Extraction of platinum and palladium from aqueous solutions using ionic-liquid-modified magnetic nanoparticles

Joana C. Almeida a,b, Celso E.D. Cardoso a,b, Márcia C. Neves a, Tito Trindade a, Mara G. Freire a, Eduarda Pereira b,*

a Chemistry Department and CIICECO-Aveiro Institute of Materials, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
b Chemistry Department and LAQV-REQUIMTE, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal

ABSTRACT

Platinum (Pt) and palladium (Pd) are noble metals with a high economic and strategic value in several technologies, including catalytic converters production. This work focused on the impact of three key variables on the performance of ionic liquid (IL)-modified magnetite nanoparticles (NPs) in removing Pt(IV) and Pd(II) from aqueous solutions, in which the optimal operational conditions were identified through a Response Surface Methodology (RSM). Experimental conditions were defined by a Box-Behnken Design of 3 factors-3 levels (pH of 4, 6 and 8; sorbent dose of 100, 300 and 500 mg/L; and element concentration of 0.4, 1.2 and 2.0 mg/L). The results have shown high capacity of IL-based NPs to remove Pd. The optimal conditions leading to the total removal of Pd(II) have been found as: 1 h of sorption, pH 6.34–6.77, 391–418 mg/L of sorbent, and 1.2–1.7 mg/L of platinum-group elements (PGEs). The optimal operating conditions obtained by RSM were then tested on more complex matrices, such as bottled water and sea water with salinity 15. It was found that NPs have a high potential in removing Pd(II) from bottled water; however, in solutions with salinity 15, the efficiency decreases significantly due to competition between Pd(II) and other ions present in solution.

1. Introduction

Platinum (Pt) and palladium (Pd) are well known for their high value in various industries, namely by their catalytic role in reducing vehicle emissions to contributions in electronics manufacturing [1]. The demand for Pt and Pd is expected to grow due to the intensive exploitation of these metals for emerging technologies. Metal extraction from ores, as compared to their production from scrap, is not a sustainable process because mining requires high energy input and large amount of water, thus leading to increased impact on the biosphere and more waste produced per tonne of material extracted [2]. Recycling these metals from end-of-life products will contribute to environmental sustainability, also making this approach an economical opportunity. Currently, the extraction of Pt and Pd from secondary sources, such as aqueous wastes resulting from recycling autocatalysts, relies primarily on hydrometallurgical processes. These processes involve the use of leaching solutions to extract the metal species from the source material and, subsequently, their separation from those metal enriched solutions. Hydrometallurgical processes pose challenges due to their reliance on volatile organic phases and hazardous reagents, thus causing environmental concerns [3]. Consequently, there is the need to develop environmentally-friendly and cost-effective techniques for separating Pt and Pd chemical species from aqueous solutions that result from recycling processes.

There are many prevalent techniques for the recovery of PGEs from aqueous wastes, including chemical precipitation, coagulation, flocculation, electrochemical methods, ion-exchange, sorption, photocatalysis, and biological processes. Apart from their own limitations, such as high operational cost, low efficiency, or the generation of large amounts of residues, sorption is generally seen as highly efficient, economical, easy to apply and has a wide variety of materials that can be used as sorbents [4].

In the past years, magnetic nanosorbents have emerged as promising materials for a variety of applications, being explored for potential applications in biomedicine, environmental remediation, energy storage, and catalysis [5]. Regarding environmental applications, they are particularly effective for removal and extraction processes, thanks to their large specific surface area and the ability for surface
functionalization to capture target pollutants of distinct chemical nature, such as heavy metals, dyes, and organic pollutants presented in wastewater from different industries [6,7]. However, this class of nanosorbents stand out for allowing the implementation of magnetic assisted separation technologies in water treatment units. Hence, the added benefit of easy removal from solution using an external magnetic field has further fuelled interest in their use [8-13]. Noteworthy, improvements on the sorption efficiency of these nanosorbents can be achieved by tailoring their surface chemistry, by grafting functional chemical groups to their surfaces with strong affinity for target pollutants [14]. In this regard, ionic liquids (ILs), due to their wide chemical diversity, offer a promising strategy for nanosorbents' functionalization, leading to magnetic SILs.

While SILs have already been used for the removal of different pharmaceutical drugs, such as acetylsalicylic acid and sodium diclofenac [15,16], and metals like Hg(II), Pt(IV) and Pd(II) [17,18], there is a gap in exploring their magnetization for environmental applications. To this end, we describe the first IL-based magnetic nanosorbents with the covalent functionalization of the NPs with IL moieties. In the present research, we describe the first IL-based magnetic nanosorbents with surfaces functionalized after covalent grafting of selected ILs for the extraction of Pt(IV) and Pd(II). The sorption process was optimized using a surface-response method.

