

M. Ruiz*
A.-M. Sastre**
J.-R. Degorce-Dumas***
E. Guibal***

*Dpt. Chem. Eng., E.U.P.V.G.
Universitat Politècnica de Catalunya
Avenida Víctor Balaguer
E-08800, Vilanova i la Geltru, SPAIN
** Dpt. Chem. Eng., E.T.S.E.I.B.
Universitat Politècnica de Catalunya
Diagonal 647, E-0880 Barcelona – SPAIN
*** Lab. Génie de l'Environ. Ind,
Ecole des Mines d'Alès, 6, avenue de
Clavières, F-30319 Alès Cedex - FRANCE

PALLADIUM SORPTION USING CHITOSAN DERIVATIVES

Table of Contents:

ABSTRACT
KEYWORDS
INTRODUCTION
EXPERIMENTAL SECTION
RESULTS AND DISCUSSION
CONCLUSION
REFERENCES

ABSTRACT

Glutaraldehyde crosslinked chitosan was tested for palladium sorption from dilute solutions through equilibrium experiments, kinetics in both batch and fixed-bed systems. Sorption capacities as high as 200 mg g⁻¹ (about 1.8 mmol g⁻¹) have been found. Sorption mechanism was fast and up to 90 % of the total sorption was achieved within the first 8 hours of contact. Sorption capacities are influenced by the acid used for pH control. The difference between HCl and H₂SO₄ may be related to metal ion speciation which depends on metal concentration, chloride concentration and pH. The study of palladium uptake using fixed-bed columns confirms the high affinity of this sorbent for palladium.

KEYWORDS

Chitosan; diffusion; fixed-bed columns; isotherms; kinetics; palladium sorption.

INTRODUCTION

Palladium is one of the most expensive metals, however, due to its special properties in catalytic processes, it is widely used in industry. Many processes have been developed to recover this metal in complex solutions, or aimed at its recovery from spent catalysts (Brooks, 1991). Ion exchange processes as well as liquid/liquid extraction techniques have been investigated, and the latest developments in Platinum Group Metals (PGMs) recovery have concerned impregnated resins. However, these processes are usually efficient at removing PGMs from medium to high concentration solutions. Research of alternative sorbents remains a priority in this field of hydrometallurgy. These new sorbents might be efficient at removing PGMs in complex and dilute solutions, available at low cost or easy to recycle. Chitosan is an aminopolysaccharide extracted by a deacetylation procedure from chitin, the most abundant biopolymer in Nature after cellulose (Roberts, 1992). It is characterized by its high nitrogen content, which explains, in turn, its ability to uptake several metal ions through different mechanisms such as ion-exchange or chelation processes, depending on the metal and the pH of the solution (Roberts, 1992; Piron et al., 1997). Chitosan has been widely experimented with for the sorption of noble metals, in its original form, or after chemical modification (Baba and Hirakawa, 1992; Guibal et al., 1999, Wan Ngah and Liang, 1999). Chitosan is also characterized by its ready dissolution in many dilute mineral acids, with the remarkable exception of sulfuric acid. It is thus necessary to stabilize it chemically for the recovery of metal ions in acidic solutions using a crosslinking treatment. It can be accomplished with different chemicals such as epichlorhydrin or glutaraldehyde. Glutaraldehyde has been used by several groups for cadmium recovery on chitosan beads (Hsien and Rorrer, 1997), and for molybdenum and vanadium sorption (Guibal et al., 1998). Glutaraldehyde crosslinking occurs through a Schiff's base reaction between aldehyde ends of the crosslinking agent and amine moieties of chitosan to form imine functions (Roberts, 1992). This study investigates equilibrium and kinetic performances of glutaraldehyde crosslinked chitosan for palladium recovery.

