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ZEOLITE MODIFIED WITH NACL FOR ADSORPTION OF [PTCL$_4$]$^{2-}$ IN MODEL DISSOLUTIONS OF THE CISPLATIN PRODUCTION

ZEOLITA MODIFICADA CON NACL PARA LA ADSORCION DE [PTCL$_4$]^{2} EN DISOLUCIONES MODELO DE LA PRODUCCION DE CISPLATINO

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ABSTRACT

This study was aimed at the evaluation of natural zeolite modified with NaCl as adsorbent for Pt(II) extraction from dissolutions of [PtCl$_4$]$^{2-}$ and also at the selection of the experimental conditions in which the maximum adsorption capacity is achieved, modelling cisplatin [PtCl$_2$NH$_3$], one of the most worldwide used drug in anticancer therapy. Study of the adsorption capacity was performed in static operation mode by evaluating the influence of initial concentration and pH dissolution, adsorbent doses, contact time and temperature. The selected conditions were: pH 6, 30 min contact time and 1 g·L^{-1} adsorbent dose. Adsorption capacity at 25 ^{o}C was 67 mg·g^{-1} and higher for 50 ^{o}C and 70 ^{o}C. The chemisorption was hypothesized as predominant adsorption mechanism supported by the good fitting of pseudo second order kinetic model of Ho and adsorption increasing with temperature. The process was spontaneous, endothermic and the disorder increased after adsorption. For the first time, the high potentiality of NaCl modified zeolite for solid phase extraction of [PtCl$_4$]$^{2-}$ was demonstrated.

Keywords: adsorption; cytostatics; [PtCl$_4$]$^{2-}$; model dissolutions; modified natural zeolite.

RESUMEN

Este estudio tuvo como objetivo la evaluación de la zeolita natural modificada con NaCl como adsorbente para la extracción de Pt(II) y también a la selección de las condiciones en que la máxima adsorción ocurre, a partir de disoluciones de [PtCl$_4$]$^{2-}$, modelando el cisplatino [PtCl$_2$NH$_3$], uno de los fármacos más utilizados a nivel mundial en la terapia anticancerígena. El estudio de la capacidad de adsorción se realizó en modo estático, evaluando la influencia de la concentración inicial y el pH de la disolución, la dosis de adsorbente, el tiempo de contacto y la temperatura. Las condiciones seleccionadas fueron: pH 6, 30 min de tiempo de contacto y 1 g·L^{-1} de dosis de adsorbente. La capacidad de adsorción a 25 °C fue de 67 mg·g^{-1} y superior a 50 °C y 70 °C. Se propone como hipótesis que la quimisorción es el mecanismo predominante, respaldado por el buen ajuste del modelo cinético de seudo segundo orden de Ho y el aumento de la adsorción con la temperatura. El proceso fue espontáneo, endotérmico y el desorden aumentó después de la adsorción. Por primera vez, se demostró el alto potencial de la zeolita modificada con NaCl para la extracción en fase sólida de [PtCl$_4$]$^{2-}$.

Palabras clave: Adsorción; citostáticos; [PtCl$_4$]$^{2-}$; disoluciones modelo; zeolita natural modificada.

INTRODUCTION

Platinum group cytostatics (PGC) have been successfully applied in anticancer therapy for decades.(1) But PGC are simultaneously highly toxics.(2) Information about chemical and physical characteristics that allows to predict the chemical transformation dynamic of PGC in waters, i e, the chemical specie and its oxidation state present once these compounds are arrived in natural waters is scarce. However, the Pt(II) ions detected in waters has been reason enough to incentive the worldwide interest of the scientific community in the development of new more efficient water treatment directly addressed to the removal of PGC from waters. Those contaminants have been detected in residual waters and even in natural waters due to the inefficiencies of water treatments. In particular, PGC was found in the 0,82-14 μg L^{-1} concentration range in hospital effluents and in 0,04-0,76 μg L^{-1} concentrations in wastewaters from a water treatment plant.(3)

