The Recovery Of Pd(II), Ir(III) And Rh(III) From Aqueous Solutions With Yeast-functionalised Zeolite ◎

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Abstract

Wastewaters from platinum group metals (PGMs) processing plants can contain substantial amounts of metals including the very PGMs. The recovery of such metals from wastewaters can be of great value especially due to recent declines in commodity prices. The recovery of Pd(II), Ir(III) and Rh(III) by zeolite functionalised with spent yeast waste was studied and the effect of adsorbent dosage, pH, initial concentration, contact time and competing ions was determined. The significant recovery of Pd(II) and Ir(III) was achieved at pH 2, 2 mg L^{-1} and 10 g L^{-1} adsorbent dosage. The adsorption capacity of Rh(III) increased with pH whilst that of Pd(II) and Ir(III) decreased. The presence of competing ions led to an increase in adsorption capacity due to an adsorbent-Fe-analyte synergistic effect. The adsorbent is suitable for significant recovery of Pd(II), Ir(III) and Rh(III) from PGMs wastewater.

Keywords: adsorption capacity, platinum group metals, spent yeast, wastewater

Introduction

The readily increasing costs of platinum group metals (PGMs) and declining ore grades have been eroding the economic viability of PGMs mines around the world. As a result, some mining plants have closed whilst others are still facing closure. During the processing of minerals, large amount of wastewater is released into the environment and some studies have reported that it may contain traces of valuable minerals such as PGMs (Mosai et al., 2019). Since these metals are in very low concentrations, the current methods used for mining cannot be used to recover the lost minerals hence, a need for cheaper and more efficient methods for recovery. Zeolites are negatively charged aluminium-silicate clay minerals which have micro and mesopores located by water molecules and cations such as Ca^{2+} and Mg^{2+} (Guaya et al., 2015). Zeolites are readily available in different parts of the world and have been used as natural adsorbents for the removal of metals from wastewaters (Yuna, 2016). Other studies have indicated the efficiency of zeolite can be improved through functionalisation with ligands that have high affinity for target metals (Simsek et al., 2013; Bakatula et al., 2015).

In this study, the zeolite clay mineral was functionalised with spent brewer's yeast waste and used to recover Pd(II), Ir(III) and Rh(III) from aqueous solutions. Thus, this study seeks to come up with a very attractive and cheap material for the recovery of precious metals.

Materials and methods

Chemicals

The chemicals used were of analytical reagent grade and were purchased from Sigma Aldrich, South Africa. The 10 mg L^{-1} stock solution containing Pd(II), Ir(III) and Rh(III) was prepared and preserved with concentrated nitric acid. Working solutions were prepared daily from the stock solution which was stored in the refrigerator at 4°C when not used. The 0.01 mol L^{-1} HCl and NaOH were used to adjust the pH of the working solutions. The spent yeast waste was collected from the Wits Microbrewery, Johannesburg, South Africa using polypropylene plastic containers.

Functionalisation of zeolite with yeast

The collected yeast waste (40 mL) was added to 2 g zeolite in a 100 mL polypropylene bottle and mixed for 24 h using an elliptical

bench-top shaker at 25°C. The contents were filtered using suction and the unbound yeast was removed by shaking the functionalised zeolite for 5 min with deionised water. The contents were filtered again and the zeolite was dried at 25°C for 24 h.

Characterisation

The natural zeolite used was characterised with powder X-ray diffraction (PXRD) D2 Phaser (Bruker, Germany) to determine the mineralogy of the adsorbent and X-ray fluorescence (XRF) (PAnalytical, Netherlands) for chemical composition. The functional groups of the natural and functionalised zeolite were determined using Fourier transform infrared (FTIR) spectroscopy (Tensor 27, Bruker, Germany). The amount of C, H and N on the natural and functionalised zeolite was determined using varioELcube V4.0.13 (Elementar, Germany). The surface area, pore size and pore volume were determined using TriStar 3000 V6.05 A (Micrometrics, USA).