EXPERIMENTAL SECTION

Chitosan was supplied by ABER-Technologie (France) as a flaked material, with a deacetylation percentage ca. 87 %, and the mean molecular weight was measured at 125,000. Moisture content of sorbent particles was determined to be ca. 10 %; sorbent masses are expressed on a wet basis. Chemical crosslinking of chitosan was performed by reacting chitosan flakes with glutaraldehyde aqueous solutions with differing concentrations for 24 hours. The crosslinked chitosan particles were rinsed extensively with demineralized water. This general procedure was applied to prepare crosslinked chitosan flakes at four particle sizes: $G1 < 125 \mu\text{m} < G2 < 250 \mu\text{m} < G3 < 500 \mu\text{m} < G4 < 710 \mu\text{m}$. Palladium solutions were prepared from palladium chloride (PdCl_2) which was purchased from ChemPur (Germany). The pH of the solutions was controlled using either HCl or H_2SO_4 , and NaOH concentrated solutions (5 M). The pH was kept constant during the sorption step. For sorption isotherms, 100 mL of metal ion solutions at fixed concentrations were put in contact with varying sorbent quantities (5 to 30 mg wet mass) at room temperature ($20 \text{ }^\circ\text{C} \pm 1 \text{ }^\circ\text{C}$). After 3 days of agitation, in a reciprocal shaker, the solutions were filtered through $1.2 \mu\text{m}$ filtration membranes and the filtrates were analyzed using the SnCl_2/HCl spectrophotometric method, or alternatively using ICP analysis (JOBIN-YVON JY36, France). The sorption capacity was obtained using a mass balance equation, and was expressed as mg Metal g^{-1} sorbent. For the study of sorption kinetics, a standard procedure was applied: 1 L of metal ion solution at fixed pH was mixed with a fixed amount of sorbent, in a jar-test agitated system (240 rpm): 5 mL samples were withdrawn at specified times and filtered through a $1.2 \mu\text{m}$ filtration membrane and analyzed as previously specified. For the study of sorption in continuous systems, a column (internal diameter: 7 mm) was filled with a fixed amount of sorbent and was fed with 5 L of a palladium solution (initial concentration was varied) at pH 2 (controlled with HCl).

RESULTS AND DISCUSSION

pH optimization

Palladium sorption was strongly controlled by the pH of the solution and the acid used for pH control as shown in Figure 1. For both sulfuric and hydrochloric acids the optimum pH was around pH 2, but with hydrochloric acid the sorption capacity (in the same experimental conditions) was almost doubled. Palladium is suspected to be sorbed through anion exchange mechanism. In acidic solutions chitosan is protonated and palladium, in presence of chloride anions, forms several anionic chloropalladate species which are exchanged with the counter ions. In very acidic solutions, the competition between counter ions and metal anions is very strong and the sorption capacity is decreased in weak acidic conditions: the sorbent is less protonated and palladium speciation is less favorable to the formation of highly exchangeable species. It is especially true in the case of solutions which pH is controlled with sulfuric acid: chloride ions being less abundant in solution, palladium speciation is displaced to the formation of less adsorbable species, and the sorption capacity decreases. This interpretation has been confirmed by the favorable effect of chloride ions when they are added in small amount in a solution which pH was controlled with sulfuric acid (not shown).

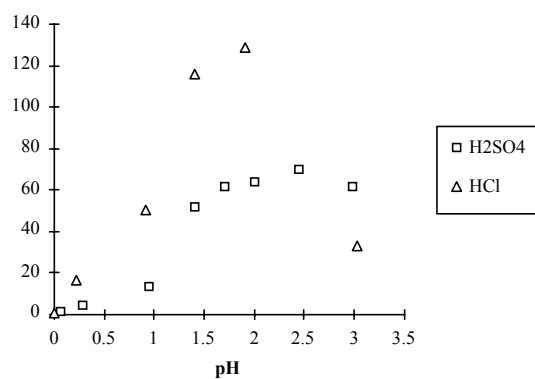


Figure 1: Influence of pH and acid used for pH control on Pd sorption (sorbent dosage SD: 0.05 g L^{-1}), $[\text{Pd}]$: 10 mg L^{-1})

Palladium sorption isotherms

Figure 2 shows the influence of sorbent particle size on sorption isotherms at pH 2 (controlled with HCl). Particle size did not significantly influence sorption equilibrium. The maximum sorption capacity tended to 180-200 mg g⁻¹ (about 1.8 mmol g⁻¹) for each size fraction. The affinity coefficient, which is proportional to the initial slope of the curves was also comparable and independent of the particle diameter. Freundlich equation fits experimental data better than the Langmuir equation. The isotherms can be described by the equation: $q = 117 C_{eq}^{1/7.42}$.