In this scenario, the development of novel more efficient technologies able to remove low concentrations of Pt(II) residues from waters is imperative. The solid phase extraction has been proposed as a viable and effective alternative for the remotion of other metals from waters.(4) In this method the selection of adsorbent material is crucial. The natural sorbents have been gaining a high popularity due to their low cost, easy management and lower environmental impact as compared with other employed synthetic sorbents.(5) Zeolites are one of the most economical and efficient natural adsorbents. Composition and structure of zeolites favor a high ionic interchange capacity with a demonstrated effectiveness in the removal of different types of contaminants.(6)

On the other hand, the chemical treatment of zeolites has been successfully applied to increase his adsorption capacity.(7) For example, the Cuban natural zeolite modified with NaCl showed high potentialities for the removal of Ni(II), Cu(II), Cd(II) and Pb(II), among others, from drinking waters.(8,9) At this point it is worthy to denote that, up to the best of our knowledge, zeolite has not been applied for the solid phase extraction of Pt(II) so far.

The present study was aimed at the evaluation of zeolite modified with NaCl as adsorbent in the solid phase extraction of $[PtCl_4]^{2-}$ in dissolutions modelling the cisplatin production and the selection of the experimental conditions in which the maximum adsorption capacity is achieved.

MATERIALS AND METHODS

Employed zeolite and its treatment

The employed sorbent was natural clinoptilolite-type zeolite from the Tasajeras deposit in Villa Clara province, Cuba.(10) Particle diameter of zeolite was between 0,2 and 0,5 mm. Before use, zeolite was chemically treated with 1 mol·L^{-1} NaCl dissolution in proportion of 1 g of zeolite with 100 mL of dissolution, during 60 min at environmental temperature and constantly shaking. Next, the mix was filtered and washed with deionized water. Finally, the modified zeolite was dried during 2 h at 60 °C. All reagents employed were analytical grade.

General procedure for $[PtCl_4]^{2-}$ adsorption on zeolite treated with NaCl

Experiments were performed in static mode. A given mass of adsorbent was in contact with a $[PtCl_4]^{2-}$ known concentration dissolution at the pH previously fixed and shaken in a shaker (100 rpm) for a given time and controlled temperature. After, the mix was filtered by gravity using a rapid qualitative filter paper. The concentration of $[PtCl_4]^{2-}$ was determined by Molecular Absorption Spectrophotometry in remaining dissolution after adsorption, following the procedure previously reported by Carmona *et al.*(11) The UV-VIS 2601 RayLeígh Spectrophotometer (China) was employed, using 1 cm thick quartz cuvettes Then, concentration of adsorbate on sorbent was calculated, knowing the initial concentration in dissolution. Each experiment was performed triplicate. Thereafter, sorption capacity and retention were calculated as usual. Each experiment was performed triplicate.

RESULTS AND DISCUSSION

Influence of $[PtCl_4]^{2-}$ dissolution pH

The $[PtCl_4]^{2-}$ adsorption capacity on zeolite and NaCl treated zeolite was determined in the 2-10 pH range, keeping the rest of experimental conditions fixed as following: volume and concentration of $[PtCl_4]^{2-}$ equal to 10 mL and 50 mg·L^{-1}, respectively, temperature of 25 ± 2 °C and contact time of 30 min (figure 1).

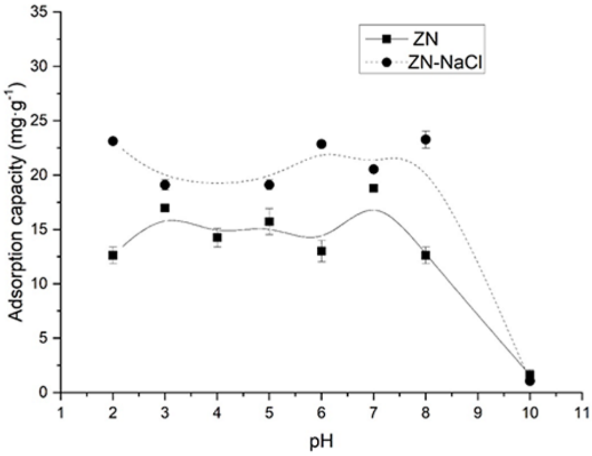

Fig. 1: Variation of $[PtCl_4]^{2-}$sorption capacity on NaCl treated and no treated zeolite with dissolution pH

