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High efficient adsorption of gold ions onto the novel functional composite silica microspheres encapsulated by organophosphonated polystyrene



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ABSTRACT

The novel functional composite silica microspheres encapsulated by organophosphonated polystyrene (SG–PS–N–P) has been successfully synthesized. SG–PS–N–P was employed to adsorb Au(III) from simulated wastewater, and it exhibited excellent performance, and the maximum adsorption capacity was 980.39 mg/g at 35 °C. The adsorption process optimization was performed using response surface methodology (RSM), and the analysis of variance (ANOVA) of the quadratic model demonstrated that the model was highly significant. Moreover, the regeneration capacities of SG–PS–N–P were investigated, and it has been found that the adsorption capability remains high after several cycles of adsorption–desorption.

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1. Introduction

Gold, historically used as a global currency, has been used in increasing industrial and medical fields due to its specific physical and chemical properties. Considering its value and scarcity, it is very necessary to recover gold from industrial scraps and wastewater (for example, the scraps from electronic devices containing gold, such as cellular phones and personal computers). There is a strong economic motivation for the removal and recovery of precious metal gold from wastewater for recycle and reuse [1,2]. Many treatment processes, such as chemical precipitation, reverse osmosis, ion exchange, adsorption, are currently used. Among these methods, adsorption is highly effective and economical, and is a promising and widely applied method [3]. Thus, it is very important to prepare effective adsorbents with strong affinities and high loading capacity for targeted precious metal ions.

Composite materials have been a significant concern because they are made from two or more constituent materials with significant physical or chemical properties, which work together to give the composite unique properties. Encapsulation technologies are becoming more and more popular in the preparation of composites, since polymer-encapsulated inorganic oxide can offer very interesting and potential applications such as adsorbents and electronic devices. Due to its excellent thermal and mechanical stability, unique large surface area and well-modified surface properties, silica was widely used as inorganic solid matrix in inorganic-organic composite materials [4,5]. Such kinds of polymer-coated silica composite materials have received a great deal of attention recently because of their excellent performance in the fields of chromatography, adsorption, and catalysis etc. [6]. Li et al. [7] reported they obtained spherical hybrid silica particles from hydrolysis of tetraethoxysilane and vinyltriethoxysilane as the precursors using NH₄OH as catalyst, and the silica particles were subsequently encapsulated with a layer of PS-DVB. The encapsulated packing was used as stationary phases in capillary electrochromatography, and displayed high column efficiencies. Do et al. [8] presented a novel synthesis of polystyrene/SiO₂ composite microparticles by dispersion polymerization in supercritical fluid. Liu et al. used reversible addition-fragmentation chain transfer polymerization to graft polystyrene onto silica nanoparticles, and epoxy groups were covalently attached to silica by condensation reaction of 3-glycidyloxypropyltrimethoxysilane with the hydroxyl on the silica particle surfaces [9]. However, many of these polymer-encapsulated silica adsorbents have low metal removal and slow process kinetics. Thus, it is necessary to develop efficient adsorbents with good affinity toward metal ions. Surface functionalization technology has been proven to be

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effective. Functional groups presenting in the polymer structure can provide binding sites to remove the metal ions from aqueous solutions and improve the adsorption properties. In the relative research work, people have found organophosphonic acids could be good candidates for chelating with transition metal ions, in which the organic parts play a controllable spacer role and the – PO_3 groups had the ability of ion exchange, and the existence of oxygen atoms and nitrogen atom in the functional group make it coordinate with a variety of transition metal ions [10]. If the organophosphonic acid groups are grafted on the solid matrix, this kind of chemical modification can overcome its shortcomings of being soluble in water, and be used in adsorption of metal ions from aqueous solutions.

Until now, to the best of our knowledge, the preparation of silica microspheres encapsulated by organophosphonated polystyrene has not been reported. In view of the abovementioned, our objective in the present work is to develop the functional composite material aminophosphonated polystyrene/silica with the high performance and to investigate its adsorption property for gold ions from simulated wastewater. Furthermore, response surface methodology (RSM) has been employed to optimize the relevant adsorption process parameters, and it is also possible to observe the effects of individual variables and their combinations of interactions on the response by using RSM [11]. Moreover, the adsorption reproducibility of this functionalized SG-PS-N-P for Au(III) ions from aqueous solutions were also carried out.

2. Experimental details

2.1. Materials and preparation

Silica gel (SG) spheres (100–200 mesh) were obtained from Qingdao Marine Chemical Plant, China. Other reagents were analytical-grade chemical products and purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd., China, they were used without further purification, and distilled water was used for all dilutions.

The synthetic routes of SG–PS–N–P were shown in Fig. 1. Prior to coating, the silica spheres were activated with nitric acid $(V_{HNO_3}: V_{H_2O} = 1:1)$ at refluxing temperature for 6 h, with 12 M hydrochloric acid at refluxing temperature for 6 h, to provide better surface reactivity of the silica substrate to polystyrene films. Then they were cooled and repeatedly washed using distilled water until there was no Cl⁻, dried in vacuum at 120 °C for 48 h before use. A suspension of 50.0 g of activated silica-gel and 50 mL of vinyl triethoxysilane (VTES) were stirred at room temperature in 200 mL of toluene solution for 12 h, first in an argon atmosphere for 30 min and then in ammonia atmosphere for the remaining



Fig. 1. Synthetic routes of functional composite silica microspheres encapsulated by organophosphonated polystyrene SG-PS-N-P.

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