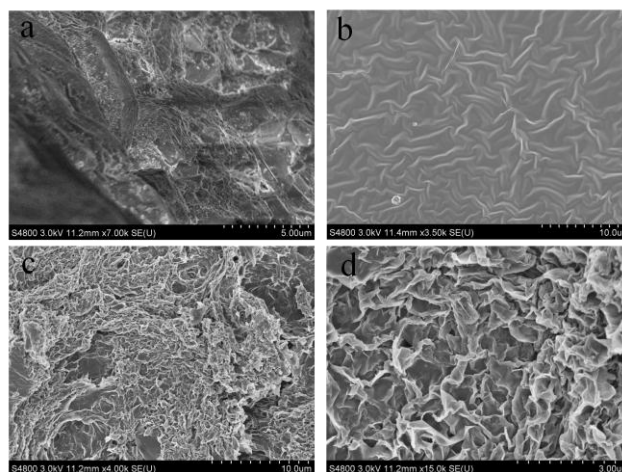


Fig. 9 SEM micrographs of NS (a), KHS (b) and GOS (c)(d).

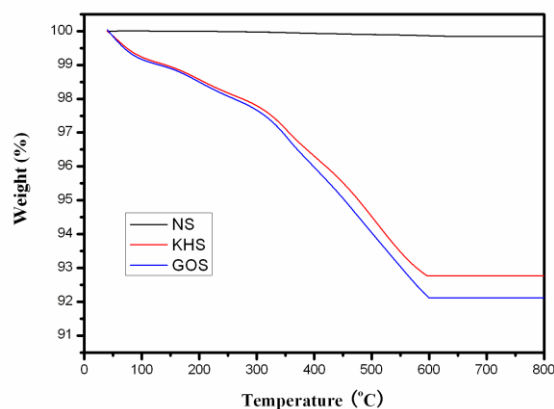


Fig. 10 TGA curves of the NS, KHS and GOS.

40 given in Fig. 3b.²⁹

AFM is a direct method to characterize the morphologies and the thickness of GO. Fig. 5 shows the tapping mode AFM images of GO. The thickness of GO is about 0.8 nm (Fig.5b), which agrees with other researchers' reports,^{30,31} suggesting the complete exfoliation of graphite oxide into individual GO sheet.

The FTIR spectra of NS, KHS and GOS are shown in Fig. 6. From Fig. 6a we can see the asymmetry stretching vibration and deformation vibration of Si-O-Si at 1200 cm^{-1} to 1100 cm^{-1} and 472 cm^{-1} , which indicated the formation of quartz sand filter. From Fig. 6b we can see that the absorption peaks at 2935 cm^{-1} , 2893 cm^{-1} and 3320 cm^{-1} ascribed to asymmetry stretching vibration, symmetry stretching vibration of C-H and stretching vibration of N-H, respectively, which demonstrates that KH550 exists in quartz sand surface. In the spectra of Fig. 6c, the characteristic absorptions of amide II (at 1550 cm^{-1}) were clearly observed, it can be concluded that the GO has been incorporated into the surface of sand. Moreover, the physical adsorbed KH550 and GO were washed with deionized water for several times in

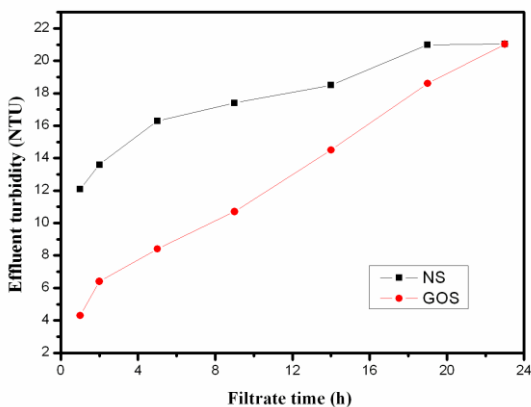


Fig. 11 Turbidity removal efficiency of NS and GOS

surface modification process, so the physical adsorption between quartz sand and GO can be eliminated.

The Raman spectra of GOS sample in Fig. 7 show the characteristic peaks located at 1339 and 1598 cm^{-1} corresponding to the D and G bands of graphene sheets, respectively,³² while barely any features are obtained from NS spectrum.