2. Experimental section

2.1. Material and reagents

All glass material used during the experiments were previously washed with nitric acid (HNO₃ 25 % v/v) obtained from Merck, Suprapur® 65 %, for at least 24 h, and then rinsed with ultra-pure water (Milli-Q water, 18 MΩ·cm). All chemicals used in this work were of analytical grade, obtained from chemical suppliers, and used without additional purification: (3-chloropropyl)trimethoxysilane (> 98 %, Acros Organics), ammonium hydroxide solution (NH₄H in H₂O, 25 %, Riedel-de-Haën), ethanol (C₂H₅OH > 99 %, Carlo Erba), gallium (Ga in 5 % HNO₃, 1005 ± 2 µg/mL, Inorganic Ventures), germanium (Ge in H₂O tr. HNO₃ tr. HF, 1003 ± 2 µg/mL, Inorganic Ventures), indium (In in 1.4 % HNO₃, 1003 ± 2 µg/mL, Inorganic Ventures), iron sulfate heptahydrate (FeSO₄·7H₂O > 99 %, Merk), methanol (HPLC grade, Fisher Scientific), niobium (NbCl₅ in 2 % HF, 1000 ± 1 µg/mL, Alfa Aesar), nitric acid (HNO₃, puriss. p.a., > 95 %, Merck), N-methylimidazole (99 %, Acros Organics), palladium (Pd in 5 % HNO₃, 1002 ± 6 µg/mL, Inorganic Ventures), platinum (Pt in 10 % HCl, 999 ± 3 µg/mL, Inorganic Ventures), potassium hydroxide (KOH, > 98 %, Pronolab), potassium nitrate (KNO₃, > 99 %, Merk), sodium hydroxide (NaOH, > 98 %, Pronolab), tetraethyl orthosilicate (C₄H₈O₄Si, TEOS, > 99 %, Sigma-Aldrich), and toluene (99.8 %, Fisher Scientific). Sorption experiments were performed using double distilled water, passed across a reverse osmosis system and further treated with a Milli-Q plus 185 water purification equipment.

2.2. Synthesis of colloidal magnete (Fe₃O₄) nanoparticles

Magnetic iron oxide NPs with an average size of 50 nm were synthesized by oxidative hydrolysis of Fe(II) in alkaline conditions, according to the procedure described in Oliveira-Silva et al. [22]. Ultrapure water was first deoxygenated under a N₂ stream, under vigorous stirring for 2 h. Then, 1.90 g (34 mmol) of KOH and 1.52 g (15 mmol) of KNO₃ were added to 25 mL of deoxygenated water in a 250 mL round flask. This mixture was heated at 60 °C, under N₂, and mechanically stirred at 500 rpm. After total dissolution, 25 mL of an aqueous solution of FeSO₄·7H₂O (4.75 g, 17 mmol) was added dropwise to the mixture and mechanical stirring was increased to 700 rpm. The resulting solution presented a dark-green colour after complete addition of the ferrous salt. After 30 min reaction, the round flask was placed in an oil bath at 90 °C, with the mixture under N₂ but without stirring, for 4 h. Finally, the resulting black powder was washed several times with deoxygenated water and ethanol. After washing, the collected powder was in an oven at 40 °C.

2.3. Coating of magnete nanoparticles

The magnete nanoparticles were then modified at the surfaces by using sol-gel methods via the alkaline hydrolysis of TEOs to obtain core-shell Fe₃O₄@SiO₂ nanoparticles, according to the procedure described in Amiri et al. [23]. Briefly, a dispersion of NPs (1.00 g) in a mixture of ethanol (80 mL) and ultra-pure water (20 mL) was prepared and left immersed in an ice bath, over 15 min under sonication (horn Sonics, VibraCell). Then, 2.15 mL of TEOs dissolved in ethanol (50 mL) and 6 mL of ammonia 25 % (v/v) were added, and the suspension was left in an ice bath for more 10 min under sonication. Afterwards, the reaction proceeded at room temperature under continuous mechanic stirring at 600 rpm for 12 h. Finally, the silica coated particles were washed by ultra-pure water and ethanol, collected by approaching a NdFeB magnet and dried at room temperature.