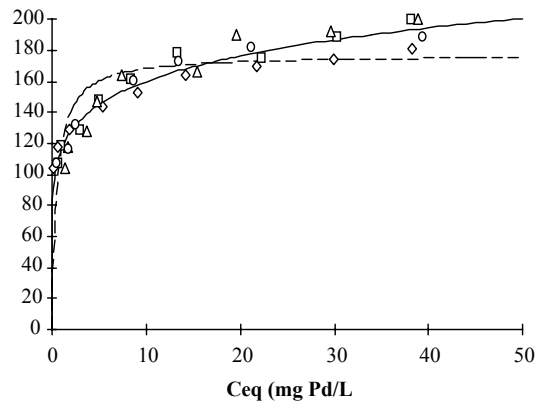


Figure 2: Influence of sorbent particle size on palladium sorption isotherms (pH 2 controlled with HCl) and modeling of sorption isotherms using both Langmuir and Freundlich models.

Palladium sorption kinetics

Though sorbent particle size did not influence sorption equilibrium, this parameter may affect the time required to reach equilibrium. Figure 3 shows the influence of increasing particle size on palladium sorption kinetics at pH 2 (controlled with HCl). Increasing particle size resulted in a decrease in the slope of the kinetic curve. The final concentration tended to 0 after a 24 hours of contact but about 90 % of the total sorption was achieved within the first 8 hours of contact. Particle size may affect both film and intraparticle diffusion due to the low porosity of the original material. The crosslinking of raw chitosan may increase the influence of this parameter.

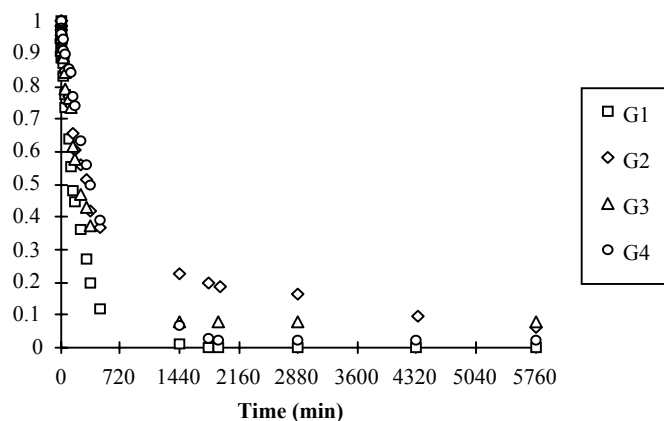


Figure 3: Influence of sorbent particle size on sorption kinetics (SD: 0.1 g L⁻¹, [Pd]: 20 mg L⁻¹)

Figure 4 confirms that increasing the crosslinking ratio (defined as the molar ratio between aldehyde and amine groups selected in the crosslinking bath) significantly increased the time required to reach equilibrium. The influence of this parameter confirms that, though the film diffusion cannot be neglected in the kinetic control, intraparticle diffusion plays a great part in the overall mass transfer resistance. Increasing the crosslinking ratio should influence the accessibility to internal sites through the formation of complementary linkages between polymer chains. However the influence of intraparticle diffusion on kinetics is less marked than it is for the sorption of other metals such as molybdate or vanadate (Guibal et al., 1998).

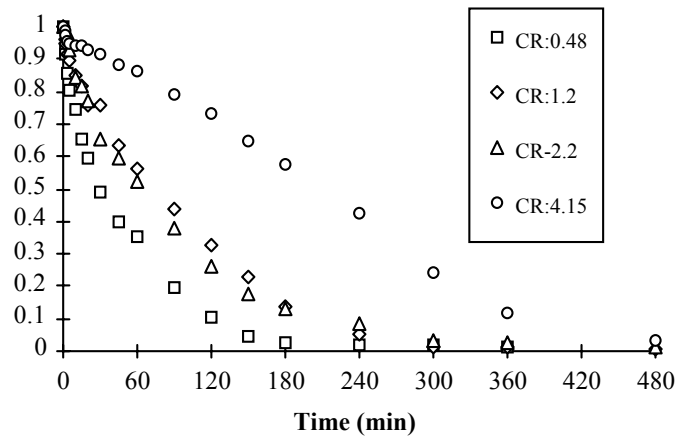


Figure 4: Influence of crosslinking ratio on sorption kinetics (SD: 150 mg L^{-1} , [Pd]: 9 mg L^{-1})