Batch adsorption studies

Batch studies were conducted to determine the effect of pH (2-9), initial concentration (0.5-10 mg L^{-1}), adsorbent dosage (5-50 g L^{-1}), contact time (0-540 min) and competing ions (Pt, Ru, Os, Hf, Au, Fe, Co, Ni, Ca, Mg, K and Zn) on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite. The raw zeolite was also used at the same conditions and the adsorption was not significant (p>0.05). The metals in the above conditions were shaken with the adsorbent to attain equilibrium and filtered. Inductively coupled plasma optical emission spectroscopy (ICP-OES) (Spectro Genesis, Germany) was used to determine the concentration of metals. The equilibrium adsorption capacity (qe (μg g-1)) and adsorption efficiency of the metals recovered by yeast-functionalised zeolite were determined using Eq. 1 and 2, respectively.

$$q_e = \frac{(C_0 - C_e)V}{M} x\ 1000 \qquad (1)$$

$$\% \ adsorption = \frac{(C_0 - C_e)}{C_0} x\ 100 \qquad (2)$$

where C_o and C_e (mg L^{-1}) are the initial and equilibrium concentrations of the metals, respectively, V (L) is the volume of the solution and M (g) is the mass of the yeast-functionalised zeolite.

Data treatment

Adsorption isotherms

The type of adsorption between the metals and yeast-functionalised zeolite was determined using the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption isotherms. The Langmuir isotherm describes the monolayer adsorption of metals onto a homogeneous surface with a fixed number of active sites. The assumption for this isotherm is that the active sites have equal adsorption energies (Latour, 2015). The Langmuir isotherm can be expressed as:

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

where qm (mg g^{-1}) is the maximum monolayer coverage and KL (L mol^{-1}) is the Langmuir isotherm constant. The affinity of the metals for the adsorbent was determined using the separation factor (R_L) which can be determined from the Langmuir constant (K_L). The affinity can be expressed as favourable ($0 > R_L < 1$), unfavourable (RL >1), linear adsorption ($R_L = 1$) and irreversible adsorption ($R_L = 0$). The R_L is expressed as:

$$R_L = \frac{1}{1 + C_O K_L} \qquad (4)$$

The Freundlich isotherm model describes the adsorption of metals onto a heterogeneous surface where the active sites are assumed to have different energies (Bakatula et al., 2015). The Freundlich isotherm can be expressed as:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad (5)$$

where K_f ((mg g^{-1})/(mol L^{-1})$^{1/n}$) is Freundlich isotherm constant and n is adsorption intensity.

The Dubinin-Radushkevich (D-R) model is used to describe the adsorption between metals and adsorbents onto a heterogeneous surface with Gaussian energy distribution (Chen, 2015). The D-R model equation is as follows:

$$ln q_e = ln X_m - K_{DR} \varepsilon^2 \qquad (6)$$

where X_m is theoretical isotherm saturation capacity (mg g^{-1}), K_{DR} is the Dubinin-Radushkevich isotherm constant (mol^2 (kJ^2)$^{-1}$), ε is the Polanyi constant which can be expressed as:

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \qquad (7)$$

where R is the universal gas constant (J (mol K)$^{-1}$)and T is temperature (K). The mean free energy of adsorption (E$_s$) can be calculated from K_{DR} as shown in Eq. 8.

$$E_S = \frac{1}{\sqrt{2K_{DR}}} \qquad (8)$$

Kinetics study

The adsorption controlling mechanism between the metals and the adsorbent was determined using pseudo first- and second-order kinetic models. The pseudo first-order model has used to describe the rate of adsorption that is controlled by the rate of surface reaction in which case, the transition of metals from free to adsorbed state is considered (Rudzinski and Plazinski 2007). The pseudo second-order model is used to describe a reaction where the adsorption reaction on the surface of adsorbent is the rate-controlling step (Liu, 2008). The pseudo first and second-order kinetic models can be expressed by Eq. 9 and 10, respectively:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (9)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (10)$$

where qt is the adsorbed amount (mg g^{-1}) at time t, q$_e$ is the adsorbed amounts (mg g^{-1}) at equilibrium and k$_1$ is the pseudo first-order rate constant (min^{-1}), k$_2$ is the pseudo second-order rate constant (g mg^{-1} min^{-1}) and k$_2$ q$_e^2$ is the initial adsorption rate.

