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Platinum and palladium recovery from dilute acidic solutions using sulfate reducing bacteria and chitosan derivative materials

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The present work focuses on the study of Pd and Pt sorption using different strains of sulfate reducing bacteria, SRB, (*Desulfovibrio* spp.) and the comparison of their sorption performance to that obtained using several chitosan derivatives. *D. desulfuricans* was the best strain: sorption capacities as high as 190 and 90 mg Metal (Me) g⁻¹ for Pd and Pt respectively were obtained under optimum experimental conditions at pH 3. At pH 2, for Pd sorption the maximum sorption capacities with HNO₃ and H₂SO₄ solutions were comparable (close to 120 mg Pd g⁻¹) and higher than the levels reached with HCl solutions (less than 70 mg Pd g⁻¹). Sorption kinetics are very fast: the equilibrium can be reached within the first 15-30 minutes of contact. For chitosan derivatives sorption capacities under selected experimental conditions (i.e. pH 2) appear to be significantly higher than with SRB between 200 and 600 mg Me g⁻¹, depending on the metal and the derivative. However, compared to SRB systems the kinetics are significantly slower: Several hours of contact are necessary to reach the equilibrium.

Keywords: Chitosan, sulfate reducing bacteria, platinum, palladium, isotherms, kinetics.

1. INTRODUCTION

Platinum group metals (PGM) e.g. Pd, Pt and Rh are of interest due to their high value and catalytic properties. Demand for PGM is increasing due to their widespread and often obligatory utilization in automotive catalytic converters. Currently the main large-scale industrial recovery processes are hydro- or pyro-metallurgical but these conventional technologies also generate liquors containing residual precious metals [1-2]. The use of low-cost sorbents has been investigated for their potential to replace current costly methods of recovering heavy metals from solutions. Natural materials or waste products from industries can be economically employed. Thus research has evaluated a variety of sorbents e.g. lignin, tannin-rich materials, chitosan, microbial biomass, algae, alginate, seaweed or zeolites [3-4].

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Metal sorbing biomasses can have a real potential as selective, competitive and cost-efficient sorbents for precious metal recovery [5-7]. An alternative approach is the use of enzymatic processes. Sulfate-reducing bacteria (SRB) are known to have a broad reducing metal activity coupled to hydrogenases or/and cytochromes [8-10]. This has been demonstrated in the case of reduction of Pd(II) to Pd(0) but the best reductive accumulation only occurred after a prior biosorption step which suggests a high metal uptake as a pre-requisite to enzymatic catalysis, especially in the case of *Desulfovibrio desulfuricans* [11-12]. The present work focuses on the optimization of sorption procedures and selection of the best strain for Pd and Pt recovery and the sorption properties will be compared to those obtained with chitosan derivatives. Indeed chitosan, which is an aminopolysaccharide produced from crustacean shell, is very efficient at removing metal ions from dilute solutions [13-17]. Sorption may involve different mechanisms including chelation (for metal cations in near-neutral solutions) or ion exchange (for metal anions in acidic solutions). The sorption properties may be enhanced by chemical modification, including amine grafting (Poly(ethyleneimine), PEI) or thiourea grafting. Sorption properties will be characterized for both SRB and chitosan derivative mediated processes by investigating the influence of the pH on sorption efficiency, and performing sorption isotherms and kinetics.

2. MATERIALS AND METHODS

2.1. SRB, growth conditions and harvesting

Desulfovibrio desulfuricans (NCIMB 8307, D.d.), *Desulfovibrio vulgaris* (NCIMB 8303, D.v.) and *Desulfovibrio fructosivorans* (DSM 2604, D.f.) were grown for 2 days anaerobically (inoculation 10 % vol/vol from 24h pre-culture) in sealed bottles under a N₂ atmosphere, as batch cultures in Postgate C medium at 30°C (*D.d.* and *D.v.*) or 37°C (*D.f.*) [18]. Harvesting was carried out by centrifugation and resting cells were obtained by centrifuging 1 L of culture and washing the cells 3 times in air with 20 mM MOPS-NaOH buffer (pH 7). Experiments were also performed with dead biomass (harvested cells were autoclaved at 120 °C for 20 minutes); sorption capacities were comparable to those obtained with living biomass. Dry weight was determined by filtration and drying to constant weight.