Sorption capacity of treated zeolite was higher (22,8 ± 0,6 $mg·g^{-1}$) than that of non-treated zeolite (16 ± 1 $mg·g^{-1}$) in the studied pH entire interval. For both adsorbents, adsorption capacity was constant without statistically significant differences for 95 % confidence level in the 2-8 pH range, after which adsorption drastically decreased. Decrease of capacity for pH > 8 can be explained by the transformation of $[PtCl_4]^{2-}$ to hydroxy complexes of Pt(II) of higher mass that could delay the sorption process and even precipitate, all of which caused the capacity reduction of Pt(II).(12,13) The selected pH was 6 in the middle of pH interval of constant capacity, which guaranteed the highest capacity with no risk due to any inaccuracy in the pH fixing. The rest of experiments were performed just with the treated zeolite, which showed highest sorption capacity.

Influence of adsorbent dose

The variation of sorption capacity and retention as a function of adsorbent dose is shown in Fig. 2. In this experiment the fixed conditions were: pH = 6, contact time =30 min, temperature of 25 ± 2 °C and dissolution concentration of 50 $mg·L^{-1}$.

Adsorption capacity and retention increased up to a maximum value for dose of 1 $g·L^{-1}$. Diffusion of adsorbate particles from the dissolution to adsorbent surface was favored with dose increase in this interval, probably because the diffusion of adsorbate particles increased, while the number of active sites also increased. All of which conduced to the increase of sorption capacity and retention. In contrast, sorption capacity fast decreased for dose higher than 1 $g·L^{-1}$, whereas retention kept practically constant. This means that, once the dose reached 1 $g·L^{-1}$ value, no adsorbate particle remained in dissolution. Therefore, the retention did not change, while sorption capacity decreased because the adsorbent mass increased and there were not more particles to be adsorbed. The maximum retention was of 33 ± 2 %. Thus, the adsorbent dose selected was 1 $g·L^{-1}$.

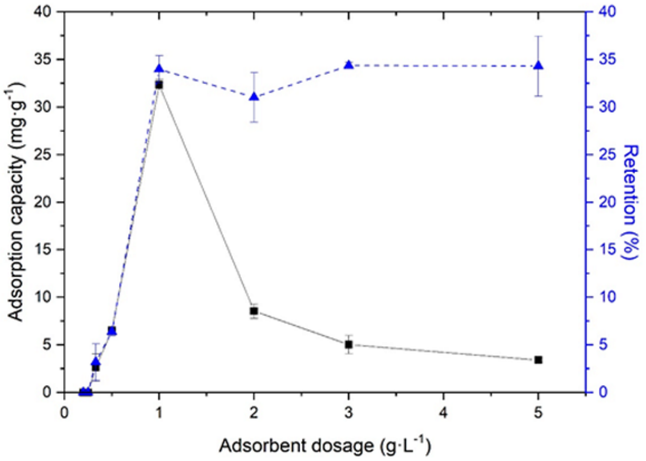

Fig. 2: Influence of adsorbent dose on the adsorption capacity and the retention of $[PtCl_4]^{2-}$ in NZ-NaCl

Influence of contact time. Kinetic model

In this experiment adsorption capacity was studied as a function of contact time for 10, 20, 30 and 40 min, with the rest of conditions set as: dissolution pH of 6, dissolution concentration of 50 $mg·L^{-1}$, adsorbent dose = 1 $g·L^{-1}$ and temperature of 25 ± 2 °C. Experiment results are shown in figure 3.