In this work, XPS analysis of the quartz sand before and after surface modified were employed to confirm the interface bonding way between graphene and the quartz sand surface. The results of the XPS analyses are shown in Fig. 8. Table 1 shows the detailed data corresponding to Fig. 8. It is shown in Fig. 8 that nitrogen and carbon content are not present at the surface of the unmodified quartz sand. In contrast, KHS contains nitrogen and carbon. Furthermore, there is a significant depletion in oxygen content and a slight decrease in silicon content on the KH550 modified quartz sand surface in comparison to the unmodified quartz sand, while for GOS, the carbon content increased to 52.43. This is further affirmed that the GO is well bind to the surface of quartz sand.

Fig. 9 corresponds to SEM images of NS, KHS and GOS. Specifically, Fig. 9a shows the extremely rough and uneven of the unmodified quartz sand surface, while the KH550 modified quartz sand surface possesses comparatively a flatter surface (Fig. 9b) due to a thin layer of KH550 grafted on the surface of quartz sand filter. In the Fig. 9(c) and (d), we can see that a lot of graphene coating on the surface of quartz sand and more tiny pores appear on its surface. This result is accordant with the analyses results of XPS and FT-IR.

TGA curves of the NS, KHS and GOS are shown in Fig. 10. The TGA data for GOS showing a weight loss of ~8.0% contrasted with that of NS. Comparatively, 7 % weight loss of KHS could be observed, which can strongly prove that GO has grafted on the sand surface.

3.2 Effectiveness of the GOS for pollutants removal

3.2.1 Turbidity removal

In order to investigate the performance of the new material in the field of water treatment, its removal to turbidity was studied (Fig.11). The turbidity of raw water is 21.03 NTU. The result

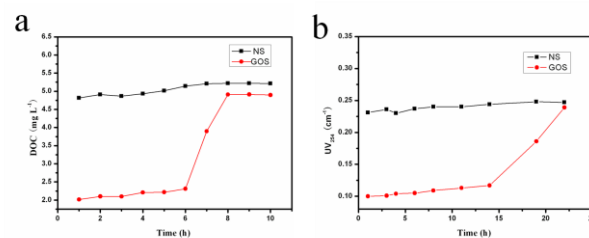


Fig. 12 Removals of DOC (a) and UV₂₅₄ (b)

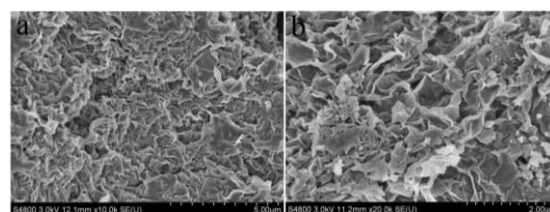


Fig. 13 SEM micrographs of GOS (after water treatment).

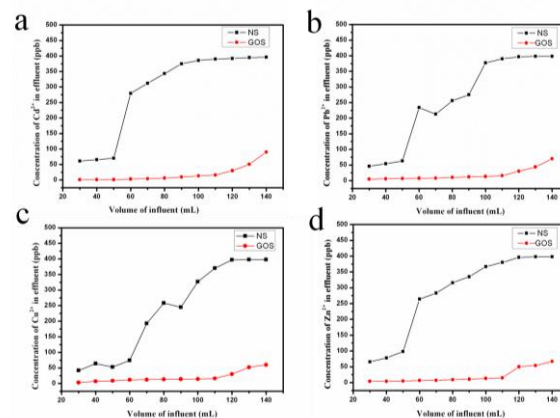


Fig. 14 Cd²⁺ (a), Pb²⁺ (b), Cu²⁺ (c), and Zn²⁺ (d) removal efficiency of NS and GOS

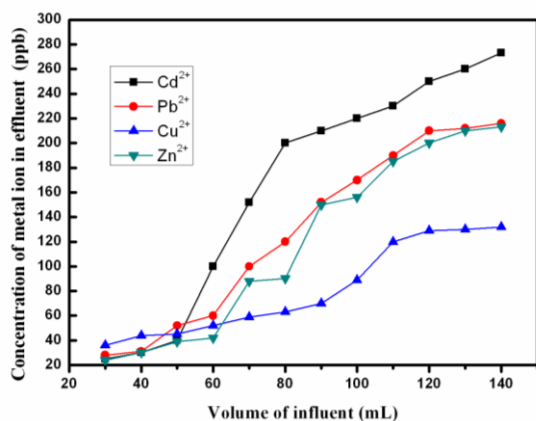
showed that as compared with NS filter media, the GOS is more efficient in treatment of water. The turbidity removal efficiency of GOS is about 38% higher than NS. This may be because of the introduction of GO make the surface of quartz sand has more holes and raise the dirt holding capacity.

