



The recovery of Pt(IV) from aqueous solutions by APDEMS-functionalised zeolite

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Abstract

The recovery of Pt(IV) from aqueous solutions by zeolite functionalised with 3-aminopropyl(diethoxy)methylsilane (APDEMS) was studied at various adsorbent dosage, pH, time, concentration and competing ions was studied. The adsorbent was highly efficient at pH 2 and the maximum adsorption was reached at 180 min. The adsorption of Pt(IV) was not affected by the presence of competing ions instead, other precious metals and trace elements were adsorbed. The strong Pt-adsorbent interaction concluded from kinetic and isotherms models makes the adsorbent suitable for the recovery of Pt(IV) and other metals from mining wastewater.

Keywords: Pt(IV), recovery, platinum group elements, APDEMS-functionalised zeolite

Introduction

Large amount of water is used during mineral processing and the resulting wastewater is discharged into the environment (Lottermoser 2003). The discharged water normally contains significant concentrations of metals. Studies have shown that platinum group metals (PGMs) are discharged along with wastewater as by-products of nickel and copper mining (Xiao and Laplante 2004). Moreover, PGMs mining plants lose significant amounts of PGMs during processing (Hunt et al. 2013). Thus, the accumulation of PGMs could be quite significant in the environment and their recovery could add value to the economy of many countries dependant on them. PGMs are widely used in jewellery, catalytic converters, laboratory equipment and medicine (Chassari et al 2005; Xiao and Laplante 2004). The production of PGMs has increased over the years due to their increasing demand and since only a few countries (South Africa, Canada and Russia) have large reserves, there is a danger of the scarcity of their minerals worldwide and thus a need for recovery from wastewater solutions (Alonso et al 2009).

Zeolites are aluminosilicate clay minerals which are among the cheapest naturally available adsorbents. They consist of SiO_4 and AlO_4

frameworks which are linked through oxygen atoms in a three-dimensional array. The overall charge of zeolite is negative due to the replacement of Si^{4+} with Al^{3+} and is balanced by cations such as Ca, Mg, Na and K in the cavities of the zeolite (Malamis and Katsou 2013). Zeolites have been found to be good adsorbents for trace metals due to their high cation exchange capacity and molecular sieve properties (Bakatula et al. 2015). Moreover, studies have shown that the adsorption capacities of zeolites can be improved by modification where the zeolite acts as a support (Ren et al. 2016). Platinum has been found to interact strongly with nitrogen and thus, the aim of the study to use zeolite functionalised with 3-aminopropyl(diethoxy)methylsilane (APDEMS) which has a primary amine group to recover Pt(IV) from aqueous solutions.

Materials and methods

Chemicals

The chemicals used in this study were of analytical reagent grade and were obtained from Sigma Aldrich, South Africa. The 10 mg L^{-1} platinum stock solution was prepared from Pt(IV) standard and deionised water in 1 L volumetric flask and was stored in the refrigerator (4°C) until required. Working solutions with specific concentrations were pre-



pared daily from the stock solution through serial dilutions. The pH of the solutions was controlled with 0.01 mol L⁻¹ NaOH and 0.01 mol L⁻¹ HCl. The stock solution of the mixed metals was prepared in the same way.

Functionalisation of zeolite and characterisation

The zeolite was purchased from Sigma Aldrich (Steinheim, Germany). The chemical functionalization was achieved by mixing 5g zeolite with 10 mL of 3-aminopropyl(diethoxy)methylsilane (bp: 85 – 88°C) in a glass vial and the contents were interacted at 180°C for 30 min in an automated Microwave-assisted Extraction monowave 450 (Anton Paar, South Africa). The contents were cooled to room temperature and filtered using 0.45µm cellulose natrete filtech filter paper using suction and rinsed with ethanol. The functionalised zeolite was then dried at 100°C for 24 h.

The natural and functionalised zeolite were characterised with fourier transform infrared (FTIR) spectroscopy in the range of 4000 – 400 cm⁻¹ for the determination of functional groups, the mineralogy was determined with powder X-ray diffraction (PXRD) D2 Phaser (Bruker, Germany), X-ray fluorescence (XRF) (PAnalytical, Netherlands) was used to determine the chemical composition, varioELcube V4.0.13 (Elementar, Germany) was used for elemental analysis. Textural properties (surface area, pore size and pore volume) were analysed with Micromeritics Flow Prep 060 instrument (Aachen, Germany). The point of zero charge (PZC) was also determined using KCl for ionic strength, HNO³ and NaOH to control pH.