2.4. Modification of Fe₃O₄@SiO₂ nanoparticles with ILs

The modification of Fe₃O₄@SiO₂ nanoparticles with ionic liquids was performed in a one-step reaction, based on the synthesis procedure previously reported by Comès et al. [24] for non-magnetic NPs. The Fe₃O₄@SiO₂ nanoparticles (1.5 g) were suspended in 100 mL of dried toluene, followed by the addition of 5 mL of 3-chloropropyltrimethoxysilane (25 mmol), and 2 mL of N-methylimidazole (25 mmol). This suspension was mechanically stirred at 700 rpm and refluxed for 24 h at 95 °C. After refluxing, the reaction was stopped, the NPs were collected using magnet, and washed with toluene (50 mL), methanol (50 mL), water (50 mL), and again with methanol (25 mL). The obtained nanoparticles functionalized with the IL, Fe₃O₄@SiO₂-(C₆H₄Im)Cl, were dried at 80 °C for 8 h prior to their characterization and sorption experiments.

2.5. Characterisation techniques

The chemical and physical characterization of IL-modified NPs was performed using various techniques. The crystalline phase in the powdered sample was identified by X-Ray diffraction (XRD) using an Empyrean PANalytical diffractometer (Cu Kα X-radiation, λ = 1.54060 Å; λ₂ = 1.54443 Å). The registration of the diffraction patterns was performed with a step size of 0.026°, in continuous mode, in the 15 ≤ 2θ ≤ 95° range. Fourier Transform Infrared (FT-IR) spectra (in the range 4000–400 cm⁻¹) were recorded using a Bruker TENSOR 27 spectrophotometer, equipped with an Attenuated Total Reflectance (ATR) accessory, after 256 scans with resolution of 4 cm⁻¹. The morphology of the NPs was appraised by transmission electron microscopy (TEM) (Electron Microscope JEOI, 2200FS, working at 200 kV). Samples were prepared by direct deposition of an aliquot drop of an ethanolic suspension of particles over a grid of copper coated with a carbon film and then let to evaporate the solvent at room temperature. Elemental analysis for carbon, hydrogen and nitrogen contents (in weight percentage) were performed with a Truspec Micro CHNS 630-200-200 elemental analyser. Analysis parameters were: sample amount about 2 mg; combustion furnace temperature of 1075 °C; afterburner temperature of 850 °C. Regarding the detection method, infrared absorption was used to determine the amount of carbon and hydrogen while the amount of nitrogen was determined by thermal conductivity. The specific surface area (SBET) of NPs were performed on an automated surface area analyser (Quantachrome Autosorb IQ2) by means of nitrogen adsorption-
desorption. Prior to the measurements, the samples were degassed overnight at 100 °C. Zeta potential measurements of the colloidal samples were performed using a Zetasizer Nano ZS (Malvern Instruments). The pH of the colloid was varied between 2 and 10, either using NaOH or HNO₃ aqueous solutions. The temperature was kept at 25 °C, and three replicate measurements of zeta potential were performed for each sample. Measurements of hysteretic cycle to evaluate the magnetic properties of NPs were performed using SQUID magnetometer at 27 °C. The magnetization was normalized to the total mass of the sample.

2.6. Experimental design

The sorption experiments were carried out to evaluate the sorption performance of IL-modified NPs on a solution of Pt(IV) and Pd(II) for a contact period of 24 h. The working solutions were prepared by diluting a specific volume of commercial stock solutions of Pt and Pd and other critical chemical elements (Ga, Ge, In and Nb) in ultra-pure water. Different amounts of NPs (100, 300 and 500 mg/L) were placed in contact with three different PGE concentration solutions (0.4, 1.2 and 2.0 mg/L). The sorbent dose was set as low as possible to ensure low costs with the material and low residues generations. For the element concentration, values were chosen within the range found in secondary sources, where the concentration of Pt and Pd are typically around 1 ppm [25]. Additionally, pH was adjusted to 4, 6 or 8 with HNO₃ 2 % (v/v) and NaOH (1 and 10 mol/L). These pH values cover a range relevant to practical applications, namely different industrial effluents, allowing us to explore the impact of pH on sorption efficiency. Solution samples were taken in predetermined periods (15 min, 1 h and 24 h) after NPs addition (0 h), immediately placed under the influence of a magnet for 5 min, then acidified with HNO₃ (65 %) to guarantee pH < 2, and stored at 4 °C for further quantification of PGEs. Control solutions (ultra-pure water containing only the chemical elements, in absence of sorbent) were always run in parallel with the assays to evaluate potential experimental losses of PGEs (by precipitation or sorption on the vessels walls) or contamination.

The removal efficiency of PGEs by IL-modified NPs in solutions with more complex matrices (bottle and sea waters) was further studied. The PGEs saline solutions (with salinity 15) were prepared by diluting the required amount of real sea water, after filtration, in distilled water.

