Title: Removal of Hg（II）from desulfurization slurry by EDTA functionalized graphene oxide sheet: synthesis, adsorption mechanism and reproducibility

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Abstract: Ethylenediaminetetraacetic acid (EDTA) functionalized graphene oxide (GO) has been synthesized through a facile silanization reaction. The chemical composition and morphology of the EDTA-GO was investigated by Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy and Raman spectroscopy. To evaluate the effects of catalytic adsorptionof Hg(II) by EDTA-GO, bath catalytic adsorption studies were performed to optimize the major parameters such as pH values, initial concentration, temperature, contact time and the amount of adsorbents. The maximum uptake removal of Hg(II) was 93.35%. Moreover, the adsorption kinetics, isotherms and thermodynamics of Hg(II) were also investigated. Furthermore, the excellent reproducibility indicated that EDTA-GO has a promising application in desulfurization slurry treatment.

Keywords: Graphene oxide, Adsorption isotherm, Reproducibility.

1. Introduction

Mercury is a highly toxic metal that can accumulate in ecological systems and adversely influence the environment[1].Two main sources，from where these metals enter into waterways，are industrial discharges and particulates in the atmosphere[2].

It is believed that catalytic adsorption capacity of an adsorbent is affected mainly by the available surface area and complexity of the groups on its surface. Ethylene diamine tetraacetic acid (EDTA) is famous for forming stable chelates with metal ions[3,4]. Therefore, to develop more efficient and low-cost adsorbents for the catalytic adsorption of Hg(II) ions from aqueous solution, EDTA functionalized carbon disulfide modified GO (EDTA-GO) composite was prepared[5,6]. EDTA-GO is founded to be an ideal adsorbent for Hg(II) catalytic adsorption[7].

A new method was reported here to develop sorbents which combine the advantages of high surface area of GO and EDTA will be one of the most excellent ways to deal with heavy metal pollution. The synthesized EDTA-GO was characterized by SEM, FTIR, BET, XRD, EDS. The kinetic, isotherm and thermodynamic studies were carried out to investigate the catalytic adsorption interactions between EDTA-GO with Hg(II). Bath adsorption tests were discussed in details. The interference of coexistent metal cations and desorption of EDTA-GO were discussed. Through this work, an innocuous adsorbent EDTA-GO for Hg(II) catalytic adsorption was achieved and it may have potential application in desulfurization slurry treatment.

2. Experimental

Preparation of EDTA functionalized graphene oxide (EDTA-GO) In this experiment, an improved method was applied for the synthesis of EDTA-GO, which was named two step reaction syntheticism. About 300mg graphite power was taken and dissolved in 100ml deionized water, ultrasonic treatment for about 30min.Subsequently, ethylenediamine(0.5ml) dissolved in ethylalcohol(200ml) with slow stirring. Then gradually add the above mixed solution in to Homogeneous graphene aqueous solution with stirring, a maintaining the reaction temperature at 50℃， magneticstirring reaction for more than 12 h and cool down to the room temperature. This procedure was treated as the first step.

The second step which was called high temperature load procedure. Take the mixed solution obtained from the first step in teflon lined autoclave, ethylenediamine(0.5ml) , carbon bisulfide (0.5ml) added, a maintaining the reaction temperature at 80℃for about 12 h. Afterwards, when the Teflon lined autoclave

cool down to the room temperature, collect the reaction mixture. Finally, the product was washed by deionized water and desiccated by freeze-drying for further experiments.

3. Results and discussion

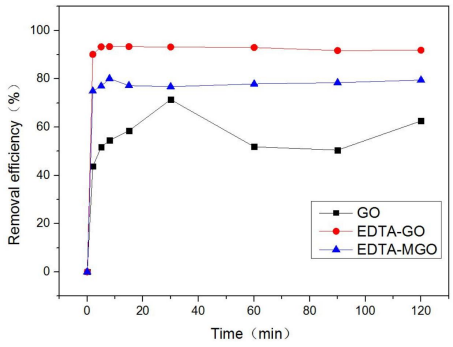

Figure 1. Effect of time and kinds of adsorbents on adsorption behavior of Hg(II):temperature=27℃； Hg(II) concentration=400ug/L; pH=7.

Table 1. Pseudo-first-order, pseudo-second-order and Elovich order rate constants for Hg(II) adsorption on EDTA-GO adsorbent

Pseudo-first-order			Pseudo-second-order			Elovich		
K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 ($gmg^{-1}min^{-1}$)	q_e (mg g^{-1})	R^2	A (mg g^{-1} min^{-1})	B （g mg^{-1}）	R^2
18.5	18.505	0.9891	0.8832	18.6392	0.9999	1.0681	4.0987	0.9788

4. Conclusions

The EDTA groups to the GO surface through silanization process can significantly increase the catalytic adsorption capacity of GO for Hg(II) in desulfurization slurry. The EDTA groups together with -OH and -COOH groups on the GO surface can make EDTA-GO an excellent catalytic adsorption adsorbent for removal of Hg(II).The XRD, SEM and XPS properties envidenced that EDTA were successfully loaded on the surface of GO. The adsorption was affected by various parameters such as intial concentration of Hg(II), pH values, contact time, and temperature.

Kinetic data showed a good correlation to a pseudo-second-order queation and the overall catalytic adsorption process of Hg(II) were controlled not only by intra-particle diffusion but involved some chemisorption. Intra-particle diffusion may be the rate-controlling step. Thermodynamic results illustrated that the catalytic adsorption process was endothermic and spontaneous. The regeneration tests showed that the adsorbents retained 89.58% of the initial adsorption capacity after four regeneration cycles.

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