Results and discussion

Characterisation

The PXRD results showed that the dominant minerals of the zeolite were clinoptilolite ((Na,K,Ca)$_{2-3}$Al$_3$(Al,Si)$_2$Si$_{13}$O$_{36}$·12H$_2$O), quartz (SiO$_2$) and sanidine (K(AlSi$_3$O$_8$)). The results from XRF indicated that the zeolite was mostly composed of silica (SiO$_2$) (68.5%)

and alumina (Al$_2$O$_3$) (11.6%). Since the yeast waste contains high amounts of amino acids, the possible interaction was through the oxides of the zeolite and these amino acids. The FTIR spectra of the natural and functional zeolite indicated that the functionalisation was successful since, there were N-H and C-N bands at 1535 and 1637 cm^{-1}, respectively on the functionalised adsorbent, indicative of the amino acid groups in the yeast. Due to the smothering of the zeolite pores by the spent yeast, the surface area and pore volume of the adsorbent decreased whilst the pore size increased. The amount of C, H and N increased after functionalisation due to high amount of amino acids.

Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption of Pd(II), Ir(III) and Rh(III) at pH 2 by yeast-functionalised zeolite was studied and the results are presented in Fig. 1. The adsorption capacity of the metals decreased as the dosage increased but, the adsorption efficiency increased with dosage due to increased amount of binding sites. The Pd(II) adsorption capacity was higher than that of Ir(III) and Rh(III) thus, the yeast functional groups on zeolite had high affinity for Pd(II) at pH 2. The adsorption efficiencies of Pd(II) were in the range of 69-91% as the dosage increased from 50 to 500 mg. The adsorption efficiencies of Ir(III) were found to be 33, 54, 59, 62 and 61% at 50, 100, 200, 300 and 500 mg of yeast-functionalised zeolite, respectively and those of Rh were found to be 17,25, 35, 39 and 61%, respectively. The lower adsorption efficiencies of Ir(III) and Rh(III) can be attributed to high oxidation states and high atomic and ionic radii of the metals thus, only a few could be taken up by the active sites. The recovery of the metals with yeast-functionalised zeolite was in the order: Pd(II) > Ir(III) > Rh(III).

Effect of pH

The effect of pH on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite was studied and the results (Fig. 2) indicated that the adsorption capacity of Pd(II) and Ir(III) decreased as pH was increased due to the change of species and adsorbent surface. At lower pH, the metals
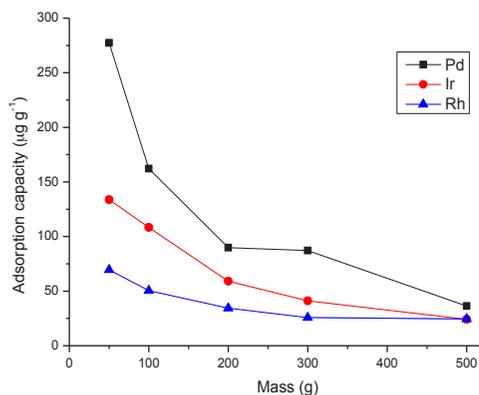
Figure 1 *Effect of mass on adsorption of metals*
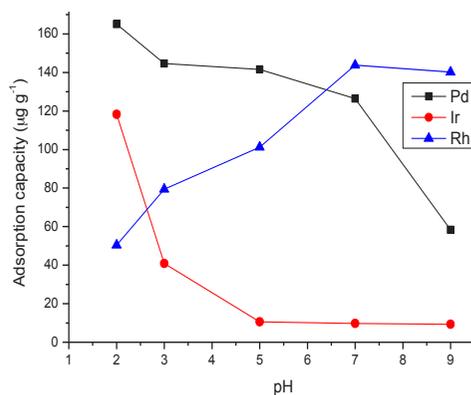
Fig. 2 *Effect of mass on adsorption of metals*

exist as $PdCl_6^{4-}$ and $IrCl_6^{3-}$ due to high HCl concentration which was used to adjust the pH. The platinum mining wastewater has high concentration of HCl which is used during processing and thus, the metals exist in their chloride species (Mosai et al., 2019). Since these species are negatively charged, they will interact electrostatically with the positively charged surface which is due to high concentration of hydronium ions (H_3O^+). Thus at highly acidic regions, the amino acids will be positively charged and interact strongly with negatively charged species. The adsorption capacity of Pd(II) and Ir(III) decreased as pH was increased due to repulsions of the negatively charged hydroxide species and the negatively charged surface. However, the adsorption of Rh(III) increased with pH. A study by Labib et al. (2018) indicated that at higher pH, Rh(III) forms aqua/chloro complexes $([RhCl_2(H_2O)_4]^+$ and $[RhCl(H_2O)_5]^{2+})$ which are positively charged and would electrostatically interact with the negatively charged surface. Thus, to substantially recover Rh(III) from wastewater, pH should be adjusted.