3.2.2 Organic matter removal

Total organic matter in water might be classified into particulate organic fraction and dissolved organic fraction. Particulate organic matter (POM) could be easily removed even through the sand-filtration; whereas dissolved organic matter (DOM) is one of the major concerns in drinking water treatment due to its difficulty to be removed. During the experiments, the raw water had average dissolved organic carbon (DOC) and UV₂₅₄ concentrations of 5.398 mg L^{-1} and 0.248 cm^{-1} , respectively. As shown in Fig. 12(a) and (b), DOC was reduced to 2.0 mg L^{-1} through the GO treatment and about 60% of the raw water UV₂₅₄ was removed at the beginning. Furthermore, it could be observed

Table 2 The removal efficiency of used GOS.

Time(h)	Turbidity (NTU)	DOC (mg L ⁻¹)	UV ₂₅₄ (cm ⁻¹)
1	8.4	2.55	0.132
2	9.2	3.24	0.148
5	10.5	4.01	0.152
7	11.2	4.25	0.167
9	13.8	4.31	0.171
12	14.9	4.73	0.182
15	15.7	4.81	0.193
18	17.5	4.85	0.198
21	19.6	4.96	0.216
23	20.6	5.02	0.221

**Fig. 15** Cd²⁺, Pb²⁺, Cu²⁺, and Zn²⁺ removal efficiency of used GOS.

that the removal efficiency of the GOS for DOM was rather stable during the 6 hours of operation. Therefore, it was reasonable to infer that the DOM was removed mainly through graphene on the sand. After experiment, the surface morphology of GOS has been included in Fig. 13. It is obvious that the GO didn't peel off from the sand. In addition, GO has a hydrophilic surface with plenty of oxygen-containing groups, and good dispersion in water. Both hydrogen bonding and π - π interaction were thought to be responsible for the adsorption of DOM on GO.

3.2.3 Adsorption of Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ by NS and GOS

In order to find out whether GOS sample could effectively adsorb heavy metal ions, adsorption studies were extended to Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺. Comparative study of NS and GOS were experimented (Fig. 14). Aqueous solutions (400 ppb) of Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ were prepared by dissolving Pb(NO₃)₂, Cd(NO₃)₂, CuSO₄ and ZnCl₂ in ultrapure water at 25 °C and pH 5, further diluted to the required concentration just before usage. The results revealed that both NS and GOS exhibit high adsorption capacity for Cd²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ when the influent volume is less than 50mL. It is obvious that the adsorption capacity of GOS was higher than that of NS during the experiment.

3.2.4 Recyclability of GOS

As an effective adsorption material, the adsorption recyclability has been studied. The above metal ions adsorbed GOS was

thoroughly rinsed with water and dried in a vacuum. Then it was put into a 10mL nitric acid solution at pH 1 for desorption. After two days, the metal ions was completely desorbed from the GOS, it was removed from the acid solution, thoroughly rinsed with water and dried in the freeze drier. The regenerated GOS was then subjected to repeated adsorption cycles as described above to investigate the recyclability of the GOS. The results in Table 2 and Fig. 15 show that the adsorption ability of GOS changed obviously during the continuous use. The decrease in adsorption ability can be attributed primarily to two factors: a decrease in the number of binding sites after each desorption step and the degradation of the GOS themselves.

4. Conclusions

In this work, we synthesized Graphene/sand composites using acyl chloride-functionalized GO and modified quartz sand, GO firmly combined in the surface of quartz sand by chemical bond. This creates a new kind of porous carbon-based multi-functional adsorption material. Through a series of adsorption test, we conclude that the nanostructured GO coating can significantly increase the retention of turbidity, organic matter and heavy metals over the parent sand granules. This kind of technique combine together the excellent function of nanostructures material with the traditional quartz sand, and have very widely applied foreground in the water treatment.

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Notes and references

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