Statistical Optimization, Kinetic and Isotherm Studies on Selective Adsorption of Silver and Gold Cyanocomplexes Using Aminoguanidyl-Chitosan Imprinted Polymers

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Abstract

Aminoguanidyl-chitosan imprinted polymers (AGCIPs) were synthesized and applied to the selective extraction of silver and gold cyanocomplexes from aqueous solutions. Batch adsorption parameters for the recovery of silver and gold cyanocomplexes from aqueous solutions by the AGCIPs viz., contact time, solution pH, initial metal concentrations and temperature, were optimized by a two-level fractional factorial design and the Box-Behnken matrix. The equilibrium data correlated well with Langmuir isotherm model; and the maximum adsorption capacities for silver cyanide calculated from the Langmuir equation were 429.2 mg Ag g⁻¹ and 319.5 mg Ag g⁻¹ at pH 6.9 and 10, respectively; whereas they were 319.5 mg Au g⁻¹ and 312.5 mg Au g⁻¹ for gold cyanide in the same order. Adsorption kinetics suggested that these materials predominantly display a pseudo-second-order kinetic mechanism, while thermodynamic parameters revealed that the adsorption process was spontaneous and of exothermic nature. Investigation on the adsorption selectivity showed that the selectivity coefficients of AGCSIP (gold cyanide) with respect to Ag(CN)₂⁻, Fe(CN)₆³⁻, and Hg(CN)₂⁻ were 8.675, 26.005 and 5694.667 respectively whereas for AGCIP (Silver cyanide) they were 3.017, 75.478 and ∞ for Au(CN)₂⁻, Fe(CN)₆³⁻, and Hg(CN)₂⁻ respectively. This indicates that AGCSIPs have excellent selectivity for silver and gold cyanide complexes. Regeneration and reusability studies also revealed that 2M solution of KNO₃ at pH 10.5 could be used to regenerate the AGCIPs; and these materials could be recycled up to five times without significantly diminishing their adsorption capacity.

Keywords: Aminoguanidyl-chitosan imprinted polymers; Silver and gold cyanocomplexes; Selective adsorption; Experimental design; Equilibrium isotherm; Kinetics

Introduction

The recovery of precious metals, particularly gold and silver, from their primary and secondary sources has always attracted a great deal of attention due to their scarcity. Since both sources contain various coexisting metals, selectivity towards target species plays a crucial role in their extraction.

Nowadays hydrometallurgical processes are extensively used to recover precious metals. In these processes, the cyanidation method...
is still the dominant technique for gold and silver ores as well as metal containing waste treatments [1]. The recovery of gold and silver from the alkaline cyanide leachate is usually accomplished through precipitation, solvent extraction, adsorption on activated carbon and ion-exchange [2]. Among these, adsorption on activated carbon and ion-exchange has been extensively employed and proved to be more effective compared to other separation methods [3,4]. However, these adsorbents are costly, not selective and require expensive labor and time [5]. This prompted the conception of this study which aims to develop efficient, cheaper and environmentally friendly sorbents for the recovery of silver and gold in the cyanidation process.

In the last decade chitosan-based materials have received increased attention as a versatile class of adsorbent that can be used in the hydrometallurgical processes [6]. The main advantage in using chitosan-based materials is their availability at low cost and their versatility. But native chitosan could not be used as anion exchanger for precious metals in the cyanidation process, since its cationic behavior is limited to acidic condition (pK near 6.2) [7]. However it can be modified, in a number of ways, with various ligating groups to produce chitosan-based materials which display higher specific affinity towards the target species [2,8-10].

Nowadays ion imprinted polymers (IIPs), have received much attention as sorbents for solid phase extraction due to several potential reasons viz. high affinity and selectivity for the target ion, high adsorption reproducibility without loss of recognition memory, low cost and stability [11]. IIPs are prepared by cross-linking a polymer derivative containing a metal ion template with a bifunctional reagent; then the metal ion is removed from the polymer matrix thus generating a specific bonding site that is complementary in size and shape to the target metal ion [12].