2.7. Elements quantification

The quantification of Pt and Pd in solution was performed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), using a Horiba Jobin Yvon Activa M spectrometer (radial configuration) equipped with a Burgener MiraMist nebulizer. Calibration curves were established using 5 standards, with concentrations between 20 and 2000 μg/L, prepared by the dilution of Pt and Pd commercial certified stock solutions into acidified water (1 % HNO₃ v/v). Only calibration curves with a correlation coefficient above 0.999 were accepted. The limit of quantification was considered as the lowest standard of calibration curve (20 μg/L). The coefficient of variation between sample replicates (at least, three replicates were investigated) did not exceed 5 %.

The amount of PGEs retained by the sorbent material per unit of mass, q (μg/g), considered that all of the Pt and Pd removed from the solution were bond in the sorbent, was estimated using the Eq. (1):

\[
q = \frac{(C_0 - C_t)}{m} \times V
\]  

(1)

where \(C_0\) (μg/L) is the initial concentration of PGEs in solution, \(C_t\) (μg/L) is the concentration of PGEs at time \(t\), \(m\) is the mass of sorbent (mg) and \(V\) is the solution volume (L).

The removal efficiency, \(R\) (%), for Pt and Pd in IL-modified NPs was calculated as follows (Eq. (2)):

\[
R = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

(2)

where \(C_0\) is the initial concentration and \(C_t\) is the concentration in the liquid fraction at a certain time \(t\).

2.8. Response Surface Methodology

Statistical modelling techniques, such as Design of Experiments (DoE) and Response Surface Methodology (RSM), are widely used for optimizing sorption processes [26–28]. DoE is helpful in the early stages of research, helping to identify key experimental variables that significantly impact the response studied. RSM, on the other hand, is used to build a statistical model that describes the relationship between these variables and the target response, based on the experimental results generated by DoE. The response is then optimized through this model by finding the optimal levels of the variables that maximize or minimize the response [26]. The Box-Behnken design is a commonly used method to perform DoE and RSM due to its precision and efficiency, although it may have limitations in predicting extreme points [27].

The Box-Behnken design of 3 factors-3 levels was used in this work. This approach allows to obtain the most relevant experiments to evaluate the different factors, but with a significant reduction of the number of experiments needs, what makes the experimental procedure more efficient [28]. The 3 independent variables studied were the solution pH, the dose of sorbent, and the initial concentration of PGEs, and each variable is placed as three equidistant values (−1; 0; 1), as presented in Table 1. The impact of these variables was evaluated on the performance of IL-modified NPs, for the responses studied, which were the removal efficiency of PGEs and the extent of the accumulation (PGEs concentrations in NPs). The solution pH, the dose of sorbent, and the initial concentration of PGEs were selected for experimental design because they, along with temperature and contact time, are among the parameters that most significantly affect sorption [29]. However, the temperature was not included in this experimental design due to the associated increase in costs. The effect of contact time was also assessed.
in this study. To improve the precision, 3 replicates in the central point were carried out. The experiments generated by Box-Behnken design are showed in Table 2.

To simplify the analysis, RSM uses codified values for variables instead of the real values; the input variables are transformed to have a mean of zero and a standard deviation of one. The codified values of the independent variables ($X_k$) are calculated by the equation represented below:

$$X_k = \frac{(x_k - x_0)}{\Delta x_k}$$  \hspace{1cm} (3)

where $x_k$ corresponds to the uncodified value of the independent variables, $x_0$ is the variable value at its centre point, and $\Delta x_k$ is the step change between levels for the $k$ variable.

RSM describes the effects of variables (linear, quadratic and combined effects) through a second order polynomial function, expressed by the Eq. (4), that allows to predict the optimized conditions:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=i+1}^{k} \beta_{ij} X_i X_j$$  \hspace{1cm} (4)

where $Y$ is the response variable studied, $X_i, X_j, \ldots X_k$ are codified values of the independent variables, $\beta_0$ is a constant, $\beta_i, \beta_{ii},$ and $\beta_{ij}$ are the regression coefficients for the linear, quadratic, and interaction terms [26–28].

