Renewable Energy 71 (2014) 61–68

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Mercury adsorption from fuel ethanol onto phosphonated silica gel prepared by heterogenous method

Fujun Cao, Ping Yin*, Xiguang Liu, Chunping Liu, Rongjun Qu**

School of Chemistry and Materials Science, Ludong University, Yantai, Shandong 264025, PR China

ARTICLE INFO

Article history:
Received 6 July 2013
Accepted 13 May 2014
Available online

Keywords:
Adsorption
Fuel
Thermodynamics
Ethanol
Mercury ion
Heterogenous synthesis method

ABSTRACT

Ethanol is one of the most important renewable biofuels contributing to the reduction of negative environmental impacts generated by the worldwide utilization of fossil fuels, and the presence of metal ions in fuel ethanol has significant effect on the performance and the quality of fuel. In the present work, silica gel functionalized by poly(triethylenetetraminomethylenephosphonic acid) SG-Cl-T-P was successfully developed by heterogenous synthesis method, and the adsorption capacity of Hg(II) from fuel ethanol via SG-Cl-T-P was examined. The adsorption isotherms were fitted by the Langmuir model, the Freundlich model and the Dubinin–Radushkevich (D–R) model. Furthermore, the adsorption study was analyzed kinetically. The thermodynamic parameters, including the Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated, they were -3.24 kJ mol^{-1} (35 °C), 29.25 kJ mol^{-1}, and 106.20 J K^{-1} mol^{-1}, respectively.

1. Introduction

Due to air pollution, climate change and energy depletion, increasing global concerns were focusing on developing a kind of clean, renewable and sustainable energy system. Fuel ethanol is considered to be a good candidate because it has several physical and chemical properties similar to those of gasoline and diesel. Moreover, ethanol is biodegradable and renewable, which can be produced from renewable biomass resources, thereby attaining the independence from petroleum-based fuel. Therefore, ethanol is one of the most important renewable biofuels contributing to the reduction of negative environmental impacts generated by the worldwide utilization of fossil fuels, and there has been a rapid growth in demand for fuel ethanol since 2000 [1,2]. Rising oil prices, low accessibility of energy resources, environmental and climate warming concerns, interests in energy diversity and security have made fuel ethanol an attractive alternative, particularly in industrial countries [3,,4]. However, the presence of metal ions in fuel ethanol has significant effect on the performance and the quality of fuel, and metallic species in ethanol can accelerate the corrosion of engines or promote the formation of gums and sediments [5,6]. Therefore, cleaning treatment of fuel ethanol plays an important role for its effective utilization and engine maintenance, and it is essential to develop cost-effective treatment methods to remove metals from fuel ethanol. Adsorption is highly effective and economical, and is a promising and widely applied method [7–12].

Recently, silica gel was widely used as inorganic solid matrix in inorganic–organic composite materials due to the excellent mechanical and thermal stability, unique large surface area, a firm chemical union with metals and well-modified surface properties [13,14]. Such kinds of modified silica gel materials have received a great deal of attentions recently because of their superior properties and excellent performance in the field of chromatography, adsorption, and catalysis [15–18]. On the surface of active silica gel, there are a large number of silanol groups, which could react with silane coupling reagents that act as precursors for further immobilization of organic ligands [19]. The reaction of silane coupling reagents with surface silanol groups leads to the existence of desirable terminal functional groups on the surface of silica gel, where special chelating properties can be finally obtained, and this is mainly related to the structure of the organic ligands, the nature of the functional groups present and the incorporated donor atoms. Furthermore, it has been studied that the behaviors of these synthesized chemically modified silica gels used as adsorbents are mainly dependent on the presence of active donor atoms such as O, S and N of the incorporated organic moieties [20,21]. In a word, these inorganic–organic hybrid materials contain inorganic backbones and organic ligands that could selectively bind target metal ions. They could be used as effective adsorption and separation

* Corresponding author. Tel.: +86 535 6696162; fax: +86 535 6697667.
** Corresponding author.
E-mail addresses: yinping426@163.com (P. Yin), rongjunqu@sohu.com (R. Qu).

http://dx.doi.org/10.1016/j.renene.2014.05.028
0960-1481/

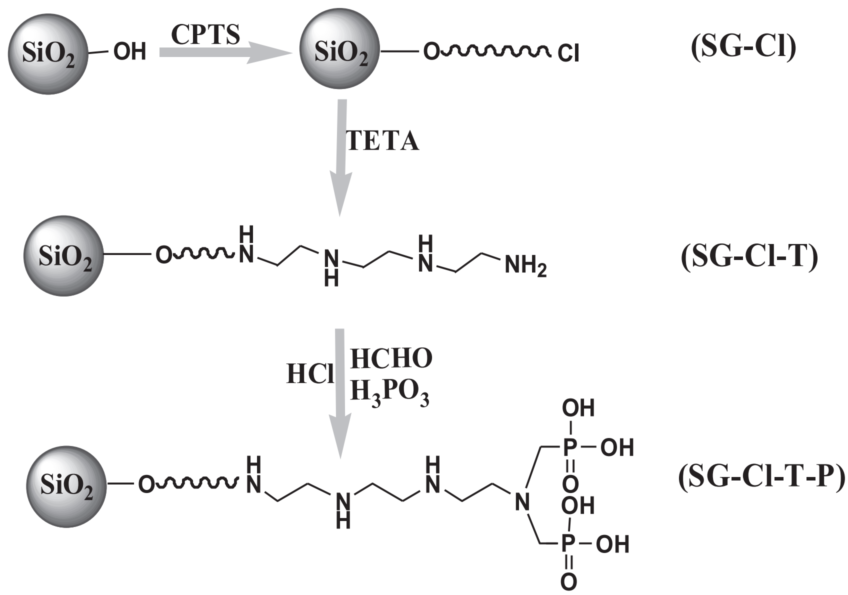

Fig. 1. Synthetic routes of SG-Cl-T-P by heterogenous method.

