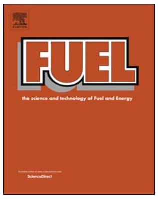
Fuel 219 (2018) 205–213

Contents lists available at ScienceDirect

Fuel

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



Full Length Article

Removal of Fe(III) from ethanol solution by silica-gel supported dendrimer-like polyamidoamine polymers

Rongjun Qu[a,*], Changmei Sun[a], Fang Ma[b], Ying Zhang[a], Chunnuan Ji[a], Ping Yin[a]

[a] School of Chemistry and Materials Science, Ludong University, Shandong 264025, China
[b] College of Business, Yantai Nanshan University, Shandong 265713, China

ARTICLE INFO

Keywords:
Silica-gel functionalized with polyamidoamine
Iron ion
Ethanol solution
Kinetics
Equilibrium

ABSTRACT

The adsorption properties of silica-gel supported hyperbranched polyamidoamine dendrimers (SiO_2-G1.0, SiO_2-G2.0 and SiO_2-G3.0) for the removal of Fe(III) from ethanol solution have been investigated. The effect of adsorbent mass, contact time, initial Fe(III) ion concentration, and temperature have been demonstrated. The adsorption kinetics of the three adsorbents was well described by the pseudo-second-order model. Langmuir isotherm model was more suitable to describe the equilibrium data, and suggested the monolayer adsorption. The mean free energy calculated from D-R isotherm model demonstrated the adsorption processes of was preceded by physical adsorption or chemical adsorption for different generation product in different temperatures. Thermodynamic parameters demonstrated that the adsorption process was exothermic, spontaneous, and random increasing process with the increase of temperature. The adsorption mechanics for Fe(III) is was greatly affected by the solvent. Furthermore, the desorption rate of the SiO_2-G1.0 maintained more than 90%, and reflected excellent reusability.

1. Introduction

From the end of 2012 to early 2013 in northern China, persistent fog and haze has sparked the attention of people for the increasingly serious environmental problems. Automobile exhaust is one of the incentives for this continuous fog and haze. In fact, it has long been desired to develop a new kind of clean, renewable and sustainable energy sources to replace the existing oil in order to resolve the issues of air pollution and energy depletion. Ethanol is considered to be potential candidate as alternative fuel in the spark-ignition engines since it is liquid and has several physical and chemical properties similar to those of gasoline and diesel fuels. Moreover, as a biodegradable and renewable fuel, ethanol can be produced from many low-cost biomasses such as wood, sugar cane, corn, sugar beet, and other grains [1–4]. As a fuel for spark-ignition engines, ethanol is far better than gasoline in anti-knock characteristics and reduction of UHC (Unborn Hydrocarbon) and CO emissions. Gasoline–ethanol mixtures, which contain up to 20% ethanol by volume, can be safely used and effectively lower the pollutant emission without major modifications to engine design. Brazil is the most successful and earliest country in promotion of gasoline–ethanol fuel in vehicle, followed by the United States, Canada, France, Spain and other European countries. In early 21st century, China also began on the development of gasoline–ethanol fuel exploration [5].

Although ethanol fuel has many advantages, the metals such as Cu, Ni, Fe, Zn and Na including in alcohol, which were mainly introduced during the transport and/or storage, distillation and refinement process of ethanol [6–9], makes the corrosion problems to engines more severe with alcohol than with ordinary gasoline fuels [10]. In addition, the overall automotive emission relative to metals' burning has an adverse environmental impact, which can decline the air quality and have an effect on human health [11]. Therefore, the presence of metals in ethanol has significant effect on the fuel performance and fuel quality.

Brazilian scientists did some pioneer work in exploring new adsorbents for removal of deleterious metal ions from ethanol fuel. Several adsorbents with heterocyclic functional groups were prepared and used in removal of Cu(II), Ni(II), Fe(II), Zn(II), Cd(II) and Mn(II) from ethanol in recent years [12–15].

As one of highly branched well-defined polymers with unique topology structure versatile physicochemical properties, polyamidoamine (PAMAM) polymers have strong coordination capability with metal ions due to the presence of numerous chelating moieties of amino and amido groups in their structures [16–18]. However, the PAMAM polymers are not suitable for the functional groups to prepare directly adsorbents for metal ions, because they are too costly due to their complex preparation process. To this end, we have prepared a series of silica-gel-supported dendrimer-like PAMAM polymer adsorbents via a

---

* Corresponding author.
E-mail addresses: rongjunqu@sohu.com, qurongjun@eyou.com (R. Qu).

https://doi.org/10.1016/j.fuel.2018.01.131
Received 18 October 2017; Received in revised form 28 January 2018; Accepted 30 January 2018

so-called ‘divergent method’ recently and investigated their adsorption properties for Au(III), Pd(II), Pt(IV), Ag(I), Cu(II), Zn(II), Hg(II), Ni(II) and Cd(II) in aqueous solution [19]. Then Our group reported the adsorption of Cu(II) from ethanol by silica gel. In order to further expand the applications of this series of silica-gel-supported dendrimer-like PAMAM polymer adsorbents supported amino-terminated PAMAM dendrimers for the first time [20]. Afterward, a series of silica gel supported ester- and amino-terminated PAMAM dendrimers (SiO_2-G0.5 ~ SiO_2-G3.0) were synthesized and used for the removal of Co(II), Hg(II) and Ag(I) from ethanol by Niu group [21,22]. In this paper, we did further investigation on the feasibility of the silica-gel-supported dendrimer-like PAMAM polymer adsorbents for the removal of Fe(III) from ethanol solution. Fe(III) is the most likely to be introduced into ethanol during the process of transport and/or storage. In addition, as a kind of trivalent metal ion, the solvation states and binding mechanism with adsorbents of Fe(III) is predicatively different from those of the divalent metal ions such as Hg(II) and Cu(II). The aim of the present paper is to give detailed results of amino-terminated silica-gel-supported dendrimer-like PAMAM polymer adsorbents for removal Fe(III) from ethanol solution which have rarely been reported. Some affecting factors including adsorbent mass, contact time, concentrations of solution on adsorption were investigated. To the best of our knowledge, there have been so far few reports about the applications of amino-terminated silica-gel-supported dendrimer-like PAMAM polymer adsorbents in removal of Fe(III) in non-aqueous solution system such as ethanol.