In this paper two aminoguanidyl modified chitosan ion imprinted polymers (AGCIPs), are proposed as low cost environmentally friendly biopolymers, for the selective recovery of gold and silver cyanocomplexes from aqueous solutions. The synthesis of these new materials was done using aminoguanidyl modified chitosan as a biopolymer, glutaraldehyde (GLA) as a crosslinker and silver and gold cyanide as ion templates. The characterization was done by analytical techniques such as FT-IR, XRD, SEM, BET and zeta potential. It is noteworthy mentioning that aminoguanidyl-chitosan imprinted polymers (AGCIPs) have never been used before, in the extraction of gold and silver cyanide. A number of studies involving guanidyl based organic synthetic polymers for the recovery of gold and silver cyanocomplexes from aqueous solutions, can be found in the literature [8,13,14]; But to the best of our knowledge, such studies involving the synthesis and uses of aminoguanidyl-chitosan imprinted biopolymers have never been reported. In order to optimize parameters (contact time, solution pH, initial metal concentrations and temperature) affecting the extraction efficiency of silver and gold cyanocomplexes anions from aqueous media, a response surface design combined with an advance multivariable optimization method was used in this study. The multivariable approach, when compare to the single variation method, has the advantage of reducing the processing costs by saving time and chemicals [15,16]. The adsorption isotherms, kinetics, thermodynamics as well as selectivity and reusability studies of the AGCIPS materials were also investigated.

Experimental

Chemicals and solutions

Chitosan (medium Mw ~ 9000, N-deacetylation degree > 75%) and glutaraldehyde (50%) were obtained from Sigma-Aldrich Chemicals, Saint Louis, Mo, USA. Potassium dicyanoargentate and potassium aurou氰ide were supplied by South Africa Precious Metal, Ltd, South Africa. 1-Cyanoguanidine and hydrochloric acid were purchased from Riedel-de Haén (Germany). Acetic acid (97%), ethanol, acetone, sodium hydroxide, thiourea, sodium nitrate, sulphuric acid, metal salts of Hg(CN)₂, and K₃Fe(CN)₆ were purchased from Merck South Africa. Working solutions, as per the experimental requirements, were freshly prepared from the stock solution for each experimental run. A Spectra scan silver and gold standard solutions (1000 mg L⁻¹) (Industrial Analytical Pty, Ltd, South Africa) were used to prepare working standard solutions at concentrations of 10-100 mg L⁻¹ for Ag and Au. Reagents used were of analytical grade, and ultrapure water (18.3 µΩ cm⁻¹ at 25°C) was obtained from an Elxir/Milli-Q Element system (France).

Instrumentation

Inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Arcos, model Arcos FH512- Germany) was used to determine the concentration of metal ions. Temperature controlled water bath-shaker (LABCON, shaking water bath-25 L, USA) was used to agitate the sample solutions. pH of the solutions was adjusted using 0.1M HCl or NaOH using a Hanna pH meter (Italy). FT-IR Attenuated Total Reflection (ATR) (Perkin Elmer, USA) was used to analyze the functional groups in the adsorbent. ¹⁴C NMR spectrum was recorded at 75 MHz, on a Bruker AV 400 spectrometer (USA). Zeta potentials of the polymers were measured by a Malvern Nanosizer (ZENN 3600, UK). The surface morphology of polymers was characterized by Scanning Electron Microscope (SEM Thermo Scientific, model 6658A-1NUS- SN, USA). X-ray diffraction (XRD) analysis was conducted using a Philips Panalytical Xpert PRO powder diffractometer, employing Cu Kα radiation of wavelength 1.54. Nitrogen adsorption/desorption experiments were carried out using Micrometric ASAP 2020 Surface Area and Porosity Analyzer (USA).

Procedure

Synthesis of aminoguanidyl-chitosan hydrochloride: Aminoguanidyl chitosan hydrochloride was prepared by dissolving 2.0 g of chitosan (12.00 mmol NH₂) and 2.04 g of 1-cyanoguanidine (24.24 mmol) in 100 mL of (0.15M) HCl solution. The solution was heated for 2 h at 100°C. After cooling to room temperature, the aminoguanidyl chitosan hydrochloride was precipitated in acetone. Then, the wet solid was purified with ethanol in a Soxhlet extractor for 24 h. Finally, the product was dried under vacuum to constant mass. The preparation of aminoguanidyl chitosan hydrochloride is illustrated in Scheme 1 (step 1).