materials for selective heavy metal ions removal. Although it has been reported that modified mesoporous silica gels have strong adsorption capabilities for heavy metal pollutants, however, there are not many data about the removal of heavy metal from ethanol solutions [7].

In the present research, we explored silica gel chemically modified by organophosphonic acid SG-Cl-T-P by heterogenous synthesis method, and found that it had excellent adsorption capability for mercury ions from fuel ethanol solutions. The adsorption capacity of Hg(II) via SG-Cl-T-P was examined, and the experimental data were correlated to different kinetic and adsorption models, and the corresponding parameters were determined. Kinetic studies are important to understand the factors and transport mechanisms that influence Hg(II) interactions with an adsorbent, such as mesoporous silica gel chemically modified by aminophosphonic acid, and to determine the conditions the conditions that influence these interactions. Moreover, thermodynamic calculations of the adsorption process are needed to understand spontaneity, heat of adsorption and the mechanism of adsorption using different thermodynamic parameters.

2. Experimental details

2.1. Materials and instruments

Silica gel (SG) of chromatographic grade (80–100 mesh size) was obtained from Qingdao Silicon Create Fine Chemical Co., China. Organic solvents toluene was redistilled just before use. 3-Chloropropyltrimethoxysilane (CPTS) (Jianghan Chemicals Factory, China), triethylenetetramine (TETA) (Shanghai Chemical Factory, China) and the other reagents (Shanghai Sinopharm Chemical Reagent Co., China) were used without further purification. Stock solutions of Hg(II) (0.1 mol L^{-1}) were prepared by dissolving $HgCl_2$ in ethanol solutions. Porous structure parameters were characterized using an automatic physisorption analyzer ASAP 2020 (Micromeritics Instruments Corporation, USA) by BET and BJH methods through N_2 adsorption at 77 K. The N analysis of products was analyzed by elemental analyzer Vario EL III (Elementar Co, German). The morphology of the compounds was examined on JEOL JSF5600LV scanning electron microscope (JEOL Co., Japan), JEOL Co., Japan. The EDXAS was performed on a NORAN LEVER-2 EDX analytical instrument (Electronics Co., Japan). The concentration of Hg(II) was determined using a GBC-932A atomic absorption spectrophotometer (GBC Co., Australia), equipped with air–acetylene flame.

2.2. Preparation of SG-Cl-T-P by heterogenous synthesis method

The synthetic routes of SG-Cl-T-P by heterogenous synthesis method were presented in Fig. 1. Silica gels were activated with nitric acid aqueous solution (HNO_3:H_2O = 1:1) at refluxing temperature for 3 h, then dipped in the hydrochloric acid aqueous solution (HCl:H_2O = 1:1) at room temperature for 6 h, finally washed with distilled water and dried in muffle at 160 °C for 12 h. Under a nitrogen atmosphere, a mixture of 30.0 g of activated silica gel and 30.0 mL of CPTS were stirred at 96 °C in the 120 mL of toluene solution for 12 h, and then the solid was filtered off and transferred to a Soxhlet extraction apparatus for reflux-extraction in ethanol for 24 h. The solid product was dried in vacuum at 50 °C over 48 h, and it was referred to as SG-Cl.

Under a nitrogen atmosphere, a mixture of 20.0 g of activated silica gel and 46.7 mL of triethylenetetramine were stirred at 90 °C in the 200 mL of ethanol solution for 12 h, and then the solid was filtered off and transferred to a Soxhlet extraction apparatus for reflux-extraction in ethanol for 24 h. The solid product was dried in vacuum at 50 °C over 48 h, and it was referred to as SG-Cl-T. Fifteen grams of SG-Cl-T were added to 120 mL ethanol at room temperature for 12 h, then 3.0 g of paraformaldehyde, 8.4 g of phosphorous acid and 3.4 mL of hydrochloric acid were added. After being refluxed at 90 °C for 12 h, the final product (SG-Cl-T-P) was filtered off, then washed thoroughly with distilled water and finally dried under vacuum over 48 h at 50 °C.

2.3. Adsorption isotherms of Hg(II) from fuel ethanol by SG-Cl-T-P

The adsorption isotherms were investigated using 0.02 g of the adsorbent with various Hg(II) ion concentrations (0.5–4.0 mmol/L) and a contact time of 24 h and 15–35 °C. The concentration of Hg(II) was detected by means of atomic absorption spectrometer, and the adsorption amount was calculated according to Eq. (1):