2.2. Sorption procedures for SRB system

Pd and Pt solutions were prepared in distilled water from Na₂PdCl₄ and Na₂PtCl₆ salts, respectively, using HCl, HNO₃ and H₂SO₄ for pH control. For sorption isotherms, known volumes of metal solutions (V, usually 10 mL) at variable initial metal concentrations (C₀, 5-50 mg L⁻¹) in sterilized and sealed bottles were put in contact with a fixed amount of sorbent (m, 1.5 mg, i.e. sorbent dosage: 150 mg L⁻¹) under agitation (150 rpm) at 30 °C. The pH was maintained constant. Samples were collected by filtration after 4 days of contact and analyzed using the SnCl₂/HCl spectrophotometric method for Pt/Pd determination (C_{eq}) [19]. The mass balance equation was used for determining the sorption capacity (q, metal concentration on the biomass, mg g⁻¹ or mmol g⁻¹): $q = V/m (C_0 - C_{eq})$. The influence of chloride concentration was tested on biosorption performance at pH 2, using *D. desulfuricans* with addition of increasing amounts of NaCl. Sorption kinetics were carried out at a metal concentration of 50 mg metal L⁻¹ under agitation (150 rpm) at 30 °C and pH 2 (controlled with either HNO₃ or HCl) in the absence or the presence of NaCl (1 M) using *D. desulfuricans*. Kinetic experiments were also carried out using the same procedure with solutions containing 25 and 10 mg metal L⁻¹. Samples were regularly collected by filtration and analyzed.

2.3. Preparation of chitosan derivatives

Chitosan was supplied by Aber Technologies (France) as a flaked material with a deacetylation percentage of about 87 % and a molecular weight of $125,000 \text{ g mol}^{-1}$. Chitosan gel beads were prepared using a neutralization process consisting of a two-step procedure [20]: (a) the dissolving of chitosan (4-5 % w/w) in acetic acid (excess of acetic acid to completely dissolve the polymer), (b) the distribution of the viscous solution (filtered and de-bubbled) through a thin nozzle into a neutralization bath (NaOH 2M). The beads were collected after 16 hours of contact with the neutralization bath and then rinsed with several demineralized water baths up to constant pH. The size of the beads was $2.5 \text{ mm} \pm 0.2 \text{ mm}$ and the water content was approximately 95 %.

Chemical cross-linking of chitosan was performed by reacting 5 g of chitosan beads (dry mass) with 1.5 g of glutaraldehyde dissolved in 100 mL of demineralized water, for 24 h. For the synthesis of poly(ethyleneimine) grafted chitosan beads (PEI-GA), PEI was dissolved in dimethylacetamide (DMA). The beads were also mixed with DMA in order to exchange water with DMA and then favor the diffusion of PEI in the beads: 5 g of chitosan beads were added to 5 g (the amount was varied for some experiments using alternatively 3 g or 5g of PEI) of PEI dissolved in 100 mL of DMA. The mixture was reacted for 24 h. The chitosan beads were then rinsed with 30 mL of DMA, and reacted for 6 h with 1.5 g of glutaraldehyde dissolved in 50 mL of DMA: glutaraldehyde is thought to establish new linkages between the amine groups of the biopolymer and some amine groups of PEI. For the synthesis of thiourea derivative chitosan beads (PEI-Th-GA), the standard procedure consists of the addition of (a) 5 g of PEI (b) 1.5 g of thiourea and (c) 5 g of chitosan to 100 mL of DMA. The components were pre-reacted for 24 h and rinsed with 30 mL of DMA before the addition of 1.5 g of glutaraldehyde dissolved in 50 mL of DMA. Following the treatments, the sorbents were extensively rinsed with demineralized water. Because of the instability of previous derivative containing thiourea, the grafting of sulfur groups was carried out according to the procedure described by Cardenas *et al.* (2001) with chitosan flakes. This technique uses epichlorohydrin as crosslinking agent. Chitosan (20 g) was contacted with 1 L of acetic acid/acetate buffer (pH 4.6); 40 mL of epichlorohydrin dissolved in 1 L of acetone were added, and the slurry mixed at $35 \text{ }^\circ\text{C}$ for 36 h. Thiourea (20 g) was then added and the stirring continued for 6 h at $60 \text{ }^\circ\text{C}$. After that period, 46 g of thiourea were added and the system was stirred for 12 h at the same temperature. Then, 500 mL of NaOH (1 M) were added and the slurry was agitated for 4 h at $60 \text{ }^\circ\text{C}$. The solid product obtained (TDC) was filtered and successively washed with acetone, demineralized water and methanol. Finally, it was dried in an oven at $60 \text{ }^\circ\text{C}$.