Scheme 1: Procedure used for the synthesis of silver and gold cyanocomplexes IIPs.
Synthesis of aminoguanidyl-chitosan imprinted polymer (AGCIP) and control polymers (CP): The aminoguanidyl chitosan hydrochloride (3.00 g) was dissolved with constant sonication in 50 mL acetic acid solution (2% V/V) and then transferred into a 250 mL round bottom flask containing 50 mL of potassium dicyanoargentate or potassium aurocyanide solutions, to give metal cyanide solution of 2000 mg L⁻¹. The mixture was stirred continuously at 60°C for 12 h. Then, 3.42 mL glutaraldehyde solution (1.81 g, 18.11 mmol) was added to the mixture to form a gel. The process was followed by filtering and intensive washing of the precipitate with acetone to remove any unreacted glutaraldehyde. The precipitate was again stirred, this time with a 2M solution of NaNO₃ at pH 10.5, to strip the template anion. This stage was monitored with an ICP-OES spectrophotometer. The residue was subsequently mixed with 0.1M solution of hydrochloric acid for 5 h to remove non-crosslinking aminoguanidyl chitosan. The precipitate obtained was filtered out and washed with distilled water and acetone; then dried inside a vacuum oven at 60°C for 12 h. The resulting material was ground and sieved to collect the particles which were later used for this study. The preparation process is shown in Scheme 1 (step 2 and 3). The aminoguanidyl-chitosan control polymer (CP) was similarly synthesized in the absence of templates.

Design of experiments
Aiming to achieve the highest adsorption uptake for silver and gold cyanocomplexes using a batch system, several variables in the adsorption process should be optimized. However, in this study, the variables chosen for optimization were: kind of adsorbents (e.g., imprinted polymers versus control) (A), contact time (B), initial metal concentration (C), pH (D) and temperature (E). The optimization was conducted using multivariate method. Firstly, the half full 2ⁿ factorial design with two central points was carried out to screen the influential variables on the extraction efficiency. The extraction efficiency (%EE) of silver and gold cyanocomplexes was taken as the response of the design experiments. The factor levels were coded as -1 (low), 0 (central point), and +1 (high) and presented in Table S1 (Supplementary data). The experimental data were processed by using the MINITAB Statistical Software program release 16.1 (Trial version, USA).

After identifying the significant variables according to the half factorial design, the response surface analysis (RSM) was applied in order to optimize the silver and gold cyanocomplexes extraction. The experimental sets were evaluated using Box-Behnken design with five replicates at centre points (Table 1). The design of experiments was carried out using MINITAB Statistical Software program release 16.1 (Trial version, USA).

Adsorption experiments
Batch tests based on fractional factorial and Box-Behnken designs were conducted at random to study the effect of the pre-selected five operating variables on the silver and gold cyanocomplexes adsorption capacity of the AGCIPs. All equilibrium adsorption experiments were individually conducted for precious metal cyanides in a thermostatic water bath at agitation rate 200 rpm. The adsorption of silver or gold cyanocomplex was tested by shaking 10 mg of the adsorbent and 10 mL of silver or gold cyanocomplex solutions at various pHs, initial metal concentration, contact time, temperature (Table S1, Supplementary data). Aliquots for analysis were filtered, and the residual Ag/ Au concentration was measured by ICP-OES. The extraction efficiency (%EE) was determined as given in equation 1.

Isotherm data were carried out by adding 10 mg adsorbent to 10 mL of 50-1000 mg L⁻¹ silver or gold metal ions at pH 6.9 for 60 min.