The results were obtained using the software Design-Expert version 13 (Stat-Ease Inc.) and Minitab Statistical Software version 19. Analysis of variance (ANOVA) allows to assess the significance of the factors, while Fisher’s test and its associated probability $p(F)$ were used to evaluate the interactions between the factors. The goodness of the adjustments was checked using the coefficient of determination, $R^2,$ and the adjusted coefficient of determination, $R^2_{adj}$ (Eqs. (5) and (6), respectively):

$$R^2 = 1 - \frac{\sum (\hat{y}_i - y_i)^2}{\sum (y_i - \bar{y})^2}$$  \hspace{1cm} (5)

$$R^2_{adj} = 1 - (1 - R^2) \frac{(N_{exp} - 1)}{(N_{exp} - N_{F} - 1)}$$  \hspace{1cm} (6)

where $\hat{y}_i$ are the values calculated by the model obtained, $y_i$ are the experimental values, $\bar{y}$ is the mean of the experimental values, $N_{exp}$ is the number of experimental data points, and $N_{F}$ is the number of parameters.

3. Results and discussion

3.1. Structural and chemical characterization of magnetic nanosorbents

The powder X-ray patterns of the synthesized Fe$_3$O$_4$ NPs (Fig. 1) match the reported data for inverse spinel cubic magnetite (JCPDS file No. 19-0629). These colloidal NPs, which were used as the ferrimagnetic cores for the final nanosorbents, preserve their chemical identity after the silica coating and IL functionalization, as shown by the respective XRD diffractograms (Fig. 1).
The FTIR spectra of Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$, and Fe$_3$O$_4$@SiO$_2$-[C$_3$C$_1$Im]Cl are presented in Fig. 2. Regarding the Fe$_3$O$_4$ NPs, the strong and broad band peaked at 540 cm$^{-1}$ is due to the Fe–O stretching lattice vibration [9]. The band at around 1050 cm$^{-1}$ in the spectra of coated particles is due the asymmetric Si–O–Si stretching vibration mode of amorphous SiO$_2$ [9]. The bands attributed to the O–Si–O deformation mode of amorphous SiO$_2$ and the symmetric Si–O–Si stretching vibration are also shown at 430 cm$^{-1}$ and 790 cm$^{-1}$, respectively [9]. On the spectra of functionalized NPs, the attenuation of the band observed at 935 cm$^{-1}$ on the spectra of Fe$_3$O$_4$@SiO$_2$, associated to the bending vibration absorption of Si–OH [15], indicates that the functionalization of silica occurred. The spectra of Fe$_3$O$_4$@SiO$_2$-[C$_3$C$_1$Im]Cl also present a weak band at 1556 cm$^{-1}$, attributed to the frequency of the imidazole ring, being in agreement with the literature reporting materials functionalized with imidazolium-based ILs [15].

The TEM images of Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$ and Fe$_3$O$_4$@SiO$_2$-[C$_3$C$_1$Im]Cl NPs are presented in Fig. 3. The original Fe$_3$O$_4$ NPs show a spheroidal shape with an average diameter about 65 nm. Core/shell type NPs are clearly observed after SiO$_2$ coating of the Fe$_3$O$_4$ cores, as shown by the shells of about 22 nm thickness. Note that after IL functionalization of the outer shells, no significant differences were observed on the morphological characteristics, as probed in the TEM images, though agglomeration had occurred on the powdered samples.

Table 3 shows the results of elemental analysis for quantitative determination of carbon, hydrogen and nitrogen present in the samples. The residual amount of carbon, hydrogen and nitrogen detected in Fe$_3$O$_4$ and Fe$_3$O$_4$@SiO$_2$ NPs are probably from vestiges of reagents used in the synthesis. The carbon and nitrogen contents (in weight fraction percentage) in the functionalized NPs (1.959 % and 1.101 %, respectively) increased as compared to the non-functionalized NPs, which corroborates the successful surface functionalization of the nanosorbents.

The specific surface area of the synthetized NPs was determined by nitrogen adsorption, using the BET (Brunauer-Emmett-Teller) method, and whose results are shown in Table 3. Although the values for the
porosity. Overall, Fe$_3$O$_4$@SiO$_2$ and Fe$_3$O$_4$@SiO$_2$-[C$_6$C$_1$Im] Cl NPs have low porosity.

Zeta potential measurements showed PZC values of 2.59 for Fe$_3$O$_4$@SiO$_2$ and 8.89 for Fe$_3$O$_4$@SiO$_2$-[C$_6$C$_1$Im] Cl NPs (Fig. 4). The higher PZC value displayed by functionalised NPs as compared to Fe$_3$O$_4$@SiO$_2$ is consistent with the presence of cationic moieties due to IL functionalization of the silica shells. The results of magnetic measurements performed on powders of Fe$_3$O$_4$, Fe$_3$O$_4$@SiO$_2$ and Fe$_3$O$_4$@SiO$_2$-[C$_6$C$_1$Im] Cl are shown in Fig. 5. All samples show magnetic hysteresis, as expected for such ferrimagnetic materials.