2.4. Sorption procedures for chitosan derivatives system

The pH of the solutions was controlled using HCl and NaOH concentrated solutions. For sorption isotherms, known volumes of metal ion solution (150 mL) at fixed concentrations were contacted with varying sorbent quantities (from 3 to 35 mg, wet mass) at room temperature (20°C). After 3 days of agitation, the solutions were filtered through $1.2 \text{ }\mu\text{m}$ membranes and the filtrates were analyzed using ICP-AES (Jobin-Yvon JY36, France). For the study of sorption kinetics, one liter of metal ion solution at fixed pH was mixed with a fixed amount (100 mg) of sorbent in a jar-test agitated system. Five-milliliter samples were withdrawn at specified times, filtered through a $1.2 \text{ }\mu\text{m}$ membrane and analyzed as previously specified. For the study of the influence of competitor anions, chloride ions were added in the form of NaCl. The isotherms were modeled using the Langmuir equation:

$$q = \frac{q_m b C_{eq}}{1 + b C_{eq}}$$

where q_m (mmol g^{-1}) and b (L mmol^{-1}) are the constants of the model.

3. RESULTS AND DISCUSSION

3.1. Selection of SRB strain and influence of the acid used for pH control

Figure 1 compares the sorption capacities at pH 2 for Pt and Pd for 3 different strains of *Desulfovibrio* using different acids for pH control. Maximum sorption capacities were obtained with *D. desulfuricans*, regardless of the acid used for pH control and metal. Comparing the sorption capacities for Pt and Pd on the basis of molar units, it appeared that the biomasses have a greater affinity for Pd than for Pt, regardless of the strain.

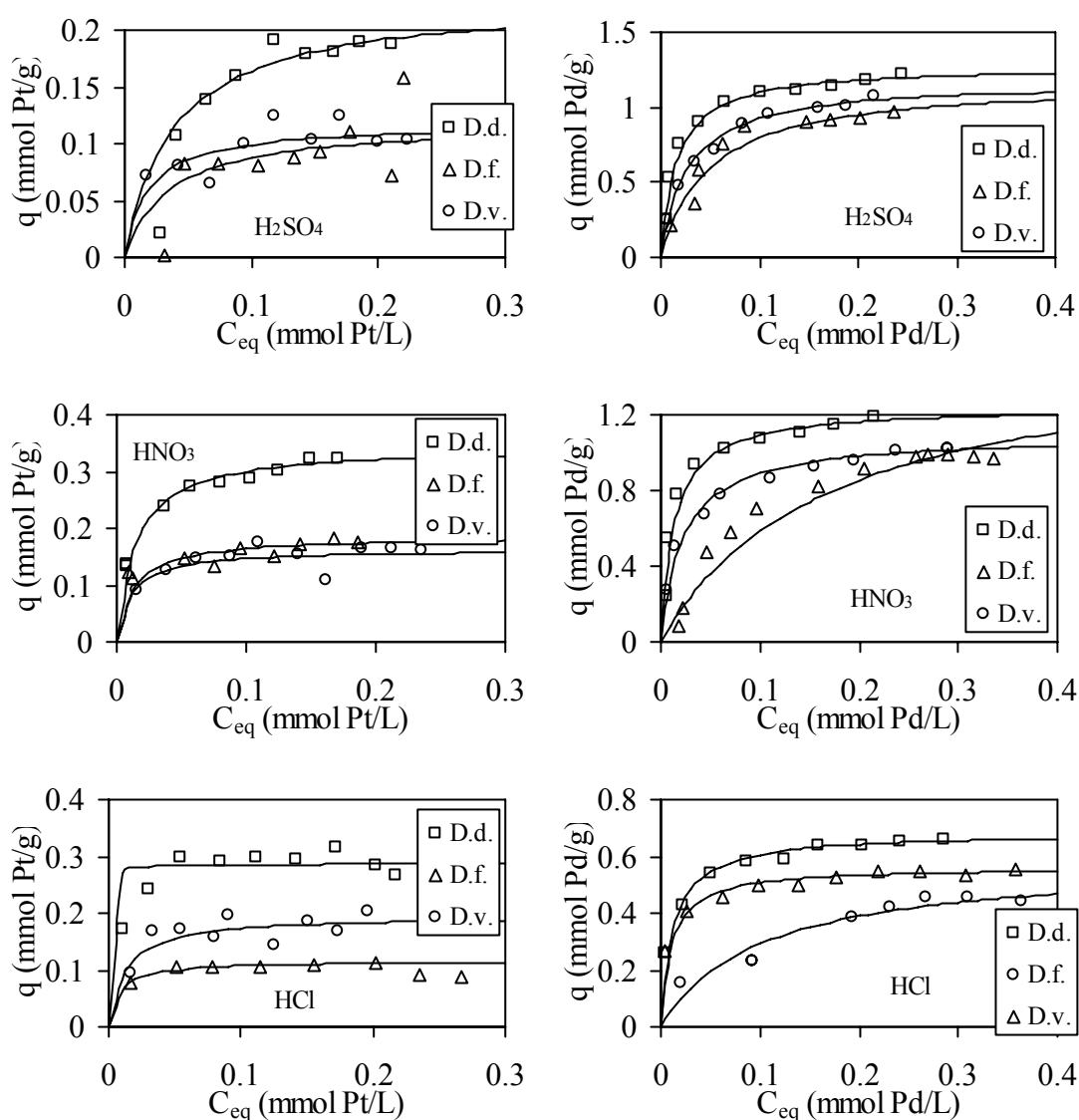


Fig. 1. Influence of the acid used for pH control and SRB strain on Pt and Pd sorption isotherms (at pH 2) (q : biomass total sorption capacity)