Batch adsorption studies

The study was carried out by placing the adsorbent and 10 mL Pt(IV) solution at various conditions in 50 mL polypropylene containers which were shaken at room temperature with an elliptical benchtop shaker (Labcon, USA) to attain equilibrium and the contents were filtered with 0.45 µm cellulose nitrate Filtech filter paper and the filtrate was analysed with inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro genesis, Germany).

Effect of adsorbent mass (50 – 500 mg) on the adsorption of Pt(IV) by APDEMS-functionalised zeolite was determined at pH 2 and room temperature (25°C). Effect of pH (2 – 9), concentration of Pt(IV) (0.5 – 5 mg L⁻¹) and contact time (0 – 540 min) on the adsorption of Pt(IV) was determined. Competing ions (Rh(III), Pd(II), Ir(III), Ru(III), Os(III), Fe(III), Ca(II), Mg(II), K(I), Co(II), Ni(II), Hf(IV), Zn(II) and Au(I)) were prepared with Pt(IV) and exposed to APDEMS-functionalised zeolite to determine their effect on adsorption or recovery of Pt(IV).

Data treatment

The adsorption capacity, q_e (mg g⁻¹) and the adsorption efficiency were calculated using equations 1 and 2, respectively.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

$$\text{adsorption efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where C_0 and C_e are initial and equilibrium concentrations of metals (mg L⁻¹), V is the volume of the solution used (L) and M is the mass of the adsorbent (g).

Adsorption isotherms

The type of adsorption occurring between Pt(IV) and APDEMS-functionalised zeolite was determined with Langmuir, Freundlich and Dubinin Radushkevich (D-R) adsorption isotherms. The Langmuir isotherm describes the monolayer adsorption between adsorbents and substances (Mushtaq et al. 2016). The Freundlich isotherm describes the non-ideal and reversible adsorption of elements onto the heterogeneous surface (Chen 2015; Mushtaq et al. 2016). The Dubinin-Radushkevich (D-R) isotherm describes the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Chen 2015). The Langmuir, Freundlich and Dubinin Radushkevich (D-R) adsorption can be expressed as, respectively:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_m} \right) C_e + \left(\frac{1}{K_L q_m} \right) \quad (3)$$

$$q_e = K_f C_e^{\frac{1}{n}} \quad (4)$$

$$\ln q_e = \ln X_m - K_{ad} \varepsilon^2 \quad (5)$$



where q_e (mg g^{-1}) is the quantity of the adsorbate adsorbed per gram of adsorbent at equilibrium, q_m (mg g^{-1}) is the maximum monolayer coverage capacity and K_L is the Langmuir isotherm constant (L mol^{-1}), K_f ($(\text{mg g}^{-1})/(\text{mol L}^{-1})^{1/n}$) is the Freundlich isotherm constant and n is the adsorption intensity, K_{ad} ($\text{mol}^2 (\text{kJ}^2)^{-1}$) is the Dubinin-Radushkevich isotherm constant, X_m (mg g^{-1}) is theoretical isotherm saturation capacity and ε is the Polanyi constant.

Kinetic models

The adsorption process controlling mechanism between Pt(IV) and APDEMS-functionalised zeolite was determined with pseudo first- and second order kinetic models represented by equations 6 and 7, respectively (Bakatula et al 2015). The correlation coefficient (R^2) and the closeness of the experimental adsorption capacity, q_{exp} to the calculated, q_{cal} were used to determine the model that best describes the kinetic data.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where q_t (mg g^{-1}) and q_e (mg g^{-1}) are the adsorption capacities at time t and equilibrium, respectively, k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the rate constants.

Results and discussion

Characterisation

The results from XRF showed that silica (SiO_2) (68.49%) and alumina (Al_2O_3) (11.48%) are main components of the zeolite. Other

chemical components are K_2O (3.79%), Na_2O (1.47%), CaO (1.22%), Fe_2O_3 (1.09%) and loss on ignition of 11.03%. The PXRD results are shown in Fig. 1. The zeolite was mainly composed of clinoptilolite, quartz and sanidine. From these results, it was clear that the natural zeolite can be classified as clinoptilolite. The FTIR spectra of the raw and functionalised zeolite are shown in Fig. 2. The peaks at 695 and 964 cm^{-1} which are present in both the raw and functionalised zeolite are due to the Si-O and Al-O-Si and Si-OH groups (Guaya et al. 2015). The success of functionalization was confirmed by the peaks at 790 and 765 cm^{-1} which are due to Si-O-Si bonds of the zeolite and APDEMS. The peak at 1644 cm^{-1} can be attributed to the deformation vibration of water. The peaks beyond 3300 cm^{-1} are due to the hydroxyl groups of the zeolite. The $-\text{CH}_2$ and $-\text{CH}$ stretching vibrations of APDEMS are represented by the peaks at 2925 and 2872 cm^{-1} . The peaks at 1182 and 1257 cm^{-1} on the functionalised zeolite can be attributed to Si- CH_2 and Si- CH_3 , respectively. The presence of the nitrogen groups is represented by the peaks at 1575 cm^{-1} ($-\text{NH}$ vibration) and 3366 cm^{-1} (primary amines). Moreover, the elemental analysis showed that the C and H percentages were high on the functionalised zeolite and that of N was observed on APDEMS-functionalised zeolite which was not present on the raw zeolite. These results show that the functionalization of raw zeolite was successful. The surface area of the raw zeolite decreased from 16.28 to 2.17 $\text{m}^2 \text{g}^{-1}$ due to functionalization with APDEMS and this also confirmed the success of the addition of