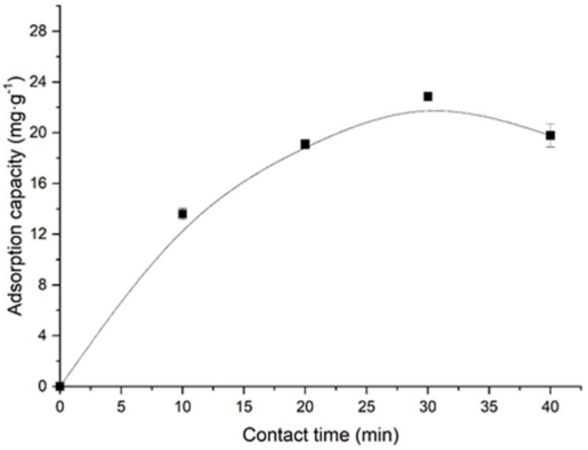

Fig. 3: Variation of $[PtCl_4]^{2-}$adsorption capacity on NaCl treated zeolite with contact time

Adsorption capacity increased fast in the first 20 min contact time. This first step is explained by a significant number of active sites available on adsorbent surface at the beginning of the process. In a second step, after 20 min, a slight increasing tendency up to a maximum adsorption around 30 min followed by a tendency to the stabilization around 40 min was observed. In this second step the number of actives decreased. The selected time was 30 min for which a maximum capacity of 22,9 ± 0,3 mg g^{-1} and retention of 45 ± 2 % was achieved.

The pseudo second order model of Ho adjusted well the experimental data (figure 4). This model has been usually employed to describe chemisorption process such as ionic interchange and others, in which covalent bonds are involved that shares or interchanges electrons, apparently, between adsorbate and adsorbent.(14)

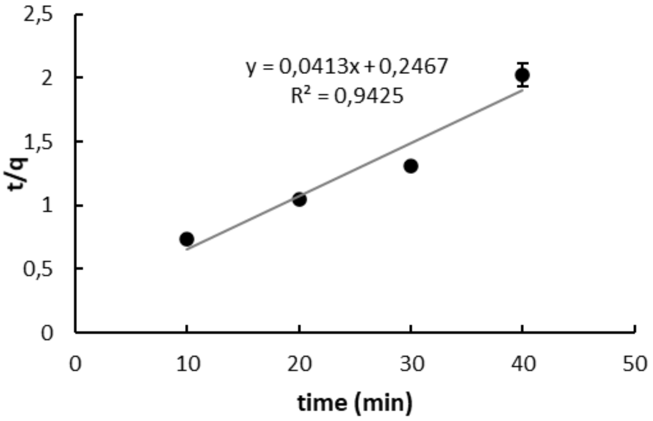

Fig. 4: Linear fit to Ho's pseudo-second-order theoretical kinetic model

The adsorption capacity derived from Ho model was 24 ± 1 mg·g^{-1} that matched very well with that determined experimentally of 22,9 ± 0,3 mg·g^{-1}. This good matching confirmed the adequacy or model of Ho to experimental data.

Influence of $[PtCl_4]^{2-}$ dissolution initial concentration. Adsorption isotherms

Influence of initial concentration was studied in the 50-300 mg L^{-1} range and the following optimized conditions: dissolution pH of 6, 30 min contact time, 1 g L^{-1} adsorbent dose. This experiment was performed for three temperatures: 25, 50 and 70 °C (figure 5).

Adsorption capacity increased with initial concentration in the 50-200 mg L^{-1} range for all studied temperatures. For concentration higher than 200 mg L^{-1} the saturation of adsorbent was reached for 25 °C, meaning that no more active sites were available for higher adsorbate concentration. Note that adsorption capacity kept practically constant. In contrast, capacity increased continuously in the whole concentration range up to 300 mg L^{-1} for temperatures of 50 and 70 °C. Adsorption isotherms are shown in figure 6.