Palladium sorption was higher in sulfuric and nitric acid solutions than in hydrochloric acid media. Bacterial strains have a greater affinity for Pt in nitric and sulfuric acid solutions. These differences may be explained by differences in the composition of cell walls or/and by the effect of metal speciation. Indeed, PGM are very sensitive to the composition of the solution with respect to the formation of complexes (especially chloro-complexes), which in turn may affect the sorption mechanism (chelation versus ion-exchange) and the affinity of metal species for sorption sites. Table 1 reports the parameters of the Langmuir equation that was used for the modeling of sorption isotherms in Figure 1.

Table 1

Influence of the acid used for pH control at pH 2 on the Langmuir parameters for the modeling of Pd and Pt sorption isotherms using *D. desulfuricans* (D.d.), *D. fructosivorans* (D.f.) and *D. vulgaris* (D.v.).

| Acid | Bacteria | Pt | | | Pd | | |
|--------------------------------|----------|-------|-------|-------|-------|------|-------|
| | | q_m | b | R^2 | q_m | b | R^2 |
| HNO ₃ | D.d. | 0.343 | 68.5 | 0.996 | 1.24 | 73.1 | 0.997 |
| HNO ₃ | D.f. | 0.185 | 78.0 | 0.980 | 1.59 | 5.85 | 0.816 |
| HNO ₃ | D.v. | 0.163 | 88.5 | 0.900 | 1.09 | 44.5 | 0.998 |
| HCl | D.d. | 0.287 | 1800 | 0.986 | 0.682 | 80.4 | 0.999 |
| HCl | D.f. | 0.116 | 126.3 | 0.970 | 0.583 | 10.1 | 0.940 |
| HCl | D.v. | 0.195 | 76.9 | 0.944 | 0.562 | 93.2 | 0.998 |
| H ₂ SO ₄ | D.d. | 0.228 | 25.6 | 0.985 | 1.27 | 62.3 | 0.998 |
| H ₂ SO ₄ | D.f. | 0.118 | 28.5 | 0.593 | 1.17 | 21.1 | 0.972 |
| H ₂ SO ₄ | D.v. | 0.118 | 52.9 | 0.928 | 1.77 | 36.8 | 0.995 |

3.2. Comparison of chitosan derivatives for Pt and Pd sorption at pH 2

Figure 2 compares Pt and Pd sorption properties at pH 2 (controlled with HCl, which is the best medium for PGM sorption, as shown in previous work) for different chitosan derivatives. Experiments were performed at low metal concentration. It is interesting to observe that sorption capacities as high as 3 mmol Me g⁻¹ were obtained and that sorption isotherms were characterized by a pseudo-rectangular shape: the saturation plateau was obtained at residual concentrations as low as 0.05 mmol Me L⁻¹ (especially for PEI and TDC). The Langmuir equation failed to fit experimental data at low Pt concentration in the case of TDC.

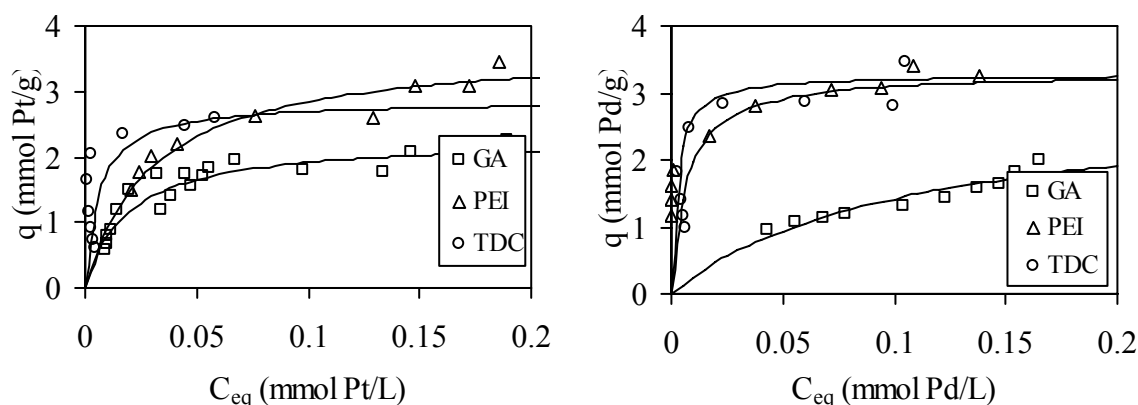


Fig. 2. Pt and Pd sorption isotherms at pH 2 for GA, PEI and TDC chitosan derivatives.