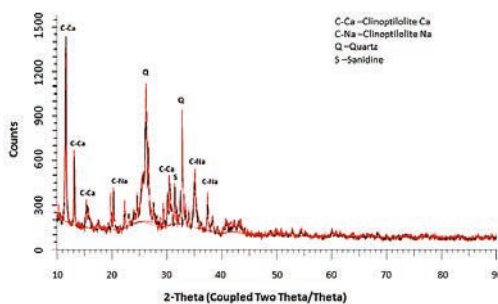


Fig. 1 PXRD pattern of zeolite

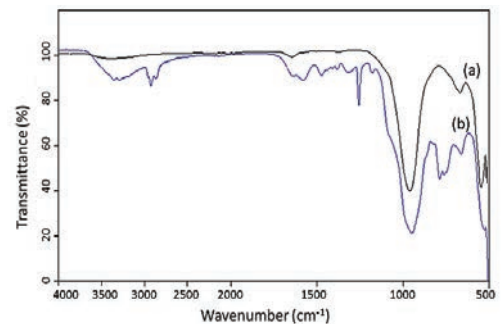


Fig. 2 FTIR spectra of raw zeolite (a) and functionalised zeolite (b)



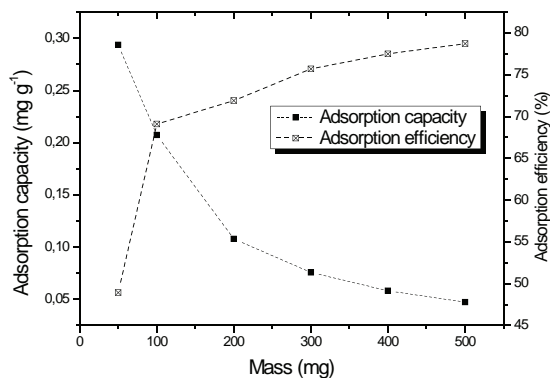


Fig. 3 Effect of mass on the adsorption of Pt(IV) by APDEMS-functionalised zeolite

the ligand on zeolite. This reduction can be attributed to the smothering of the pores by APDEMS as the pore size and pore volume also decreased from 12.97 to 4.50 nm and 0.052 to 0.0045 cm³, respectively.

Effect of adsorbent mass

The effect of adsorbent mass on the adsorption or recovery of Pt(IV) was studied and the results are shown in Fig. 3. The adsorption efficiency increased with increasing adsorbent mass but the adsorption capacity decreased. For subsequent experiments, 10 g L⁻¹ adsorbent mass was used as the adsorption capacity and the adsorption efficiency were significant.

Effect of pH

Studies have shown that pH can affect the behaviour and hence the adsorption efficiency of adsorbents (Bakatula et al. 2015; Ren et al. 2016). The adsorption capacity decreased with increasing solution pH and this could

be attributed to the speciation of Pt(IV) and the surface charge (Fig. 4). At acidic pH, the surface groups were protonated and thus, –NH³⁺ which had high affinity for the anionic Pt(IV) species (PtCl₆²⁻) resulted. The anionic chloride species were more prevalent at acidic pH due to the addition of HCl. During the processing of PGMs, concentrated acids are used for extraction and thus, the discharged water is highly acidic (Nguyen et al. 2016). Thus, the adsorbent will work well and significantly recover Pt(IV) from mining wastewaters which are highly acidic. PZC was found to be 5.3. The adsorption capacity decreased significantly beyond pH 2 and this can be attributed to the low amount of chloride species favourable for adsorption as well as electrostatic repulsion between the Pt species and the surface groups.