### Table 1: Optimization of silver and gold cyanocomplexes adsorption AGCIPs using Box-Behnken design with five-central points.

| Experiment | Time (min) B | pH D | X or E (°C) E | %EE Ag(CN)₃⁻ | Au(CN)₂⁻ |
|------------|--------------|------|--------------|----------------|-----------|
| 1          | 0            | -1   | -1           | 85.126         | 87.042    |
| 2          | 1            | 0    | -1           | 85.175         | 93.244    |
| 3          | 0            | 0    | 0            | 84.370         | 89.230    |
| 4          | -1           | 0    | +1           | 76.961         | 54.986    |
| 5          | 0            | +1   | +1           | 20.228         | 49.702    |
| 6          | 0            | +1   | -1           | 23.575         | 64.787    |
| 7          | +1           | 0    | +1           | 89.820         | 70.126    |
| 8          | -1           | 0    | +1           | 19.128         | 45.056    |
| 9          | 0            | 0    | 0            | 81.103         | 89.541    |
| 10         | 0            | -1   | +1           | 78.425         | 82.899    |
| 11         | 0            | -1   | 0            | 81.358         | 69.012    |
| 12         | 0            | +1   | 0            | 77.002         | 75.030    |
| 13         | 0            | 0    | 0            | 80.472         | 89.224    |
| 14         | 0            | 0    | 0            | 85.565         | 89.641    |
| 15         | 0            | 0    | 0            | 76.839         | 87.194    |
| 16         | +1           | +1   | 0            | 25.428         | 63.000    |
| 17         | -1           | 0    | -1           | 82.099         | 59.987    |

| Levels     | Time (min) B | pH D | X (mg L⁻¹) C | or X: (°C) E | %EE |
|------------|--------------|------|--------------|-------------|-----|
| -1         | 10 (2)       | 50 (16) | 90 (30)     |             |     |
| 0          | 6            | 8     | 10           |             |     |
| +1         | 105          | 157.5 | 210          |             |     |
|             | 25           | 37.5  | 50           |             |     |

Note: The bracket star ( *) denote to the condition for adsorption silver cyanide by the polymer. X stands for the factors temperature (°C) or initial concentration (mg L⁻¹) for adsorption silver and gold cyanocomplexes by the imprinted polymers, respectively.
The effect of imprinting on selectivity was defined by:

\[ k_d = \frac{C_i - C_f}{C_f} \times \frac{V}{m} \]  

(3)

where \( K \) is the distribution coefficient and \( V \), the volume of the solution used for the extraction and \( m \), the mass of the polymer used for extraction. The selectivity coefficient (\( \beta \)), for the binding of a particular metal ion in the presence of a competing ion can be obtained by:

\[ \beta_{\text{Ag(CN)}_2 \text{ or Au(CN)}_2} = \frac{k_{\text{Ag(CN)}_2 \text{ or Au(CN)}_2}}{k_{\text{competing} \text{ ion}}} \]  

(4)

The relative selectivity coefficient \( k' \):

\[ k' = \frac{k_{\text{Ag(CN)}_2 \text{ or Au(CN)}_2}}{k_{\text{non-imprinted}}} \]  

(5)

The results allow an estimation of the effect of imprinting on selectivity.

**Effect of different desorbents on the desorption of silver and gold cyanocomplexes-imprinting ions**

Batch sorption/desorption experiments were conducted using different desorption solutions of Thiourea (0.5M)/H_2SO_4 (2M), NaOH (1.0M) and NaNO_2 (2M) at pH 10.5. The adsorbed silver and gold cyanocomplexes (100 mg L\(^{-1}\) metal ions) (20 mg dry adsorbents) were washed with deionized water several times, dried and transferred into stoppered reagent bottles. To this, the desorption agent (10 mL) was added, and the bottles were shaken in a shaker (200 rpm) at room temperature (25-27°C) for 2.0 hrs. The concentration of Ag or Au ions desorbed from the imprinted polymers into aqueous phase was quantified by ICP-OES. The desorption ratio (%) could be calculated from the following equation:

\[ \text{Desorption ratio} = \frac{\text{amount of ions desorbed to the elution medium}}{\text{amount of ions adsorbed onto the sorbent}} \times 100 \]  

(6)

**Results and Discussion**

**Synthesis and characterization of the polymers**

**Synthesis and characterization of the AGCIPs:** For the synthesis of AGCIPs, we adopted a three step strategy, which involved the formation of electrostatic interaction between imprinted cyano-anions and guanidyl groups of chitosan followed by the freezing of the complex configuration by a cross-linking process with glutaraldehyde, and finally the removal of the templated anions to give the aminoguanidyl chitosan-imprinted polymers (AGCIPs) (step 2 and 3 in Scheme 1).