3.3. Influence of pH on sorption performance

Figure 3 shows the influence of pH on Pt and Pd sorption by *D.desulfuricans* (selected for its highest affinity for PGMs) with HNO₃, HCl and H₂SO₄ solutions. As expected increasing the pH resulted in an increase in sorption capacities due to the weaker competitor effect of counter anions brought to the solution by the acid used for pH control. The differences between the different acidic solutions decreased at increasing the pH since the amount of acid used for pH control (and consequently the addition of counter anions) also decreased. Sorption capacities were again lower in HCl solutions. This result contrasts with other experiments performed with ion-exchange resins (chitosan sorbents) for which the control of the pH with HCl enhances the formation of chloro-complexes, readily adsorbable on protonated amine groups. It may indicate that the sorption mechanism is different to that observed with chitosan material. These results confirm the greater affinity of the sorbent for Pd than for Pt.

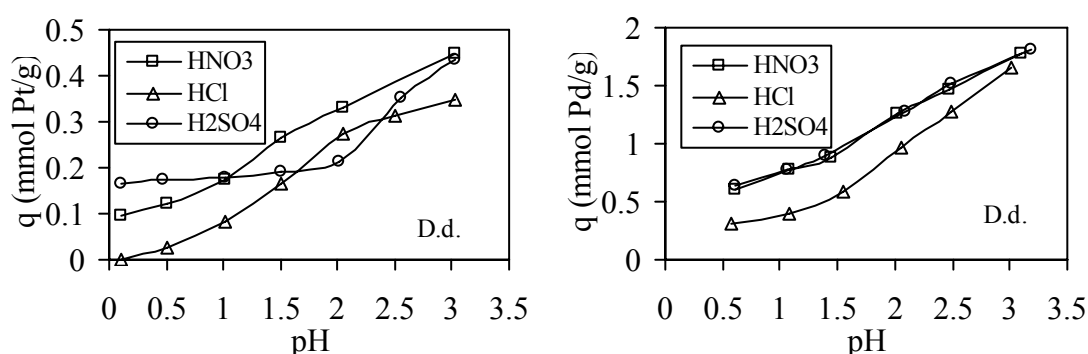


Fig. 3. Influence of pH and acid used for pH control on Pt (left figure) and Pd (right figure) sorption capacity (Co(Pd/pt): 50 mg Metal L⁻¹; Sorbent dosage: 150 mg L⁻¹).

The influence of the pH on the sorption of Pt and Pd was also investigated. The PEI and TDC (glutaraldehyde cross-linked material) was significantly less efficient at sorbing PGMs than the other derivatives, see above). Table 2 shows the parameters of the Langmuir equation that were used for the modeling of sorption isotherms in Figure 4. In most cases, except for TDC and platinum at low metal concentration, the Langmuir equation fitted well experimental data.

Table 2

Influence of the pH (controlled with HCl) on the Langmuir parameters for the modeling of Pd and Pt sorption isotherms using GA, PEI and DTC derivatives of chitosan.

| pH | Sorbent | Pt | | | Pd | | |
|----|---------|----------------|-------|----------------|----------------|-------|----------------|
| | | q _m | b | R ² | q _m | b | R ² |
| 1 | PEI | 1.11 | 27.4 | 0.984 | 1.64 | 37.85 | 0.991 |
| 2 | PEI | 3.69 | 33.25 | 0.980 | 3.28 | 408.8 | 0.995 |
| 3 | PEI | 1.94 | 2725 | 0.983 | 2.68 | 114.7 | 0.992 |
| 4 | PEI | 2.65 | 1130 | 0.992 | 2.20 | 74.3 | 0.955 |
| 1 | TDC | 2.21 | 196.9 | 0.988 | 2.54 | 295.5 | 0.997 |
| 2 | TDC | 2.86 | 161.6 | 0.940 | 3.31 | 146.8 | 0.975 |
| 3 | TDC | 2.90 | 100.8 | 0.801 | 3.00 | 194.4 | 0.996 |
| 2 | GA | 2.28 | 52.85 | 0.978 | 2.91 | 9.48 | 0.871 |

Maximum sorption capacities were obtained at pH 2 for the PEI derivative of chitosan, with a significant decrease at pH 1 and pH 3. At pH 4, the results should be considered with caution since precipitation may occur. On the other hand, with TDC the sorption isotherms were influenced negligibly by the pH (in the range pH 1-3): the difference in maximum sorption capacities did not exceed 10-20 %. This may be explained by the different mechanisms involved in metal uptake for PEI and DTC. For PEI, sorption occurs through anion-exchange on protonated amine groups; this mechanism is very sensitive to the pH of the solution, and to the presence of competitor anions. For TDC, sorption may be the combination of anion-exchange (on protonated amine groups) and chelation (on the thio groups). Chelation on sulfur compounds is less sensitive to pH and to the presence of competitor anions. This may explain the high efficiency of TDC for Pt and Pd sorption in a broader range of pH compared to the PEI derivative, although the sorption capacities were slightly higher for PEI than for TDC at the optimum pH (i.e. pH 2). The increase in the density of sorption sites (by grafting of supplementary amine functions) may explain this improvement in sorption properties.

