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PALLADIUM SORPTION BY AMINO-FUNCTIONALIZED MACROPOROUS COPOLYMER FROM CHLORIDE–NITRATE SOLUTIONS

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ABSTRACT

Macroporous poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) with attached diethylene triamine [PGME-deta] with high amino-group content was used for the investigation of the Pd(II) sorption kinetics from mixed chloride/nitrate aqueous solutions in acidic medium (pH 2.0) at $T=298$ K. Four kinetic models were employed in order to comprehend the mechanism of Pd(II) sorption. The maximum experimental Pd(II) sorption capacity at initial pH 2.0 and 298 K was 20 mg g^{-1} .

INTRODUCTION

Due to their high cost and low availability, precious metals separation and recovery from wastes such as spent catalysts or scraps, and extraction from ores has become vital [1]. Precious metal palladium (Pd) applications include medical, catalytic and electrical/electronic uses, due its corrosion/oxidation resistance, electrical conductivity and catalytic activity. Amongst various processes for Pd recovery, sorption is the method with great potential due to high efficiency and selectivity [2]. The prospect of the application of inexpensive and easily synthesized macroporous glycidyl methacrylate-based copolymer with amino ligand (PGME-deta) as a sorbent for the removal of Pd(II) complexes from chloride–nitrate solutions was tested in static conditions. Four kinetic models [pseudo-first order (PFO),

pseudo-second order (PSO), Boyd and Mckay] were fitted to elucidate the mechanism of Pd(II) sorption from aqueous solutions (pH 2.0) at 298 K.

EXPERIMENTAL

PGME with 20 mass% crosslinker was synthesized by suspension copolymerization in the shape of spherical beads with the average particle diameter of 150-300 μm and functionalized with diethylene triamine; PGME-deta was subsequently characterized [3]. In static conditions, 0.50 g of the copolymer was contacted with 50 cm^3 of 500 mg dm^{-3} Pd(II) solution prepared by mixing the appropriate amounts of the standard solution (1000 mg dm^{-3} $\text{Pd}(\text{NO}_3)_2$ in 0.5M HNO_3 ; pH = 0.3; Merck, Germany) and $2.1 \cdot 10^{-3}$ M $\text{NaCl}_{(\text{aq})}$ to achieve equal quantities of chloride and nitrate in the working solution. The initial pH of this solution was adjusted with 5M $\text{NaOH}_{(\text{aq})}$ to pH=2.0. After predetermined time intervals 0.50 cm^3 solution aliquots were withdrawn and, with adequate dilutions, Pd(II) in supernatant was determined by ICP-OES (Perkin Elmer, Model ICP 400).

RESULTS AND DISCUSSION

The investigations of Pd(II) sorption by porous vinylpyridine anion exchangers from chloride solutions [4], as well as on carbon adsorbents from nitric acid solutions [2] have been published.

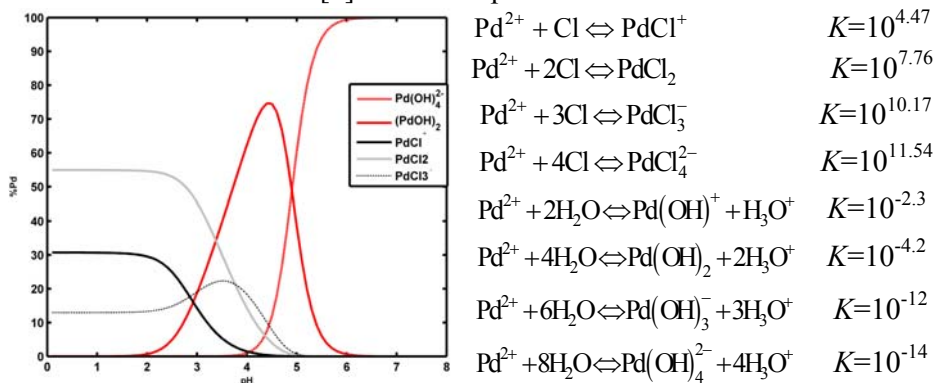


Figure 1. Speciation of palladium (500 mg dm^{-3}) as the function of pH calculated using ChemEQL 3.1 and the stability constants applied for graph construction [6]. The species comprising $\leq 5\%$ total are not shown ($\text{Pd}(\text{OH})_3^-$, $\text{Pd}(\text{OH})^+$, Pd^{2+} , PdCl_4^{2-}).