The FT-IR was also used as an important tool to ascertain the binding of metal cyanide ions to AGCIP as well as their complete removal from the imprinted polymers. The spectra of aminoguanidyl chitosan control polymers (CPs), AGCIPs before and after the ion template removal (unleached IIP and leached IIP respectively) are presented in Figures 1c-2f. When comparing the spectra of these three materials, it can be observed that CP and leached AGCIP have similar spectrum, while noticeable differences can be observed before and after the leaching process on the IIP spectra. For instance the N-H stretching vibrations peaks at 3242 cm\(^{-1}\) and 3290 cm\(^{-1}\) observed in the spectra of unleached silver and gold cyanocomplexes imprinted polymers, respectively moved to higher wave number 3334 cm\(^{-1}\) after the leaching process.

Another difference is found in the 1540 to 1665 cm\(^{-1}\) region, where the aminoguanidyl characteristic peaks observed for the silver and gold cyanocomplexes unleached polymers at 1637 cm\(^{-1}\) and -1633 cm\(^{-1}\) respectively appeared at 1643 cm\(^{-1}\) (st. vib for C=N) in the leached polymers. Furthermore the bending vibration peak of N-H that appeared at 1540 cm\(^{-1}\) and ~1543 cm\(^{-1}\) for silver and gold cyanocomplexes unleached polymers respectively is found at 1557 cm\(^{-1}\) in the leached IIPs. These results clearly confirm that the aminoguanidyl groups are strongly involved in the binding of metal cyanide complex ions. Also noteworthy is the stretching vibration of C=N groups that are observed near 2160 cm\(^{-1}\) and 2154 cm\(^{-1}\) respectively (Figures 1d-2e) in the unleached polymers, but disappeared after the leaching process, thus indicating the complete removal of the metal cyanoide ion templates from the polymer.

Another confirmation of the binding of metal cyanide complex ions is given by XRD patterns of control, unleached and leached polymer particles (Figure 2a-e). In the XRD pattern of the unleached
be protonated at pH \( < \text{pH}_{zpc} \) point of view, we expected that guanidyl groups in the polymer will be greater than that of CPs and were 38.908 Å, 44.603 Å and 14.166 Å, respectively. The BET result indicates an increase in surface area due to the imprinting of template anions-AGCIPs with a porous patterned surface due to leaching. This result is consistent with the conclusion obtained in our study were 0.998 and 0.979 for the extraction of silver and gold cyanocomplexes, respectively. These values were higher than 0.8. Thus indicating a good agreement between the predicted and observed results [22].

Analysis of Variance (ANOVA) was used to investigate the significance of the variables and their interaction in the extraction of the silver and gold cyanocomplexes. The information acquired from the ANOVA is presented in a Pareto chart (Figure 4A and 4B). Bar lengths are proportional to the absolute value of estimated effect, which helps in comparing the significance of effects. If the bar exceed the vertical reference line (P 0.05), the effect of the variable or interaction is significant [23]. On the other hand, when the value of the factor is positive it implies that increasing the factors from minimum to maximum maximizes the extraction. In contrast; the negative values mean that the factors must be kept at low levels to enhance the extraction [24].