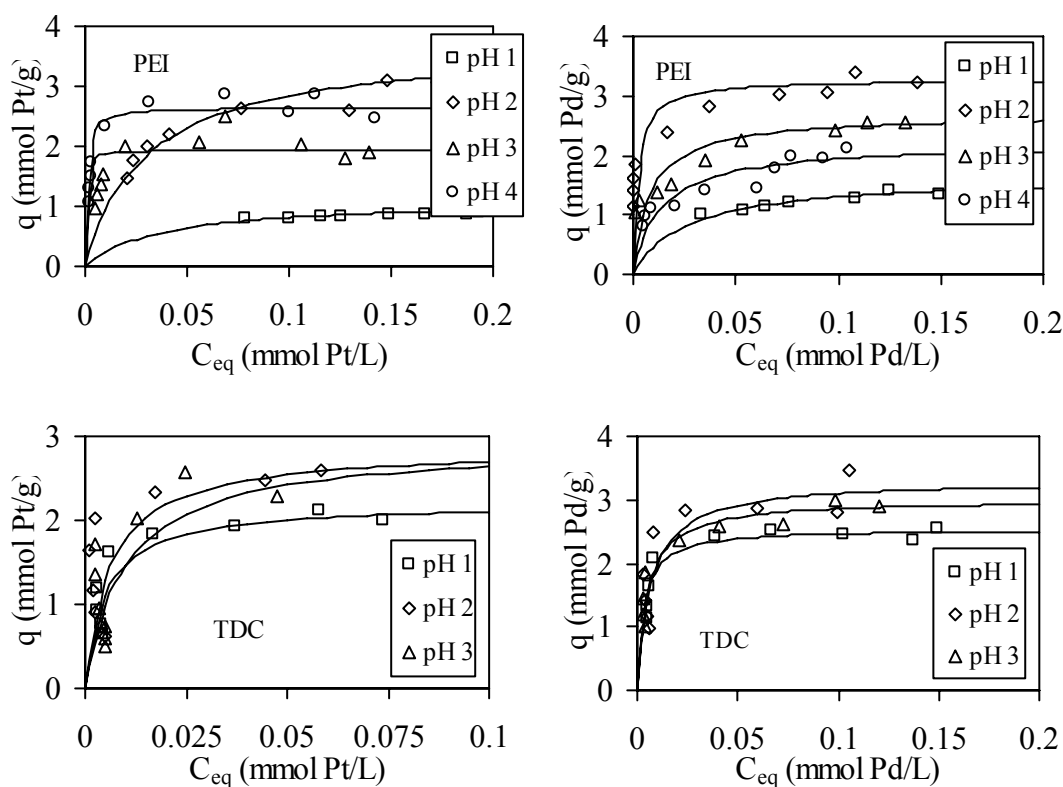


Fig. 4. Influence of pH on Pt and Pd sorption isotherms using PEI and TDC.

3.4. Sorption kinetics

The kinetics is also an important parameter in the design of a sorption process. Figure 5 shows Pt and Pd sorption kinetics using *D. desulfuricans* at pH 2 controlled with nitric acid and hydrochloric acid (with a superimposition of kinetic curve performed in HCl media in the presence of NaCl). Sorption kinetics were little influenced by the acid used for pH control. In the case of Pd sorption, a greater contact time was necessary to reach the equilibrium. The presence of NaCl strongly decreased the efficiency of sorption, especially in the case of Pd.