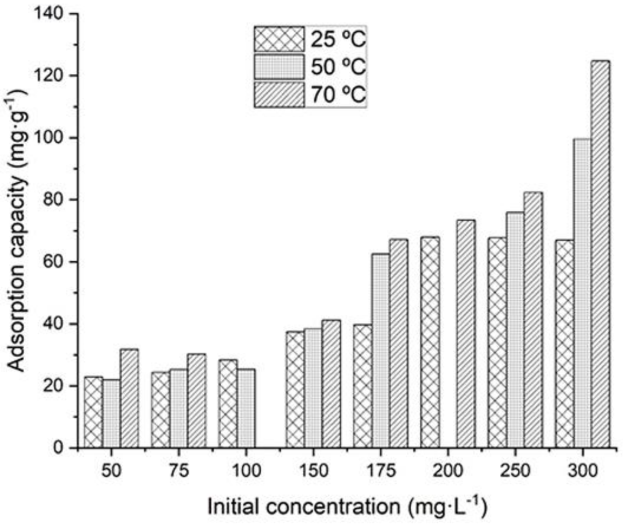

Fig. 5: Adsorption capacity *versus* initial concentration for temperatures of 25, 50 and 70 °C

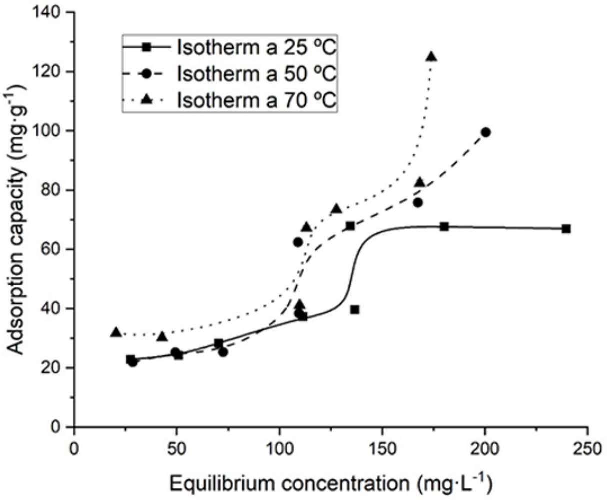

Fig. 6: Adsorption isotherms of $[PtCl_4]^{2-}$ on NaCl treated zeolite for different temperatures

In this case, adsorption capacity versus concentration at equilibrium conditions is plotted instead of initial concentration. Isotherm obtained for 25 °C of temperature presented "S" shape. This fact, revealed the possible presence of two different mechanisms involved.(15) In the first step up to approximately 125 mg·L^{-1} an ionic interchange mechanism with Na^+ ions incorporated to the zeolite by means of the NaCl treatment can be occurring because they are the major compensation cations. In a second step, between 175 mg·L^{-1} and 250 mg·L^{-1} concentration at equilibrium the same ionic interchange mechanism can be present, but in this case with other Ca^{2+}, K^+ and Mg^{2+} compensation cations also present in zeolite. In addition, another chemical interaction type, as for instance the ionic interchange with complexes formation can be also present. For temperatures of 50 and 70 °C, the inflexion concentration point was led defined than that for 25 °C, but still it could be considered at the same 125 mg·L^{-1} concentration. Maximum $[PtCl_4]^{2-}$ adsorption capacity increased with temperatures being, 67.5 mg·g^{-1} for 25 °C, and higher, 99.5 mg·g^{-1} and 124,7 mg·g^{-1}, for 50 °C and 70 °C, respectively. These obtained sorption capacities competed well with other reported for environmental control of Pt(II).(1)

The Freundlich isotherm model was well statistically fitted to experimental data with 95 % of confidence level for the studied temperatures. Then, molar Gibbs free energy by ΔGº was calculated for all temperatures by $\Delta G^o = -RT \ln K_F$ equation, where R is the universal gas constant (8,314 J mol^{-1} K^{-1}), T is the absolute temperature (K) and K_F is the Freundlich constant. After, the standard molar enthalpy (ΔHº) and standard molar entropy (ΔSº) were calculated as the intercept and slope, respectively, of the ΔGº versus T straight line fitted (table 1).

