Fuel 226 (2018) 331–337

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Comparison studies of adsorption properties for copper ions in fuel ethanol and aqueous solution using silica-gel functionalized with 3-amino-1,2-propanediol

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ARTICLE INFO

Keywords:
Silica-gel functionalized with 3-amino-1,2-propanediol
Copper ion
Ethanol
Aqueous
Adsorption

ABSTRACT

Silica-gel functionalized with 3-amino-1,2-propanediol (SG-AP) was used as adsorbent for the removal of copper ions from both aqueous and ethanol solutions. The adsorption isotherms and adsorption kinetics were comparatively investigated by using batch method. The static saturated adsorption amount for Cu^{2+} in ethanol is less than that in aqueous, indicating a much lower adsorption rate. The experimental data were fitted to pseudo-first-order and pseudo-second-order kinetic models. The results indicated that all the adsorption data in both solutions fitted well with the second-order kinetic model, implying that SG-AP is suitable to apply in the low initial concentration of copper ions in aqueous or ethanol solution. The adsorption isotherms were fitted by the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models. It was showed that the adsorption processes in both aqueous and ethanol solutions were favorable and Freundlich model was much appropriate. From the D-R isotherm model, the calculated mean free energy *E* showed that the adsorptions occurred in aqueous via physical processes, while those in ethanol mainly via chemical processes. Desorption study showed that SG-AP had good durability as well as good efficiency for repeated use.

1. Introduction

Increasing global concerns due to environmental pollution and the aggravation of the fossil fuel energy crisis have generated much interest in developing a clean, renewable and sustainable energy system. From this point of view, ethanol is considered to be good candidate as alternative fuel in the sparkignition engines [1,2]. Brazil is the most successful country in promotion of gasoline–ethanol fuel in vehicle, followed by USA, Canada and some European countries.

During the application of ethanol fuel, people found that it can corrode engine to be more serious than ordinary gasoline due to more metal ions including Cu, Pb, Ni and Fe contained in it. These metals ions were introduced to ethanol inevitably during the process of production, transportation, and storage [3–6]. Among the metal ions in ethanol, copper ions possess rather high concentration as well as much unfavorable impression to engine or environment. Some research showed that copper ions can catalyze the oxidation reactions of unsaturated hydrocarbons in gasoline with oxygen and with each other to form the significant gums, leading to fuel decomposition and poor engine performance [7]. Furthermore, copper and other heavy metal ions will be discharged into environment along with the exhaust gases, resulting in serious threaten to human beings and bio safety. Therefore, the removal of copper and other heavy metal ions in ethanol fuel became a key issue and drive people to explore novel adsorbents with low cost and high adsorption capabilities for metal ions in ethanol.

Brazilian researchers did some pioneer work on this issue. Gushikem was the first to report the adsorption and preconcentration capabilities of silica gel modified by imidazole for Cu, Ni, Fe, Zn, Cd and Mn in ethanol [8,9]. Afterwards, Dias Filho also synthesized a series of modified silica with heterocyclic functional groups to adsorb metal ions in ethanol solution [10,11]. Besides heterocyclic compound, some other types of chelating functional groups such as octahedral POSS (polyhedral oligomeric silsesquioxanes) [2] and PAMAM dendrimers [12] were also reported. We noticed that most of the reported adsorbents involved either heterocyclic compounds with high toxicity or complicated synthesis steps (e.g. the synthesis of dendrimer-like groups), which were not suitable for large-scale industrial production. Also it is noticed that a large number of adsorbents have been prepared for removal and enrichment of heavy metal ions in aqueous solution. But can those adsorbents be used as effective as in ethanol solution? If not, what's the difference between the adsorption mechanisms in the two solvent systems? Few studies have been paid attention to the above

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https://doi.org/10.1016/j.fuel.2018.04.032
Received 9 February 2018; Received in revised form 30 March 2018; Accepted 7 April 2018

issues.

In this paper, we try to answer the above questions and explore novel adsorbents for the removal of Cu(II) from ethanol fuel solution. 3-Amino-1,2-propanediol (APD) is an important medical intermediate with very low toxicity. It is similar to glycerol in structure and expected to have good copper-chelating ability. In our recent paper, APD groups were immobilized onto silica-gel via homogeneous and heterogeneous routes using two silane coupling reagents 3-glycidoxypropyltrimethoxysilane (GPTS) and γ-chloropropyltrimethoxysilane (CPTS) [13]. The preliminary study showed that the adsorbent prepared via the homogenous route with CPTS had the highest capacities for metal ions in aqueous than the others. In this paper, further studies were conducted to evaluate the capability of the adsorbent for removal of copper ions from ethanol and aqueous solutions, including the difference between adsorption equilibriums, kinetics and mechanisms in the two solvents.