Palladium sorption in fixed-bed columns

Figure 5 shows the influence of initial concentration on the shape of breakthrough curves (column depth 4.5 cm, superficial flow velocity: 0.6 m h^{-1}). As expected, increasing the initial concentration resulted in a decrease in the breakthrough bed volumes and an increase in the slope of the breakthrough curves. This sorbent allows a very efficient recovery of palladium in dynamic system: even at a concentration of 47.5 mg L^{-1} , the breakthrough occurred at 1000 BV.

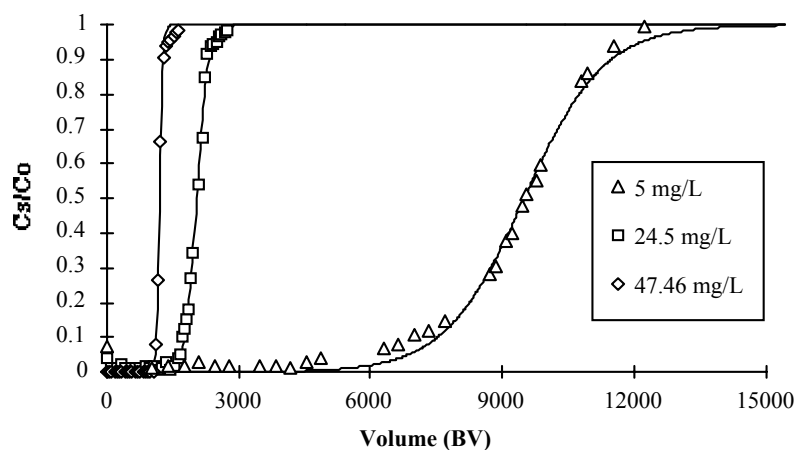


Figure 5: Influence of Pd concentration on breakthrough curves (sorbent mass: 0.5 g)

CONCLUSION

Glutaraldehyde-crosslinked chitosan is very efficient at recovering palladium from dilute acidic solutions (sorption capacity 1.8 mmol g^{-1}). The optimum pH is reached at pH 2. Sulfates anions diminish sorption capacities due to a displacement of palladate speciation to form less adsorbable metal species in comparison to chloride media. Sorption capacities are not controlled by sorbent particle size, however this parameter controls sorption kinetics due to a dual film and intraparticle diffusion mechanism. In fixed-bed systems, palladium is also efficiently recovered with breakthrough volumes higher than 1000 BV with palladium concentration as high as 47.5 mg L^{-1} .

REFERENCES

- Baba Y. and Hirakawa H. (1992) Selective adsorption of palladium(II), platinum(IV) and mercury(II) on a new chitosan derivative possessing pyridil group, *Chem. Lett.*, 1905-1908.
- Brooks C.S. (1991) *Metal Recovery from Industrial Wastes*, Lewis Publishers, Chelsea, Mich.
- Guibal E. Milot C. and Tobin J.M. (1998) Metal-anion sorption by chitosan beads: equilibrium and kinetic studies, *Ind. Eng. Chem. Res.*, 37, 1454-1463.
- Guibal E., Larkin A., Vincent T. and Tobin, J.M. (1999) Chitosan sorbents for platinum sorption from dilute solutions, *Ind. Eng. Chem. Res.*, 38, 401-412.
- Hsien T.-Y. and Rorrer G.L. (1997) Heterogeneous cross-linking of chitosan gel beads: kinetics, modeling, and influence on cadmium ion adsorption capacity, *Ind. Eng. Chem. Res.*, 36, 3631-3638.
- Piron E., Accominotti, A. and Domard A. (1997) Interactions between chitosan and uranyl ions. Role of physical and physicochemical parameters on the kinetics of sorption, *Langmuir*, 13, 1653-1658.
- Roberts G.A.F. (1992) *Chitin Chemistry*, MacMillan, London.
- Wan Ngah W.S. and Liang K.H. (1999) Adsorption of gold(III) ions onto chitosan and N-carboxymethyl chitosan: Equilibrium studies. *Ind. Eng. Chem. Res.*, 38, 1411-1414.