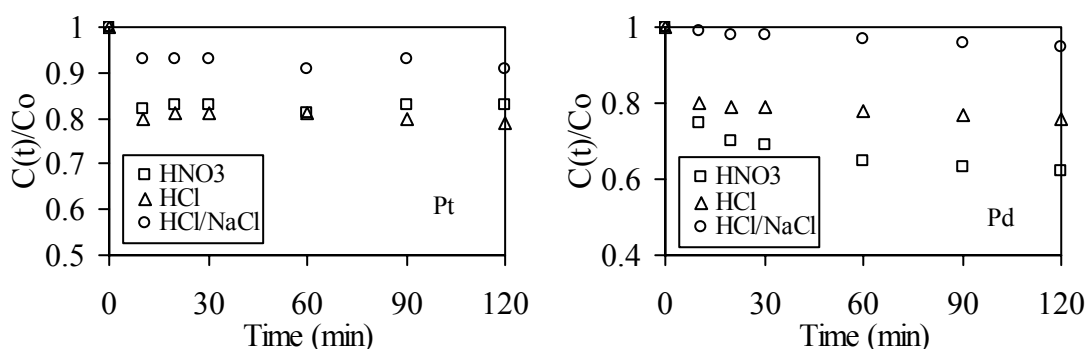


Fig. 5. Influence of the acid used for pH control on Pt and Pd sorption kinetics at pH 2 using *D. desulfuricans* ($C_0(\text{Pt/Pd})$: 50 mg Metal L⁻¹; Sorbent dosage: 150 mg L⁻¹).

In most cases, more than 90 % of total sorption was achieved within the first 10 minutes of contact. Sorption kinetics was significantly faster with SRB than for chitosan derivatives (see below). The initial concentrations did not significantly influenced sorption kinetics, regardless of metal (Figure 6). The same contact time (about 10 minutes) was sufficient to achieve the same percentage of metal uptake (90 %). The sorption was restricted to the external surface of the cells. The uptake was almost instantaneous (no effect of intraparticle diffusion resistance).

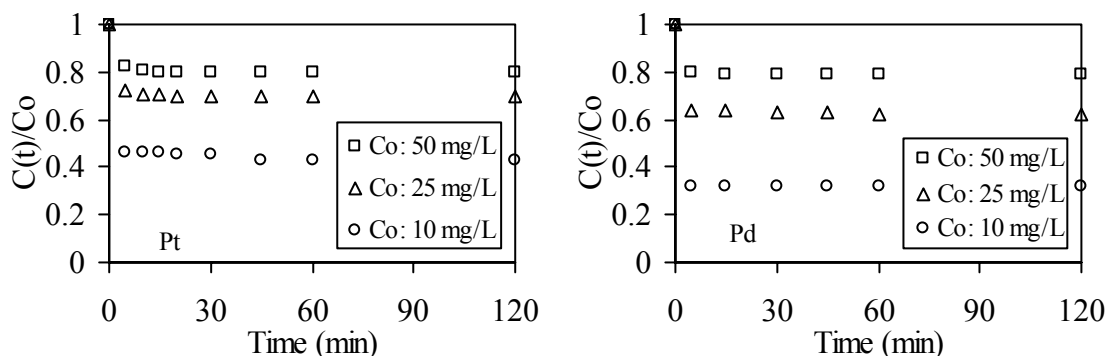


Fig. 6. Influence of metal concentration on Pt and Pd sorption kinetics using *D. desulfuricans* at pH 2 controlled with HCl (relative concentration decay curves: $C(t)/C_0 = f(t)$).

In the case of chitosan derivatives the reaction required a greater contact time to reach equilibrium: for PEI more than 24 hours of contact were necessary to achieve the complete removal of Pd and Pt. For TDC material, at the same sorbent dosage, the equilibrium was reached within 6 hours of contact. It is difficult to compare the data since sorbent dosage (100 mg L⁻¹) was sufficient to completely remove Pt and Pd. As a consequence it is possible that the sorbents were not fully saturated, or at least that the relative saturations were different for PEI and TDC. It is not possible to conclude on the predominance of the resistance to intraparticle diffusion on the kinetic control. Other experiments have shown using similar sorbents that sorption occurred in the whole mass of the sorbent. It is thus anticipated that the diffusion of metal ions to internal sites controls the time required to achieve complete recovery of PGMs. It is important to observe that PEI was prepared with chitosan gel beads of expanded structure but with greater particle size, while TDC was obtained by chemical modification of flakes with lower porous network with small particle size.

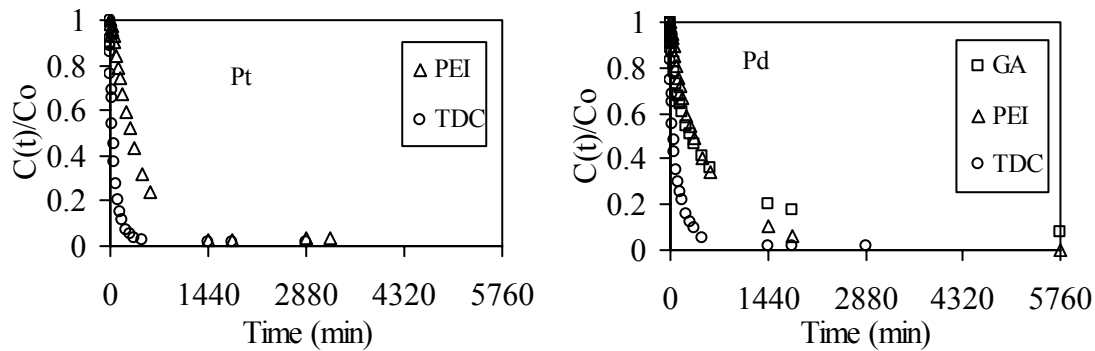


Fig. 7: Pt and Pd sorption kinetics on PEI and TDC at pH 2 (controlled with HCl, C_0 (Pt/Pd): 20-25 mg Metal L^{-1} ; Sorbent dosage: 100 mg L^{-1}).