2. Experimental

2.1. Materials and methods

Silica gel-supported 3-amino-1,2-propanediol (SG-APD) was prepared according to our previous work [13] as shown in Fig. 1. The parameters of the absorbent were as follows: BET surface area, 319 $m^2 g^{-1}$; amino content, 0.74 mmol g^{-1}; BJH desorption average pore diameter, 5.9 nm. Stock solution of Cu^{2+} were prepared by dissolving $CuCl_2{\cdot}2H_2O$ in dry ethanol or DI water. All reagents were analytical grade and used without further purification.

The concentrations of metal ions were determined using a 932B-model atomic absorption spectrometer (AAS, GBC, Australia) equipped with an air–acetylene flame. The operating parameters were as follows: lamp current, 3.0 mA; slit width, 0.5 nm; wavelength, 253.7 nm; sensitivity, 1.60 μg g^{-1}.

2.2. Static adsorption experiments

Static adsorption experiments were carried out by shaking the adsorbent (0.05 g) in 0.001 mol L^{-1} ethanolic or aqueous metal solution (20 mL) at 100 rpm for 24 h at room temperature. After adsorption, an aliquot (10 mL) was removed and analyzed by AAS to determine Cu^{2+} concentration. The amount of metal adsorbed was calculated according to Eq. (1):

$$Q = \frac{(C_0 - C)V}{W} \quad (1)$$

where Q is the adsorption amount, mmol·g^{-1}; C_0 is the initial metal ion concentration, mmol·L^{-1}; C is the final metal ion concentration, mmol·L^{-1}; V is the volume, L; and W is the weight of adsorbents, g.

2.3. Adsorption kinetics

The adsorption kinetics was studied using a batch method by treating the adsorbents (0.04 g) in 5.0 mM ethanolic or aqueous metal solution (20 mL) at 15 °C to 35 °C. At various time intervals, an aliquot (10 mL) of the solution was removed and Cu^{2+} concentration was determined by AAS.

2.4. Adsorption isotherms

The adsorption isotherms were investigated by treating the adsorbents (0.03 g) with various concentrations of different Cu^{2+} solutions for 24 h at 15 °C to 35 °C.

2.5. Reusability studies

To investigate the reusability of adsorbed Cu^{2+} ions from SG-AP, desorption experiments were carried out as follows: after adsorption, the Cu^{2+} ion-loaded SG-AP was separated and slightly washed with ethanol or DI water to remove unabsorbed Cu^{2+} ion on the surface of the adsorbents. They were stirred with 20 mL of 0.1 mol L^{-1} of HCl containing 4% thiourea for 24 h, and the concentrations of Cu^{2+} ions were analyzed as previously. The desorption ratio of Cu^{2+} ions was then calculated as the ratio of the amount of desorbed Cu^{2+} ions to the amount of initially adsorbed Cu^{2+} ions.

3. Results and discussion

3.1. Static saturated adsorption amounts

Static saturated adsorption amount is usually used as primary

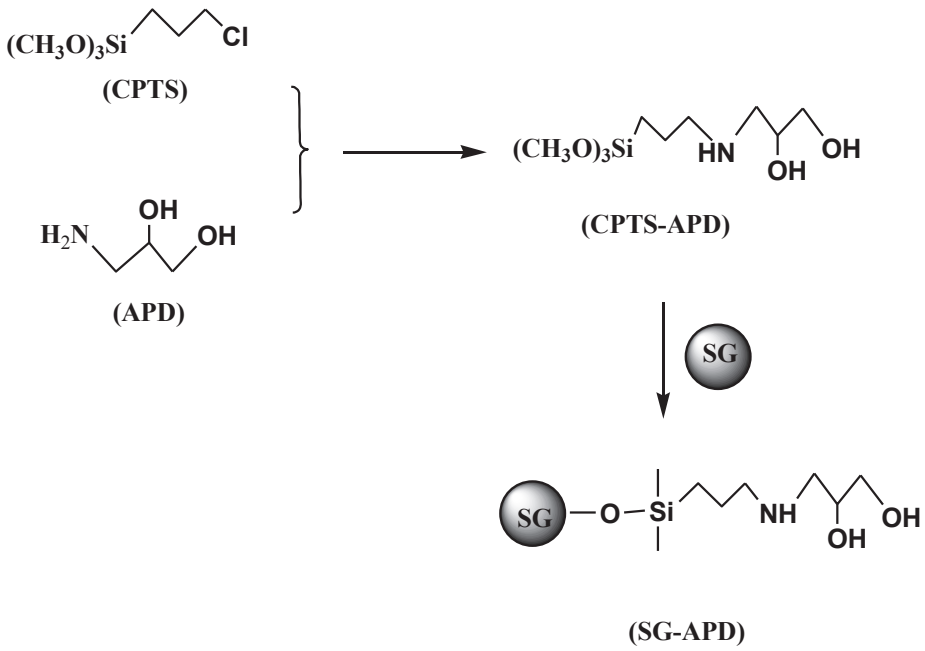

Fig. 1. Synthesis of SG-AP.