Figure 4A and 4B showed that the type of polymer (A) and the pH of the solution (D) used for the extraction of silver cyanide (+7.30 and +7.02, respectively) and gold cyanide (+13.96 and -5.27, respectively) were statically significant at 95% confidence level. In the case of gold cyanide extraction (Figure 4B), contact time (+4.44) and interaction between AB and AD were not significant at 95% confidence level. This result demonstrated that the IIPs (high level) were better than CPs (low level) for both silver and gold cyanocomplexes. Therefore, it was expected that experiment with IIPs optimized system will present higher adsorption capacities for silver and gold cyanocomplexes than CPs. On the other hand, the negative value of the pH coefficient meant that the silver and gold cyanocomplexes uptake by IIPs and CPs were favoured at low pH values (pH 6.0). The increase in the pH led to a notable decrease of both cyanide anions uptake by the two kinds of adsorbents (IIPs and CPs). The other statistically significant factors for the extraction of silver cyanide (Figure 4A) were solution temperature (-3.77) and interaction between BC (-4.93), CD (-3.11) and AD (-3.04). Contact time (+0.48) and initial concentration (+0.34) were not significant at 95% confidence level. In the case of gold cyanide extraction (Figure 4B), contact time (+4.44) and interaction between AB and AD were statically significant at 95% confidence level. However, the main effect contact time (-1.56) and temperature (+0.68) were statically significant at 95% confidence level.

For further optimization experiments on the adsorption of silver and gold cyanocomplexes, only imprinted polymers (IIPs) will be considered, and only the most three significant factors will be undertaken. These include: pH, temperature and contact time for the extraction of silver cyanide; and pH, contact time and initial metal concentration for the extraction of gold cyanide.

Surface analysis: After identifying the most significant variables using a half 2\(^{3}\) factorial designs, a Box- Behnken response surface design (RSM) was used to find the optimum condition for the highest silver and gold cyanocomplexes extraction. The list of experiments which was beneficial for anion adsorption. Whereas, at pH > pH\(_{zpc}\) solution, a relatively lower number of positively charged sites on the adsorbent surface do not favour the adsorption of anionic metal cyanides due to the electrostatic repulsion.

Statistical design of experiments

Screening of factors for silver and gold cyanocomplexes uptake by AGCIPs and control CPs polymers (Half factorial design): Table S1 (Supplementary data) depicts the results of RSM optimization where 5-factors fractional factorial was used. The regression analysis was performed to fit the response (%EE). A good fit model should have a correlation coefficient value above 0.8 [21]. The correlation coefficients obtained in our study were 0.998 and 0.979 for the extraction of silver and gold cyanocomplexes, respectively.

For further optimization experiments on the adsorption of silver and gold cyanocomplexes, only imprinted polymers (IIPs) will be considered, and only the most three significant factors will be undertaken. These include: pH, temperature and contact time for the extraction of silver cyanide; and pH, contact time and initial metal concentration for the extraction of gold cyanide.
Figure 3: Scanning electron micrographs of silver cyanide AGCIP (a), gold cyanide AGCIP (b) and CP (c), magnification × 10000.

Figure 4: Pareto chart of standardized effects for variables related to the extraction of silver cyanide (A) and gold cyanide (B).
Figure 5A, 5B, 5D and 5F show the interactive conformation of silver and gold cyanocomplexes using aminoguanidyl-chitosan imprinted polymers. The adsorption isotherms at two different pHs, 6.9 and 8, were measured. The adsorption isotherms at pH 6.9 showed a similar trend to those at pH 8, with a slight increase in the adsorption capacity at higher pH. The adsorption capacity of silver cyanide was lower than that of gold cyanide, with %EE values of 85.4% ± 1.2 and 92.9% ± 1.2 for silver cyanide and gold cyanide, respectively. The adsorption efficiency of silver cyanide was higher at pH 8, while the adsorption efficiency of gold cyanide was higher at pH 6.9. The adsorption isotherms were fitted to the Langmuir model, with the maximum adsorption capacity (Qmax) of 85.4 mg g⁻¹ for silver cyanide and 92.9 mg g⁻¹ for gold cyanide. The calculated adsorption energy (Ea) values were 33.2 and 40.1 kJ mol⁻¹, respectively, indicating a physical adsorption process. The adsorption isotherm data were also used to predict the adsorption capacity at different initial concentrations and contact times, with the calculated values being close to the experimental data. The effect of temperature and initial concentration on the adsorption efficiency was also studied, with the adsorption efficiency decreasing with increasing temperature and increasing initial concentration. The adsorption isotherms were used to design separation processes for silver and gold cyanocomplexes.
### Analysis of variance (ANOVA) for quadratic model for Ag(CN)\(_2\)- adsorption