Effect of concentration

The adsorption of Pt(IV) at pH 2 was observed to increase with increasing Pt(IV)

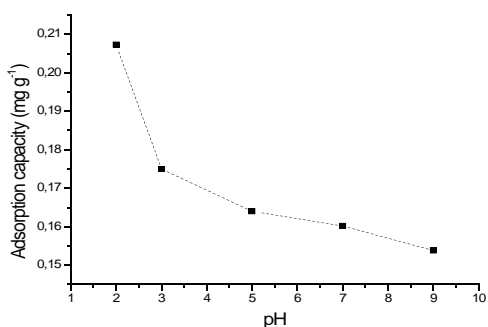


Fig. 4 Effect of pH on Pt(IV) adsorption

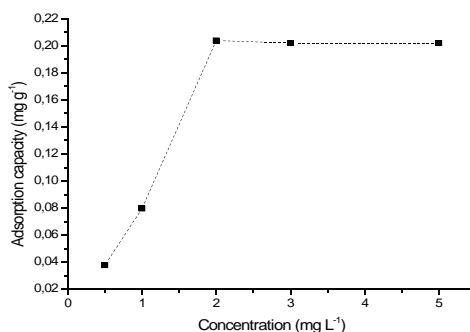


Fig. 5 Effect of concentration on Pt(IV) adsorption



Table 1 Adsorption isotherm constants

Langmuir			Freundlich			Dubinin-Radushkevich (D-R)		
q_m (mg g ⁻¹)	K_L (L mol ⁻¹)	R^2	K_f ((mg g ⁻¹)/(mol L ⁻¹) ^{1/n})	n	R^2	X_m (mg g ⁻¹)	E_s (kJ mol ⁻¹)	R^2
0.117	3.5x105	0.98	32.29	1.99	0.91	1.37	12.42	0.92

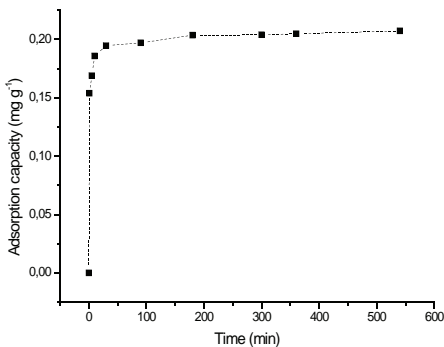
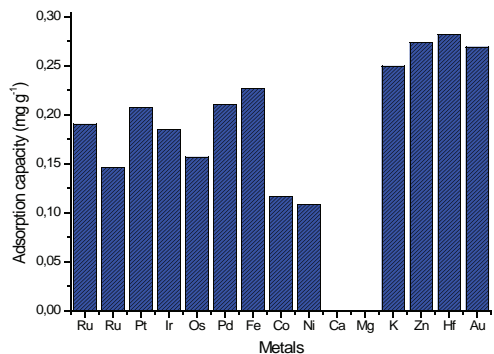
Table 2 Kinetic parameters for Pt(IV) adsorption by APDEMS-functionalised zeolite

Pseudo first-order			Pseudo second-order		
K_1 (min ⁻¹)	q_{exp} (mg g ⁻¹)	R^2	K_2 (g mg ⁻¹ min ⁻¹)	q_{exp} (mg g ⁻¹)	R^2
0.0088	0.0061	0.71	6.71	0.103	0.99

concentration from 0.5 to 2 mg L⁻¹ (Fig. 5). The increase in adsorption capacity can be attributed to the availability of binding sites (-NH₃⁺). The adsorption efficiencies were 75.6, 79.7, 78, 3, 57.7 and 40.4% at 0.5, 1, 2, 3 and 5 mg L⁻¹, respectively. The ability of the adsorbent to significantly adsorb very low concentrations of Pt(IV) makes it a suitable adsorbent for PGMs wastewater which contains very low concentrations of PGMs (Hunt and Clark 2013, Hunt et al 2015). This also means that there is a strong interaction between Pt(IV) and the adsorbent. Beyond 2 mg L⁻¹, no increase in adsorption was observed. The adsorption isotherm results (Table 1) indicated that the interaction of Pt(IV) onto APDEMS-functionalised zeolite is through monolayer adsorption since the experimental data was described better by Langmuir isotherm ($R^2 > 0.98$). The free energy change as determined from D-R isotherm was found to be 12.42 kJ mol⁻¹ indicating that the adsorption process is through ion exchange (Bakatula et al. 2015).