Table 1: Freundlich isotherm constant (K_F) and thermodynamic parameters

T (ºC)	**K_F (L·g^{-1}·mol^{-1})**	**ΔG° (J mol^{-1})**	**ΔH° (kJ·mol^{-1})**	**ΔS° (J·mol^{-1}·K^{-1})**
25	1,284	-618	5561,9	20,341
50	1,318	-741		
70	1,730	-1563		

K_F increased with temperature, according to the similar increase of adsorption capacity observed experimentally. The negative value of ΔG° with temperature classified the sorption process as spontaneous, meaning that once it begins does not need the external to the system action to be accomplished, while the increase of spontaneity with temperature is given by the increase of absolute value of ΔG. The energy of the adsorption process given by a positive value of ΔH° indicated the endothermic character of the process, while the positive value of ΔS° showed the increase of the disorder of the system after adsorption.

The adsorption capacity of Pt(II) (67,5 mg·g^{-1}) achieved with NaCl-treated zeolites in this study for 25 °C is markedly higher than those previously reported using other sorbents as for example, that obtained by Lombana *et al*. (2023). Even more, earlier investigations have shown that natural zeolites without any chemical treatment typically display limited adsorption capacities for others elements, as for example for Ni(II),(9) primarily due to the low ion exchange potential associated with compensation cations such as Ca^{2+} and K^+ naturally present in zeolites.(12) NaCl treatment enhances performance by replacing those lesser mobile ions with Na^+, facilitating greater accessibility of ions in solutions to active sites. Thus, the Na^+ present in treated zeolite exchanges easier than Ca^{2+} and K^+ with others ions in solution due to its lower ionic radius and high mobility, favouring the occupation of more accessible sites in the zeolite. While, modified clinoptilolites have demonstrated improved adsorption of other metal ions. For instance, Liu *et al.* (2019) reported approximately 30 mg·g^{-1} for Zn(II) and Ni(II),(16) and Ortiz-Núñez *et al.* (2025) achieved 28,8 mg·g^{-1} for Ni(II) using Cuban clinoptilolite.(4) The sorption capacity obtained in the present work not only surpasses those documented for zeolites but also rivals the performance of advanced adsorbents, including metal-organic frameworks (MOFs), activated carbon, and bio-based materials. For instance, Zr- and Fe-based MOFs offer capacities between 50 and 80 mg·g^{-1} but require costly synthesis and display sensitivity to extreme conditions.(17) Activated carbon modified with $ZnCl_2$ or H_3PO_4 typically reaches 20-40 mg·g^{-1} for noble metals,(18) while bioadsorbents, despite their sustainability, seldom exceed 30 mg·g^{-1} for Pt(II).(19) The achieved findings in the present study highlight the material's potential as a sustainable, and highly competitive solution for Pt(II) remediation in aqueous environments.

CONCLUSIONS

The potentialities of zeolite treated with NaCl as adsorbent for solid phase extraction of Pt(II) in chloride complex form was demonstrated, achieving high adsorption capacities of 67,5 mg·g^{-1} and 124,7 mg·g^{-1} for 25 °C and 70°C, respectively, that competed well with other reported for environmental control of Pt(II). The selected experimental conditions were: dissolution pH 6, adsorbent dose of 1 g·L^{-1}, 30 min contact time and temperature of 70 °C. The chemisorption as involved adsorption mechanism was suggested by the good fitting of the pseudo second order model of Ho. The increase of adsorption capacity with temperature support also this hypothesis. The adsorption of $[PtCl_4]^2$ on NaCl treated zeolite was a spontaneous process given by ΔG° negative value. The process was endothermic as demonstrated by ΔH° positive value and the disorder of the system increased after adsorption according to ΔS° positive value.

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INTEREST CONFLICT

The authors wish to confirm that there are not conflicts of interest associated with this manuscript submitted for consideration by the journal.

AUTHOR'S CONTRIBUTION

Alejandra Bayolo Soler: investigation, data curation, writing-original draft preparation.

Rachel Lombana Fraguela: investigation, data curation, writing-original draft preparation; review and editing.
Ania Cabrera Díaz: conceptualization, data curation, writing-review and editing.
Mario Simeón Pomares Alfonso: conceptualization writing-review and editing.
Margarita E. Villanueva Tagle: conceptualization, data curation, writing-review and editing.
All authors have read and agreed to the published version of the manuscript.