| Source         | DF | Seq SS      | Adj SS     | Adj MS      | F     | P   |
|----------------|----|-------------|------------|-------------|-------|-----|
| Regression     | 7  | 11091.000   | 11091.000  | 1584.420    | 243.710 | 0.000|
| Linear         | 3  | 7441.900    | 2638.000   | 879.340     | 135.260 | 0.000|
| Square         | 1  | 3630.000    | 3630.000   | 3629.950    | 558.340 | 0.000|
| Residual Error | 9  | 58.500      | 58.500     | 6.500       |        |     |
| Lack-of-Fit    | 5  | 11.000      | 11.000     | 2.190       | 0.180  | 0.954|
| Pure Error     | 4  | 47.500      | 47.500     | 11.890      |        |     |

### Analysis of variance (ANOVA) for quadratic model for Au(CN)\(_2\)- adsorption

| Source         | DF | Seq SS      | Adj SS     | Adj MS      | F     | P   |
|----------------|----|-------------|------------|-------------|-------|-----|
| Regression     | 8  | 4239.760    | 4239.760   | 529.970     | 244.660 | 0.000|
| Linear         | 3  | 2813.220    | 2813.22    | 937.740     | 432.900 | 0.000|
| Square         | 3  | 1371.130    | 1371.130   | 457.040     | 210.990 | 0.000|
| Residual Error | 8  | 17.330      | 17.330     | 2.170       |        |     |
| Lack-of-Fit    | 4  | 13.230      | 13.230     | 3.310       | 3.220  | 0.142|
| Pure Error     | 4  | 4.100       | 4.100      | 1.030       |        |     |

#### Models summary Statistic

|          | Ag(CN)\(_2\) | Au(CN)\(_2\) |
|----------|--------------|--------------|
| R\(^2\)  | 0.993        | 0.996        |
| R\(^2\) (adjusted) | 0.990 | 0.991 |
| R\(^2\) (predicted) | 0.988 | 0.977 |

Table 2: Analysis of variance (ANOVA) and statistical summary for quadratic models for silver and gold cyanocomplexes adsorption.
fitting evaluated using the correlation coefficient and functional error function. It was reasonable to study the adsorption isotherm at pH 10 since a typical mining leaching solution containing gold and silver as cyanide complexes are practically recovered at this pH. The mathematical equations of Langmuir and Freundlich are given in Table S2 (Supplementary data). The calculated constants, correlation coefficients (R²) and relative average error (F_exp) are listed in Table 3. Inspection of the correlation coefficients (R²) and relative average errors (F_exp) show that the correlation coefficients of Langmuir model was stronger with respect to Freundlich model at the studied pHs, for both AGCIP and CP. The q_exp calculated by Langmuir model (Table 3) at the studied pH for both IIP and CP were consistent with the experimental saturated adsorption of resins (q_cal), which also proved that the monolayer adsorption was dominant and the process is preferably chemisorption rather than physisorption.

Furthermore, the maximum sorbent capacities for silver cyanide AGCIP and CP decreased substantially with increasing pH (more than 25% at pH 10). But, the adsorption capacity for Au(CN)₂⁻ AGCIPs did not change much with increasing pH and was found to be, at higher pH, comparable with that obtained at the optimum pH (pH 6.9) (less than 2.2% at pH 10), thus indicating the strong interaction between template gold anions and active sites of the adsorbent even at relatively high pH.

The essential degree of suitability of resin towards metal ions can be expressed in terms of separation factor R_i which describes the type of isotherm and it is calculated by the equation R_i=1+(1/K_iC_i) where, C_i is the initial concentration of template anions. The values of R_i calculated for both IIP and CP at the two studied pH were in the range between 0.004 and 0.7, thus indicating highly favourable adsorption of template anions onto the studied resins. Another support for the favourability of the adsorption process is given by the values of adsorption intensity (n) which were determined from Freundlich isotherm. In this study the calculated n values were greater than unity indicating favorable adsorption conditions and reflecting a high affinity between adsorbate and adsorbent which is indicative of chemisorption.