Coercivity (Hc), remanent magnetization (Mr) and saturation magnetization (Ms) values obtained from the hysteresis loops are included in Table S1 (Supplementary Material). The saturation magnetization for magnetite NPs, around 80 emu/g at 27 °C, is within the reported values for this material [22,30]. Also, this value is very close to the value for bulk magnetite (92 emu/g).

The modified nanoparticles show lower values of saturation magnetization than the uncoated magnetite NPs. Even though they are functionalized with diamagnetic material, Fe$_3$O$_4$@SiO$_2$ and Fe$_3$O$_4$@SiO$_2$-[C$_6$C$_1$Im] Cl have magnetizations still quite high (42 and 51 emu/g, respectively). The variables ahead the red line are significative for the response R (%). For Pt, only one factor had impact on the response: the “dose of sorbent” with low initial concentration. This is mainly due to the increase of mass loading to a higher number of binding sites available for sorption of Pt, improving the sorption efficiency. Also, for higher concentration, the amount of Pt in solution is higher, which leads to a rapid saturation of active sites. For Pd, the pH is the most important factor in its removal efficiency. This is related to the NPs surface charge and the chemical species of Pd in solution. At low pH values, protonation of active sites on the sorbent occurs, while with the increase of pH the surface charge is increasingly negative.

Considering the pareto charts obtained for the accumulation of PGEs on NPs (sorption capacity, q), the pattern observed relatively to the significant factors is completely different in comparison with the response R (%). For Pt, only one factor had impact on the response: the pH was impactful at 15 min of contact, while the factor “dose of sorbent” was significant at 1 h, but both with a negative effect. For Pd, none of the variables had impact on the response studied.

Based on the information provided by the pareto charts, only the significant variables were considered to generate the reduced models. Table 5 presents the reduced models for the removal efficiency of Pt and Pd, in terms of the real values of the independent variables. Given the lack of significant model terms for Pt and Pd in the response accumulation, it was not possible to obtain the equations to predict this response.

The coefficient of determination (R$^2$) and the adjusted coefficient of determination (R$^2_{adj}$) indicates the quality of the fittings between the experimental and the calculated data. The reduced models for Pd showed high values of R$^2$ (0.9406-0.9511) and R$^2_{adj}$ (0.9169-0.9315), demonstrating a good fitting and robustness of the models. Thus, an
accurate response can be predicted by these models. The values of $R^2$ and $R_{adj}^2$ for Pt functions were lower than those for Pd. Nevertheless, these values validate the good robustness of the model obtained for the $R$ (%) at 15 min, while the estimation of the $R$ (%) 1 h is not so precise.

3.3. PGEs removal from water and optimization of operational parameters by Response Surface Methodology

The removal results obtained in the different experiments revealed a high variability according to the parameters tested (pH, dose of sorbent and initial concentration of PGEs). Therefore, there is the need to use the response surface methodology for the optimization of the experimental parameters. The three-dimensional response surfaces allow an easy visual understanding of the interactions of the three independent variables on the $R$ (%) of Pt and Pd. Fig. 7 shows the 3D response surface plots for Pt, at 15 min and 1 h. The interactive effects of dose of sorbent and initial concentration on the removal efficiency, while keeping the pH constant (at 6), show that higher removal percentages are achieved at low concentrations and using the maximum amount of sorbent. Fig. 8 shows the 3D response surface plots for Pd, at 15 min and 1 h. The interactive

![Pareto chart with the effects of variables in the responses studied (removal efficiency and accumulation of Pt and Pd on NPs) at 15 min and 1 h of exposure. In the figure: A represents the solution pH, B is the dose of sorbent (mg/L) and C is the initial concentration of PGEs (mg/L). Variables with values below the dashed line are not significant.](image-url)
effects of pH and dose of sorbents on the removal efficiency, while keeping the initial concentration constant (1.2 mg/L), revealed that the removal is more affected by the pH than by the dose of sorbent, and this effect does not change with time. Higher removals are achieved for pH around 6.5. The interactive effects of pH and initial concentration were similar to the effects of pH and dose of sorbent, and therefore, are not shown here.