Crosslinked chitosan containing approximately the same amount of nitrogen as PGME-deta (Table 1) [5] also binds chloropalladate species efficiently [6]. In the case of this study (mixed chloride-nitrate solutions), it should be mentioned that the hydrated Pd(II) ions and their mononitrate complexes are

almost absent when $\text{HNO}_{3(\text{aq})} \leq 0.01 \text{ M}$ [2]. Therefore, only graphs representing the speciation of chloropalladate complexes and Pd(II) hydrolysis products are shown in Figure 1. As for the mixed Pd-Cl⁻-OH⁻ species, it appears that these can be disregarded, too [1]. Ruiz et al. already demonstrated that the optimum pH for Pd sorption on modified chitosan was 2.0 in the presence of chloride ions, involving protonated amino groups [6]. Therefore, pH 2.0 was chosen as optimal given that the PGME-deta amino group content is high (Table 1).

Table 1. Relevant characteristics of PGME-deta [3].

$S_{Hg}, \text{m}^2 \text{g}^{-1}$	$V_S, \text{cm}^3 \text{g}^{-1}$	$d_{V/2}, \text{nm}$	C_{AG}, mmol^{-1}	%C	%H	%N
29	0.89	212	6.51	52.4	8.1	9.1

Table 2. Kinetic parameters for Pd(II) using PGME-deta (pH=2.0, $T=298\text{K}$)

PFO				PSO			
$Q_e,$ mg g^{-1}	$k_1,$ min^{-1}	$Q_e^{calc},$ mg g^{-1}	R^2	$k_2,$ min^{-1}	$h,$ $\text{mg g}^{-1} \text{min}^{-1}$	$Q_e^{calc},$ mg g^{-1}	R^2
20	0.093	6	0.879	0.053	17.6	18	0.999

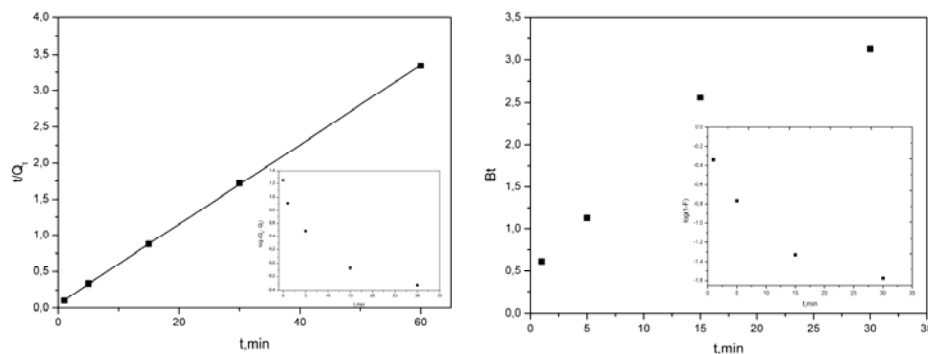


Figure 2. PFO [7] (a), PSO [8] (b), Boyd plot [9] (c) and McKay plot [10] (d) for Pd(II) sorption onto PGME-deta.

Please refer to the cited papers for abbreviations and definitions given in Tables 1 and 2 and Figure 2.

The theoretical Q_e^{calc} values calculated from the PSO model are very near to the experimental Q_e values, with $R^2=0.999$ (Table 2), indicating chemisorption of Pd(II) species on the protonated amino groups involving

valence forces through sharing or exchange of electrons as the surface-reaction mechanism [6,8] (Figure 2). Boyd and Mckay plots suggest particle and film diffusion control of Pd(II) sorption on PGME-deta [9,10].

CONCLUSION

The high amino-group content of macroporous glycidyl methacrylate based copolymer with attached diethylene triamine [PGME-deta] is the key characteristic for its capability to sorb metal ions through several mechanisms dependent on the solution pH including ion-exchange or chelation. The PSO kinetic model accurately describes the sorption behavior over the whole time period and provides a good calculated capacity compared to the experimental value of 20 mg g^{-1} , indicating chemisorption of Pd(II) species on the protonated amino groups which involves valence forces through sharing or exchange of electrons. Boyd and Mckay models confirm both particle and film diffusion as rate-controlling.

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