Effect of initial concentration

The effect of initial concentration on the adsorption of Pd(II), Ir(III) and Rh(III) by the adsorbent at pH 2 was studied and the results are shown in Fig. 3. The adsorption capacity of Pd(II) increased with concentration from 0.5 to 10 mg L-1 due to favourable adsorption. The adsorption capacity of Ir(III) and Rh(III) however, increased up to 2 mg L^{-1} and remained fairly the same beyond this. This can be attributed to the limited binding sites

for these metals which are swiftly occupied hence, no further increase in adsorption was observed. The adsorption efficiencies of Pd(II) were found to be 83, 83, 81, 74 and 64% at 0,5, 1, 2, 5 and 10 mg L^{-1}, respectively. The adsorption efficiencies for Ir(III) and Rh(III) were less than 25% beyond 2 mg L^{-1}.

The type of adsorption occurring between the metals and yeast-functionalised zeolite was determined using adsorption isotherms and the data is presented in Table 1. The correlation coefficients (R^2) were high for Langmuir isotherm, indicating that the adsorption of the metals to the adsorbent was through monolayer adsorption. The metals were removed from aqueous solutions through the metal-N interaction since, studies have indicated that PGEs have strong interactions with nitrogen (Mosai et al., 2019). The maximum adsorption coverage (q_m) of Pd(II) onto the adsorbent was higher than for Ir(III) and Rh(III) which can be attributed to high affinity of the active sites for Pd(II) hence, the adsorption capacity has been higher than that of the other metals. The correlation coefficients for Pd(II) were >0.99 for all isotherms, meaning that there is also a possibility of adsorption on different adsorption sites or different adsorption mechanisms leading to a heterogeneous adsorption. The mean adsorption energy (Es) of Pd(II) determined from D-R isotherm was 10.12 kJ mol^{-1} meaning that the interaction with the adsorbent was through chemical ion exchange. The energies of Ir(III) and Rh(III) were greater than 16 kJ mol^{-1} indicating that their interaction was possibly chemisorptive in nature (Youssef et al., 2008).
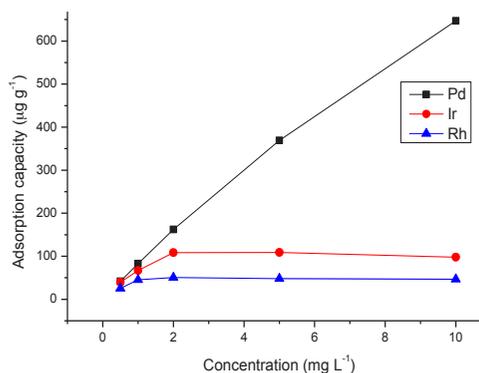
Fig. 3 Effect of concentration on adsorption of metals
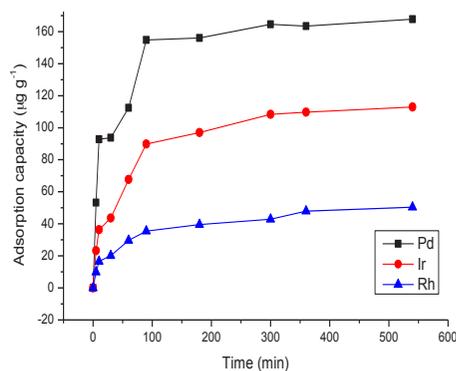
Fig. 4 Effect of time on adsorption of metals

Effect of contact time

The effect of contact time indicated that there is at first a fast rate of adsorption of the metals which was observed within 10 min (Fig. 4). Beyond 90 min, the increase in adsorption of the metals was insignificant. Even though the adsorption of the metals was substantial within 90 min, a contact time of 6 h was selected for this study to obtain the maximum adsorption. The contact time data was used to fit in the kinetic models and determine the adsorption controlling mechanism. The results in Table 2 showed that pseudo second-order described the data better since the correlation coefficient (R^2) was > 0.99 for all the metals, indicating that the interaction of the metals with the adsorbent is strong (Mosai et al., 2019). To further confirm that the data was better described by pseudo second-order, the experimental adsorption capacity ($q_{e, exp}$) was close to the pseudo second-order calculated adsorption capacity (q_e) of the metals. When the adsorption is described by pseudo second-order, the interaction between the metals and the adsorbent is so strong that the detachment of the metals is unlikely to happen, which is a good attribute of the adsorbent especially when it is handled from mining or waste sites.

