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Fibrous polyethylenimine/polyvinyl chloride crosslinked adsorbent for the recovery of Pt(IV) from acidic solution: Adsorption, desorption and reuse performances

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ABSTRACT

This study focused on evaluating the characteristics and performance of polyethylenimine (PEI)/polyvinyl chloride (PVC)-crosslinked fiber (PEI/PVC-CF) as an adsorbent for Pt(IV) sorption. To fabricate the PEI/PVC-CF, a PEI/PVC crosslinked polymer mixture was synthesized through the alkylation reaction at 80 °C for 6 h and then this polymer mixture was extruded into fibers in water. The analyses of SEM and FTIR were performed to identify the adsorptive characteristics of the PEI/PVC-CF and the binding mechanism between the Pt(IV) and adsorbent. The valuable sorption performance of Pt(IV) by the PEI/PVC-CF were demonstrated from the results of isotherm and kinetic experiments. The pseudo-first-order kinetic model was adequate to describe kinetic data obtained at 25 and 50 mg/L, and the pseudo-second-order model was suitable for 100 and 200 mg/L. The isotherm data fitted well to the Langmuir model and the maximum uptake was evaluated to be 217.31 mg/g. According to thermodynamic studies, the adsorption process of Pt(IV) by PEI/PVC-CF was endothermic and spontaneous. The mixture of HCl and thiourea was also used as an eluent for desorption of Pt(IV) from loaded-adsorbent. As a result, nearly 100% of desorption efficiency was achieved at above 20 mM thiourea concentration in 0.01 M HCl. Besides, the sorption-desorption experiments exhibited that the PEI/PVC-CF could be reused repeatedly at least five cycles. The reusability and applicability of PEI/PVC-CF was also verified in a column system.

1. Introduction

Platinum group metals (PGMs) including platinum (Pt), palladium (Pd), osmium (Os), rhodium (Rh), ruthenium (Ru) and iridium (Ir) have been used in various industrial fields due to their distinct properties, such as catalytic activity, corrosion resistance, thermoelectric stability, chemical inertness and magnificent color. The natural resources of PGMs are very limited and their amounts are only about 66,000 tons all over the world (Dong et al., 2015). Generally, PGMs are contained in basic metal sulfide minerals and their content in the ore is 2–10 g/ton (Jha et al., 2013). Due to the low availability compared to the high demand in various industries, the cost of these metals are increasing rapidly. According to the global supply and demand of PGMs in 2015, especially, the total supply of Pt was 172.3 tons, which was lower than the total gross demand (239.8 tons), and the total recycled Pt amount from secondary resources was only 48.9 tons (Matthey, 2016). Therefore, it is significantly important to recover PGMs from secondary resources. It can also prevent some environmental pollution through PGMs recovery.

PGMs dissolved in aqua regia or hydrochloric acid solution with a lot of chlorines can be recovered from industrial waste solutions using several conventional methods. Representatively, chemical precipitation, ion exchange, solvent extraction, and electrowinning have been used for the removal or recovery of metal ions from effluents. However, these methods have some drawbacks such as high cost of capital, high amount of reagents, high energy requirement, and toxic sludge generation which should be properly disposed (Das, 2010). On the other hand, adsorption, one of the

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most widely used methods, has been considered as a promising technology to remove/recover PGMs from acidified aqueous solutions or wastewaters (Morisada et al., 2012). Since the treatment efficiency of PGMs by adsorption is dependent on the adsorption performance of the adsorbent, a variety of attempts have been made to develop an excellent adsorbent.

Polyethylenimine (PEI) is a long chain polymer having primary, secondary and tertiary amine groups that can readily interact with ionic pollutants such as PGMs, dyes, and heavy metals. Thus, this polymer has been widely used to modify the surface of adsorbents to increase their adsorption performances. For instance, PEI-modified biosorbents were successfully fabricated and applied for removal/recovery of reactive dyes (Mao et al., 2011), heavy metals (Deng and Ting, 2005), and precious metals (Zhou et al., 2017). Cho et al. (2016) reported that the maximum Pd(II) uptake of PEI-coated polysulfone/*Escherichia coli* biomass composite fiber was enhanced up to 7 times compared to the polysulfone/biomass composite fiber. Also, Saleh et al. (2017) suggested that PEI-modified activated carbon could remove uranium(VI) from aqueous solution. However, these adsorbents above mentioned should be coated with PEI molecules. Their fabrication process requires several reaction paths and is relatively complicated. In addition, a large loss of expensive PEI may be generated after the adsorbent preparation. Thus, it is necessary to study and develop a simple and effective method from an economic point of view.