One of the main goals of this study was to optimize the operational parameters to maximize the removal efficiency of Pt and Pd from water. However, the removal results obtained in the experiments generated by Box-Behnken design revealed that Pt has low affinity for IL-modified NPs, and the better sorption of this element occurs in extreme conditions (at the minimum concentration and using the maximum amount of material). Thus, optimal experimental conditions were determined considered only the optimization of Pd removal by IL-modified NPs after 15 min and 1 h (Table 6). The optimized variables values were: pH 6.34, dose of sorbent of 418 mg/L and initial concentration of 1.2 mg/L, for exposure of 15 min, with expected removal of 100 % for Pd and 19 % for Pt. For 1 h of exposure, the optimal conditions differ on all variables: pH 6.77, dose of sorbent of 391 mg/L and initial concentration of 1.7 mg/L, with expected removal 100 % for Pd and 13 % for Pt.

The obtained results reveal the high affinity between the Pd and the NPs. Thus, it is possible to separate Pd from Pt through the application of NPs in various subsequent sorption-desorption cycles, which generates a

**Table 5**
Reduced models of the R (%) and the respective R^2 and R^2 adjusted as function of the significant variables (p-value < 0.05).

<table>
<thead>
<tr>
<th></th>
<th>15 min</th>
<th>1 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>reduced</td>
<td>R (%) = 18.67 + 0.11 Mass -</td>
<td>R (%) = 7.47 + 0.13</td>
</tr>
<tr>
<td>model</td>
<td>36.50 Concentration - 0.045 Mass - 1.56</td>
<td>Concentration - 0.063</td>
</tr>
<tr>
<td>Cox2</td>
<td>0.9267</td>
<td>0.8945</td>
</tr>
<tr>
<td>R^2</td>
<td>0.8973</td>
<td>0.7512</td>
</tr>
<tr>
<td>Pd</td>
<td></td>
<td></td>
</tr>
<tr>
<td>reduced</td>
<td>R (%) = -496.85 + 194.98 pH -</td>
<td>R (%) = -427.01 +</td>
</tr>
<tr>
<td>model</td>
<td>0.26 Mass + 0.053 pH*Mass - 162.15 pH - 0.20 Mass</td>
<td>16.67 pH<em>pH - 0.041 pH^2</em>Mass - 13.02 pH*pH</td>
</tr>
<tr>
<td>Cox2</td>
<td>0.9406</td>
<td>0.9511</td>
</tr>
<tr>
<td>R^2</td>
<td>0.9169</td>
<td>0.9315</td>
</tr>
</tbody>
</table>

**Table 6**
Experimental conditions determined for optimize Pd removal, at 15 min and 1 h.

<table>
<thead>
<tr>
<th>Time</th>
<th>pH</th>
<th>Dose of sorbent (mg/L)</th>
<th>Initial concentration (mg/L)</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min</td>
<td>6.34</td>
<td>418</td>
<td>1.2</td>
<td>100</td>
</tr>
<tr>
<td>1 h</td>
<td>6.77</td>
<td>391</td>
<td>1.7</td>
<td>100</td>
</tr>
</tbody>
</table>

![Fig. 7. 3-D Response Surfaces obtained with the reduced models during 15 min (on left) and 1 h (on right) of exposure of Pt to IL-modified NPs, in function of the dose of sorbent and concentration.](#)

![Fig. 8. 3-D Response Surfaces obtained with the reduced models during 15 min (on left) and 1 h (on right) of exposure of Pd to IL-modified NPs, in function of the dose of sorbent and pH.](#)
The solution is Pd and Pd may not be removed in the same manner. While the Pd species in experimental.

Fig. 9.

Comparison of R (%) of Pt and Pd determined by DoE and obtained experimentally.

<table>
<thead>
<tr>
<th>PGs</th>
<th>Time</th>
<th>pH</th>
<th>Dose of sorbent (mg/L)</th>
<th>Initial concentration (mg/L)</th>
<th>R (%) DoE</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>15 min</td>
<td>6.5</td>
<td>350</td>
<td>1.0</td>
<td>97</td>
<td>93</td>
</tr>
<tr>
<td>Pt</td>
<td>15 min</td>
<td>6.5</td>
<td>350</td>
<td>1.0</td>
<td>100</td>
<td>90</td>
</tr>
</tbody>
</table>

preconcentrate solution of Pd.

3.4. Validation of the conditions determined by DoE

The predictions of PGs removal efficiencies determined by DoE were confirmed experimentally. For that, an assay was performed under the following conditions: pH 6.5, dose of sorbent of 350 mg/L and initial concentration of 1.0 mg/L. The results of R (%) of Pt and Pd, determined by DoE and obtained in the experimental assay are presented in Table 7. The removal efficiencies obtained experimentally for Pt (22–24 %) and Pd (90–93 %) using the IL-modified NPs are closer to those obtained by DoE, but in general a little inferior.