2. Experimental

2.1. Materials and methods

Silica-gel-supported amino-terminated dendrimer-like PAMAM polymers (SiO_2-G1.0, SiO_2-G2.0, and SiO_2-G3.0) were prepared according to the Ref. [19]. The physical parameters of SiO_2-G1.0, SiO_2-G2.0, and SiO_2-G3.0 were listed in Table 1. Stock solutions of Fe(III) were prepared by dissolving $FeCl_3{\cdot}6H_2O$ in dry ethanol. The other reagents were analytical grade and used without further purification. The atomic absorption spectrometer (VARIAN, AA240, American) equipped with air–acetylene flame was employed to determine the concentrations of Fe(III) in all the adsorption experimental. Each experiment was repeated 3 times in order to verify consistent results.

2.2. Static adsorption experiments

Static adsorption experiments were carried out by shaking 0.05 g of adsorbents with 20 mL of ethanol solution of Fe(III) (concentration 1×10^{-3} mol L^{-1}). The mixture was equilibrated for 24 h on a thermostat-cum-shaking assembly at 278 K and the agitation rate was 100 rpm. After adsorption, the upper clear liquid of Fe(III) solutions was sucked by a pipette and poured into a tube. Then the Fe(III) solutions in the tube was diluted by the double-distilled water. Almost immediately, the concentrations of Fe(III) which was diluted were determined by AAS. The adsorption amount was calculated according to the Eq. (1)

$$q = \frac{(C_0 - C)V}{W} \tag{1}$$

q, the adsorption amount (mg g^{-1}); C_0, the initial concentrations of Fe (III) (mmol mL^{-1}); C, the final concentrations of Fe(III) (mmol mL^{-1}); V, volume (mL); W, the weight of adsorbents (g).

Table 1
Physical parameters of SiO_2-G1.0, SiO_2-G2.0, and SiO_2-G3.0.

Adsorbents	SiO_2-G1.0	SiO_2-G2.0	SiO_2-G3.0
Grafting percentage (%)	10.49	19.83	27.65
Amino content (mmol.g^{-1})	1.91	1.87	1.83
BET surface area (m^2 g^{-1})	266.55	157.16	121.16
Cumulative volume of pores (cm^3 g^{-1})	0.67	0.36	0.30
BJH Desorption average pore diameter (nm)	7.35	5.86	5.76
Apparent particle density (g L^{-1})	710	706	701
Particle density ρ_p (g L^{-1})	410	410	408
Mean particle diameter (d_p) (μm)	150	155	157
Particle porosity (ε_p)	0.48	0.25	0.21

2.3. Effect of adsorbent mass on adsorption

At room temperature, adsorbent dosage was varied from 10 to 60 mg and equilibrated with 20 mL of Fe(III) solution of 1×10^{-3} mmol mL^{-1} for 24 h. The percent removal of Fe(III) was calculated according to the Eq. (2)

$$\text{Percent removal (\%)} = (C_0 - C)/C_0 \times 100 \tag{2}$$

2.4. Adsorption kinetics

The adsorption kinetics was studied by using 0.03 g of adsorbents which were added to each Erlenmeyer flask containing 20 mL of 56 mg L^{-1} Fe(III) solution at three temperatures (278, 288, and 298 K) by placing the Erlenmeyer flask on a temperature controlled shaker. At various time intervals, the upper clear liquid of Fe(III) solutions was sucked and determined by AAS.

2.5. Adsorption isotherms

The adsorption isotherms were investigated by using 0.03 g of adsorbents with 20 mL of various Fe(III) (varying the initial concentrations from 5.6 to 280 mg L^{-1}of Fe(III) solution) at 278–298 K. The samples were collected at 24 h to quantify initial and final Fe(III) concentrations.

2.6. Effect of concentration of Fe(III) on adsorption

At room temperature, initial Fe(III) concentration was varied from 0.1 mmol L^{-1} to 1 mmol L^{-1} with the adsorbent dosage of 30 mg and the solution volume of 20 mL. After shaking the mixture for 24 h, the adsorbents were taken out of the solution; and the concentration of metal ions in the solution was then measured by AAS.

2.7. Regeneration

Regeneration studies were carried out by using 100 mL of 0.1 mol L^{-1} HCl as desorption solution. After the adsorbents reached equilibrium/saturation in 100 mmol L^{-1} solution containing Fe(III) metal ions, the adsorbents were taken out of the solution, rinsed with deionized water, and then immersed in 0.1 mol L^{-1} HCl solution for 2 h. After the regenerated adsorbent was rinsed with deionized water for 3 times, it would subsequently be used for the next cycle of adsorption/desorption experiment. Herein, 3 cycles of regeneration studies were performed. The desorption ratio of Fe(III) was then calculated as the ratio of the amount of desorbed Fe(III) to the amount of initially adsorbed Fe(III).

3. Results and discussion

3.1. Static saturated adsorption amounts

In theory, the binding capabilities of PAMAM dendrimers for metal ions should increase with their increasing of generation number due to the increasing of chelating functional groups. Logically, the adsorption capacities of silica-gel adsorbents functionalized with dendrimer-like PAMAM for metal ions should follow this order SiO_2-G3.0 > SiO_2-