3.5. Influence of chloride concentration on sorption performance

One purpose of this work was to develop a metal recovery technology applicable to acidic leachates obtained from solid scrap. The main characteristics of leachates from spent automotive catalysts and other wastewaters are a high concentration of chlorides and low pH, since *aqua regia* is necessary for effective PGM leaching. Hence, the influence of chloride on Pd and Pt sorption is of major concern for the evaluation of process applicability. Figure 8 compares relative sorption capacities (compared to reference performance, i.e. without NaCl addition) for the different systems with increasing concentrations of chloride. The addition of chloride strongly reduced Pt sorption capacities especially for SRB system and for PEI: when chloride concentration exceeded 0.25-0.5 M Pt sorption capacities were negligible for PEI and SRB. In the case of Pd, with PEI derivative and SRB there was also a significant decrease in sorption capacity, however it was necessary to drastically increase NaCl concentration: with SRB the sorption decrease was about 70 % at a chloride concentration of 1 M; with PEI, at a 0.5 M chloride concentration the decrease did not exceed 50 %. In the case of TDC, the addition of chloride decreased sorption capacities but even with a chloride concentration as high as 2 M, the decrease of sorption capacity did not exceed 40 %, regardless of metal. The grafting of supplementary amine groups (PEI) increased the number of sorption sites, and then decreases the competitor effect of chloride ions.

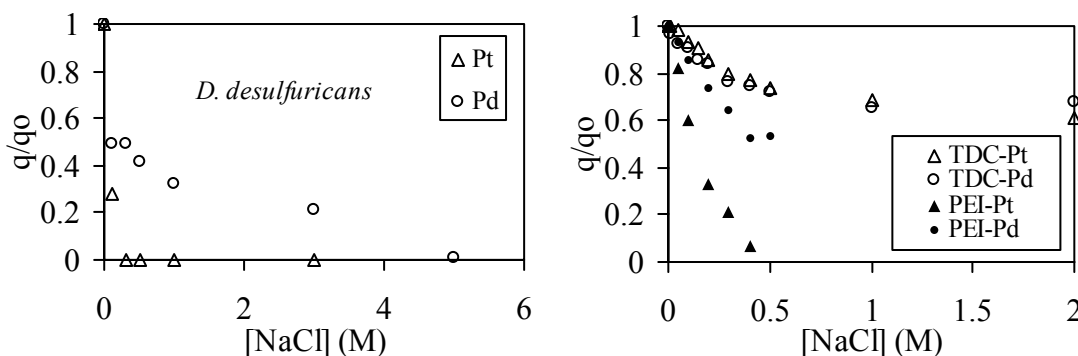


Fig. 8. Influence of chloride concentration on Pt and Pd sorption at pH 2 (controlled with HCl; for *D. desulfuricans*: C_0 (Pd/Pt): 50 mg Metal L^{-1} ; Sorbent dosage: 150 mg L^{-1} ; for chitosan derivatives: C_0 (Pd/Pt): 20 mg Metal L^{-1} ; Sorbent dosage: 40 mg L^{-1}).

In the case of thiourea grafting, new chelating groups less sensitive to the pH and the competitor effect of chloride anions, limited the influence of chloride concentration. The TDC appears to be perfectly designed for the treatment of industrial solutions containing high concentrations of chloride ions and low pH, despite the flaked conditioning that limits the use of sorbent particles in fixed-bed systems.

4. CONCLUSIONS

Sulfate-reducing bacteria (especially *D. desulfuricans*), and chitosan derivatives (more specifically thiourea derivative of chitosan) appear promising sorbents for the recovery of PGMs from dilute acidic solutions (in the range pH 1-3) containing chloride anions (below 0.5-1 M). Both sorbents have a preference for Pd over Pt, though more marked in the case of SRB. The SBR system is characterized by very fast sorption kinetics (equilibrium reached within 10 minutes of contact), while chitosan derivatives are characterized by slower kinetics but very high sorption capacities (up to 3 mmol Me g⁻¹). Experiments are currently performed on the sorption of Pt and Pd in multi-component systems and in the presence of other metals (typical industrial solutions).

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