Avny and Porath (1976) found out the fact that the crosslinked polymer of PEI and polyvinyl chloride (PVC) could be synthesized in *N*,*N*-dimethylformamide (DMF) solution at 100 °C for 24 h by alkylation reaction between the amine groups in PEI and the chlorines in PVC. This crosslinked polymer showed the ability to remove cupric and mercuric salts from aqueous solutions. Our previous work also confirmed that this crosslinked polymer solution can be easily made into fibers (Kim et al., 2015). Therefore, this study focused on the development of a fiber-type polymer adsorbent, PEI/PVC-crosslinked fiber (PEI/PVC-CF) with a high adsorption capacity, rapid adsorption kinetics, convenient separation, excellent stability and reusability. This adsorbent can be made very easily compared to other sophisticated adsorbents, there is no need to coat the fiber surface with PEI, and chemical surface modification by hazardous chemicals is not required. Instead, the mixture of PEI and PVC can only form fibers from water by extrusion without loss of raw polymer materials. The Pt(IV) adsorption performance of PEI/PVC-CF was examined in various batch experiments such as the isotherm and kinetic experiments. Its adsorption characteristics were analyzed by fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The effective desorption conditions of Pt(IV) and the reusability of the adsorbent were also evaluated.

2. Materials and methods

2.1. Materials

Polyvinyl chloride (PVC) with 40 kDa molecules and *N*,*N*-dimethylformamide (DMF, 99.8%) were purchased from Sigma-Aldrich Korea Ltd. (Yongin, Korea) and Daejung Chemicals & Metals Co., Ltd. (Siheung, Korea), respectively. Branched polyethylenimine (PEI) solution was supplied by Habjung Moolsan Co., Ltd. (Seoul, Korea) and its general properties were the same as the molecular weight of 70 kDa, the content of 50%, and the primary, secondary and tertiary amine ratios of 25, 50 and 25%, respectively. To prevent PVC hardening by the water in PEI solution, PEI was dried at 60 °C for 24 h in a drying oven before use in the experiments. Potassium hexachloroplatinate(IV) (K_2PtCl_6, 99.0%) was supplied by Kojima Chemicals Co., Ltd. (Saitama, Japan). All the other reagents used in this work were of analytical grade.

2.2. Preparation of PEI/PVC-crosslinked fiber

Each of PEI and PVC was dissolved at 40 °C for 24 h in a bottle containing 15 mL of DMF solution. The well dissolved PEI was added to 15 mL of the PVC solution and then the PEI/PVC mixture was violently stirred at 80 °C for 6 h. As a PEI/PVC crosslinked polymer was synthesized, the mixture color was changed from colorlessness to yellow. After 6 h, the mixture quickly cooled down at room temperature to stop additional alkylation reaction between PEI and PVC molecules. Thereafter, PEI/PVC crosslinked polymer solution was extruded through a plastic hub needle with 0.20 mm of inner diameter into deionized water and made into fibers. The resulting product, PEI/PVC-crosslinked fiber (PEI/PVC-CF) was separated from water and washed with distilled water several times to remove any residual DMF. PEI/PVC-CFs were then lyophilized using a freeze dryer (TFD Series, Ilshinbiobase, Korea) for 24 h and stored in a desiccator until used in this study.

2.3. Batch adsorption experiments

A stock solution (1000 mg/L) was prepared by dissolving a certain amount of Pt(IV) salt in 0.1 M HCl solution and diluted in the same way if necessary. Basically, batch experiments were carried out at 160 rpm and 25 °C in 50-mL polypropylene conical tubes. The adsorption isotherms for Pt(IV) sorption on the PEI/PVC-CF were evaluated on the conditions of 0.02 g of adsorbent and 30 mL of 0.1 M HCl containing different initial Pt(IV) concentrations (0–700 mg/L) for 24 h to achieve the maximum sorption capacity of the PEI/PVC-CF. The experiments were also performed at different temperatures such as 35 and 45 °C for the thermodynamic studies. After reaching equilibrium, the adsorbent was separated by means of centrifugation at 9000 rpm and 5 min. For adsorption kinetics, the experiments were carried out at four different initial Pt(IV) concentrations such as 25, 50, 100 and 200 mg/L. The experimental procedures were the same as mentioned above, except that the samples were collected at predetermined time intervals to find an equilibrium time for Pt(IV) sorption.

Pt(IV) concentration remaining in the supernatant was measured using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, ICPS-7500, Shimadzu, Japan) after proper dilution. The Pt(IV) amount adsorbed on the adsorbent was calculated using the following mass balance:

$$q = \frac{\left(C_i - C_f\right)V}{m} \tag{1}$$

where q is the Pt(IV) uptake (mg/g), C_i and C_f are the initial and final Pt(IV) concentrations (mg/L), respectively, V is the working volume (L), and m is the weight of adsorbent (g) used in this study.

2.4. Desorption and reuse studies

For Pt(IV) desorption studies, PEI/PVC-CF (0.02 g) was added into 30 mL of 0.1 M HCl with different initial Pt(IV) concentrations (50, 100 and 200 mg/L) and mixed at 25 °C for 24 h. After sorption, the residual Pt(IV) concentration in the supernatant was determined by ICP-AES with appropriate dilution. The Pt(IV)-sorbed PEI/PVC-CFs were rinsed with 0.1 M HCl solution to get rid of some unadsorbed Pt(IV) ions existed on the surface of the adsorbent. The Pt(IV)-loaded adsorbents were then resuspended into 30 mL of 0.01 M HCl containing different thiourea concentrations (0–30 mM). The suspension was shaken at 160 rpm for 24 h to allow Pt(IV) detachment from the loaded sorbents. Moreover, sorption-desorption experiments were performed repeatedly up to