Effect of contact time

The effect of contact time on the adsorption of Pt(IV) by APDEMS-functionalised zeolite was investigated and the results are shown in Fig. 6. A rapid increase in adsorption was observed between 0 and 30 min after which, a slow uptake was observed until 180 min. Equilibrium was reached at 180 min where the adsorption was controlled by diffusion. Thus, 180 min was chosen as the sufficient time for the recovery of Pt(IV) by the adsorbent. The kinetic data was best described by pseudo second-order indicating that chemisorption was the rate controlling mechanism ($R^2 > 0.99$) (Table 2). This was also supported by the calculated adsorption capacity (q_{cal}) (0.102 mg g⁻¹) which was very similar to the experimental adsorption capacity (0.103 mg g⁻¹). The experimental adsorption capacity determined with pseudo first-order was found to be 0.0061 mg g⁻¹ which is very different from the calculated capacity, further explaining that there is no good correlation with pseudo first-order.

**Fig. 6** Effect of time on Pt(IV) adsorption**Fig. 7** Effect of competing ions on Pt(IV) adsorption

Effect of competing ions

A mixture of 2 mg L⁻¹ Pt(IV) and other ions at pH 2 was exposed to APDEMS-functionalised zeolite to determine the efficiency of the adsorbent on the recovery of Pt(IV) in the presence of other ions. The adsorption capacity of Pt(IV) was not affected by the presence of other ions, some of which are PGMs (Fig. 7). Moreover, these PGMs and other cations except Ca and Mg were adsorbed by the adsorbent making APDEMS-functionalised zeolite a dual efficacy adsorbent. The ability to significantly adsorb Pt(IV) in the presence of other ions makes the APDEMS-functionalised zeolite a suitable adsorbent to be used in mining wastewater.

Conclusion

In this study, APDEMS-functionalised zeolite was synthesised and used to recover Pt(IV) from aqueous solutions. The characterisation results showed that the functionalization was successful. The experimental studies were carried out under the optimised conditions (100 mg adsorbent, pH 2, 2 mg L⁻¹ and 180 min) and indicated that 0.207 mg g⁻¹ of Pt(IV) was removed from aqueous solutions by APDEMS-functionalised zeolite. The adsorbent was significantly adsorbed Pt(IV) at highly acidic pH (pH 2) which makes the adsorbent very suitable for PGM mining wastewater which is highly acidic. The kinetic (pseudo second-order) and isotherm (Langmuir) models as well as the energy from D-R isotherm indicated that there was strong chermisorptive Pt-adsorbent interaction. The presence of competing ions did not affect the adsorption of Pt(IV). The adsorbent can be applied in retaining ponds into which processing solutions are discharged and fed to the processing units together with fresh ore after recovery.

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References

- Alonso E, Field FR, Roth R, Kirchain RE (2009) Strategies to address risks of platinum scarcity for supply chain downstream firms. In Sustainable Systems and Technology, 2009. ISSST'09. IEEE International Symposium on (pp. 1-6). IEEE.
- Bakatula EN, Mosai AK, Tutu H (2015) Removal of Uranium from Aqueous Solutions using Ammonium-modified Zeolite, S Afr J Chem, 68:165–171
- Chassary P, Vincent T, Marcano JS, Macaskie LE, Guibal E (2005) Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives, Hydrometallurgy 76(1-2):131-147
- Chen X (2015) Modeling of experimental adsorption isotherm data, Information 6(1):14-22.
- Guaya D, Valderrama C, Farran A, Armijos C, Cortina JL (2015) Simultaneous phosphate and ammonium removal from aqueous solution by a hydrated aluminum oxide modified natural zeolite, Chem Eng J 271:204-213
- Hunt AJ, Matharu AS, King AH, Clark JH (2015) The importance of elemental sustainability and critical element recovery, Green Chem, 17(4):1949-1950
- Lottermoser B (2003) Mine Water. In Mine wastes, Springer, Berlin, Heidelberg, pp. 83-141
- Malamis S, Katsou E (2013) A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: Examination of process parameters, kinetics and isotherms, J Hazard Mater 252:428-461
- Mushtaq M, Bhatti HN, Iqbal M, Noreen S (2016) Eriobotrya japonica seed biocomposite efficiency for copper adsorption: isotherms, kinetics, thermodynamic and desorption studies, J Environ Manage 176:21-33
- Nguyen TH, Sonu CH, Lee MS (2016) Separation of Pt (IV), Pd (II), Rh (III) and Ir (IV) from concentrated hydrochloric acid solutions by solvent extraction. Hydrometallurgy, 164:71-77
- Ren H, Jiang J, Wu D, Gao Z, Sun Y, Luo C (2016) Selective adsorption of Pb (II) and Cr (VI) by surfactant-modified and unmodified natural zeolites: a comparative study on kinetics, equilibrium, and mechanism, Water Air Soil Pollut 227(4):101
- Xiao Z, Laplante AR (2004) Characterizing and recovering the platinum group minerals—a review. Miner Eng, 17(9-10):961-979