Competing ions

The effect of competing ions on the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite was studied since, mining wastewaters contain substantial amounts of other metals. The results from this study give an indication of how the adsorbent will behave in real wastewater. The results (Fig. 5) showed that the adsorption capacity of the analytes increased in the presence of other ions and this can be attributed to the possible synergistic interaction of the analytes with other metals such as iron thus, leading to adsorbent-Fe-analyte interaction (Mosai et al., 2019). The percentage increments in adsorption were found to be 14, 27, 58% for Pd(II), Ir(III) and Rh(III), respectively. Other PGEs (Pt, Ru and Os) were substantially removed from the aqueous solutions which is a good attribute of the adsorbent. Thus, in the presence of metals such as Fe, there is a possibility of multilayer adsorption where the Fe is directly connected to the adsorbent and form bonds with the analytes. The ability of the adsorbent to remove metals such as (K, Ni, Co and Zn) means that the yeast-functionalised zeolite has dual efficacy and that is recovering precious metals whilst removing contaminants from wastewaters.

Table 1 Adsorption isotherm parameters for the adsorption of metals by yeast-functionalised zeolite

Metal	Langmuir			Freundlich			Dubinin-Radushkevich		
	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})	Es (kJ mol^{-1})	R^2
Pd(II)	0.99	53960	0.99	1308	1.37	0.99	16.7	10.12	0.99
Ir(III)	0.15	1.10x10^7	0.99	0.90	4.97	0.91	0.29	19.0	0.93
Rh(III)	0.052	2.75x10^6	0.99	0.19	7.61	0.83	0.09	22.3	0.85

Table 2 kinetic models parameters for the adsorption of Pd(II), Ir(III) and Rh(III) by yeast-functionalised zeolite

Metal	Pseudo first-order				Pseudo-second order		
	q_e (exp) mg g^{-1}	k_1 min^{-1} 10-3	q_e mg g^{-1}	R_2	k_2 g mg^{-1} min^{-1}	q_e mg g^{-1}	R_2
Pd(II)	0.20	4.10	0.12	0.75	2.93	0.17	0.99
Ir(III)	0.080	1.98	0.17	0.81	4.13	0.12	0.99
Rh(III)	0.051	0.61	0.18	0.78	1.65	0.050	0.99

Conclusion

The ability of zeolite functionalised with yeast waste to recover Pd(II), Ir(III) and Rh(III) from aqueous solutions was studied. The results obtained were compared to those of the raw zeolite and the results were significanty different. The raw zeolite poorly adsorbed the metals but, there was a substantial change when the functionalised zeolite was used. The adsorbent was hoghly efficient at 2 mg L^{-1} and a dosage of 10 g L^{-1}. The adsorbent will substantially recover Pd(II) and Ir(III) at highly acidic pH regions but the adsorption of Rh(III) will be more efficient at less acidic pH regions due to the formation of aqua/chloro complexes which are positively charged. The adsorption capacity of Pd(II) was highly preferred more than other metals due to the ability to adsorb onto different active sites of the adsorbent since, both Langmuir and Freundlich described the adsorption data well. The adsorption mechanism of all the analytes was best described by pseudo second-order kinetic model meaning that the interaction of the metals was strong due to chemical adsorption. The adsorption capacities of the analytes increased in the presence of other ions due to adsorbent-Fe-metal synergistic interaction. Desorption studies were not conducted since, the used adsorbent can be processed along with the new ore and thus, no extra chemicals required for recovery. Hence, this will be a very cheap process.

Acknowledgements
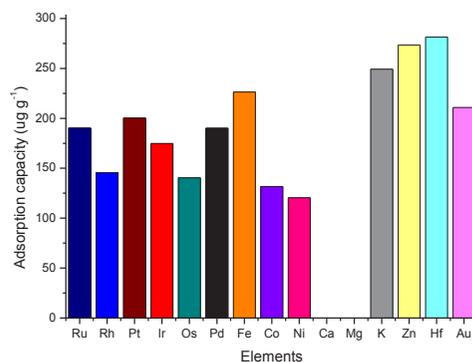
Fig. 5 Effect of competing ions on adsorption of metals

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