The differences observed between Pt and Pd, either in terms of removal or in the way in which the studied variables affect its removal, could be explained by the fact that the species of these elements have opposite charge in the starting solution. Considering the zeta potential values presented for the functionalized material, it is expected that Pt and Pd may not be removed in the same manner. While Pd species in solution is [Pd2+], the Pt species is [PtCl6]2−, revealing different sorption mechanisms. Under the given experimental conditions, as imidazolium is a ligand containing N-donor atoms, it is capable of coordination with Pd(II) [31]. The Pt(IV) removal is believed to be accomplished through the formation of ionic pairs between the functionalized NPs and the anionic Pt chlorocomplexes.

3.5. The effect of matrix ionic strength on the PGs removal

The viability of sorption process in complex matrices is a parameter of high importance for industry since the industrial effluents are very complex. The removal efficiencies of Pd and Pt were evaluated in bottled water and real aqueous solutions with salinity 15 (common salinity in coastal and transitional systems). The results of R (%) in the different matrices are depicted in Fig. 9.

Either for Pt or Pd, the sorption efficiency decreases as the complexity of the matrix increases. Despite the removal efficiency in ultra-pure water is similar to those in bottled water, in saline water almost no sorption occurs for both elements. This trend indicates that competition exists for the binding sites with other ions present in solution, such as Na+, Ca2+ and Mg2+ (which are the dominant cations) and Cl− (a common anion in saline water).

This study demonstrates that, in terms of applicability on aquatic systems or industrial effluents, the use of IL-modified NPs for the removal of Pt or Pd could not be viable. On the other hand, these materials seem highly suitable to be applied in the sorption of Pd and Pt from catalytic converter lixiviates, with the further advantage of allowing magnetic assisted separation.

4. Conclusions

This work described, for the first time, the use of ionic-liquid-supported magnetic nanosorbents for extracting Pt(IV) and Pd(II) from aqueous solutions. The optimal conditions for PGs removal were identified using DoE and RSM. The use of DoE allowed the identification of the most important variables in the removal of Pt(IV) and Pd(II). One key finding is the significant impact of pH on the removal efficiency of Pd(II), with the highest performance observed at pH around 6.5. In contrast, the removal efficiency of Pt(IV) was primarily influenced by the sorbent dose and initial concentration, with higher removal efficiencies achieved at higher dosages and lower concentrations.

The studied magnetite IL-modified NPs demonstrated strong potential for Pd removal in ultra-pure and bottled waters. However, the increase of matrix ionic strength was found to significantly reduce their performance, being a result of competitive effects with other ions in solution. The results of this study open new avenues for future research, particularly in evaluating the sorption efficiency of magnetic IL-modified NPs under the conditions of a catalytic converter lixiviate.

CRediT authorship contribution statement

Joana C. Almeida: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Conceptualization. Celso E.D. Cardoso: Investigation. Márcia C. Neves: Investigation. Tito Trindade: Writing – review & editing, Supervision, Resources, Conceptualization. Mara G. Freire: Writing – review & editing, Supervision, Resources, Conceptualization. Eduarda Pereira: Writing – review & editing, Supervision, Resources, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Fig. 9. Sorption efficiency of IL-modified NPs for Pt and Pd in different matrices: ▲ ultra-pure water, — control ultra-pure water, – bottled water, — control bottled water, ■ saline water, — control saline water. Multielemental solution of 1 mg/L Pt and Pd, pH 6.5, 350 mg SIL/L, 0, 0.25, 1 and 24 h sorption.
Data availability

No data was used for the research described in the article.

Acknowledgment

The authors acknowledge the financial support to LAQV-REQUIMTE within the scope of the projects UIDB/50006/2020 and UIDP/50006/2020, financed by national funds through the FCT/MCTES. This work within the scope of the projects UIDB/50006/2020 and UIDP/50006/2020, financed by national funds through the FCT/MCTES. This work within the scope of the projects UIDB/50006/2020 and UIDP/50006/2020, financed by national funds through the FCT/MCTES. The authors acknowledge the financial support to LAQV-REQUIMTE (Fundaçao para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) and ESF (European Social Fund) through NORTE 2020 (Programa Operacional Região Norte) for the PhD grant SFHR/BD/119947/2018 and COVID/BD/152965/2022. Celso E. D. Cardoso acknowledges FCT/MCTES (Fundaçao para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) and ESF (European Social Fund) through NORTE 2020 (Programa Operacional Região Norte) for the PhD grant 2021-06684-BD. Márcia C. Neves acknowledge FCT for the research contract CEECIND/00383/2017/CP1459/CT0031 (DOI 10.54499/CEECIND/00383/2017/CP1459/CT0031).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2024.105510.

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