Comparison of the maximum adsorption capacities of AGCSIPs with different adsorbents reported in literature

For comparison study, the values of some adsorbent capacities towards silver and gold cyanocomplexes available in the literature are shown in Tables 4 and 5. The q_exp values for adsorption silver cyanide (429.2 and 321.5 mg g⁻¹) and gold cyanide (319.5 and 312.5 mg g⁻¹) at pH 6.9 and 10, respectively are higher than those in most previous (429.2 and 321.5 mg g⁻¹) shown in Tables 4 and 5. The q_exp towards silver and gold cyanocomplexes available in the literature are preferable chemisorption rather than physisorption.

Kinetic studies

Kinetic analysis is required to get an insight of the mechanism that describes the adsorption process, which are mainly used in the modeling, and designing of continuous process. Four linearized form of kinetic models viz., pseudo-first order, pseudo-second order, intra-particle diffusion and liquid film diffusion have been used to analyze the collected experimental data during (Table S2, Supplementary data). The parameters, correlation coefficients (R²) and relative average error (F_exp) of the four different models were all listed in Table S3 (Supplementary data) and presented in Figure S2 a-d (Supplementary data). From the investigated models discussed above, the pseudo-second-order kinetics model fitted well to the adsorption data inferred from the high R² value of 0.9775 to 0.9999, as well as better predicted the value for q_t than those of first-order model given in Table S3 (Supplementary data). Thus it can be assumed that chemisorption is the rate-controlling step involving valence forces through sharing or exchange of electrons between the adsorbent surface and adsorbate ions with no involvement of a mass transfer in solution.

The plot of intra-particle diffusion which can be obtained by plotting q vs. t¹/₂ (Figure S2c, Supplementary data) is linear over the entire time range but did not pass through the origin point indicating that the intra-particle diffusion may not be the rate controlling factor in determining the kinetics of the process. The role of liquid film diffusion in governing the adsorption process was also verified using the kinetic equation. The plot of –ln(1-F) versus time (presented in Figure S2d, Supplementary data) and the fitting parameter (Table S3, Supplementary data) gave linear line with the higher correlation coefficients for IIPs ranged from 0.9781 to 0.9878. However, the corresponding calculated correlation coefficients for CPs were low (0.9257 and 0.1301). This indicates that the liquid film diffusion model can be applied to predict the adsorption kinetic for the adsorption of template anions by AGCIPs and demonstrates that the surface areas of AGCIPs are higher compared to the CPs resin.

| Isotherm | Ag(CN)₂⁻ AGC | pH 6.9 | pH 10 | Au(CN)₂⁻ AGCAGC | pH 6.9 | pH 10 |
|---------|--------------|--------|-------|------------------|--------|-------|
|         | IIP          | CP     | IIP   | CP               | IIP    | CP    |
| Langmuir |              |        |       |                  |        |       |
| q_exp   | 407.54       | 163.99 | 293.69| 101.88           | 315.17 | 52.74 | 303.79 | 31.84 |
| K_L (L mg⁻¹) | 429.185 | 150.830| 321.543| 104.822 | 319.489 | 52.826| 312.500| 35.199 |
| R²      | 0.999        | 0.887  | 0.998 | 0.990            | 0.999  | 0.998 | 0.999  | 0.909  |
| F_exp   | 0.041        | 0.158  | 0.042 | 0.058            | 0.026  | 0.084 | 0.041 | 0.163 |
| Freundlich |            |        |       |                  |        |       |
| K_0 (mg g⁻¹ (L mg⁻¹)²) | 109.648 | 46.666| 31.696| 15.849           | 109.648| 44.463| 87.096| 9.683 |
| 1/n     | 0.221        | 0.147  | 0.475 | 0.316            | 0.185  | 0.036 | 0.232 | 0.250 |
| R²      | 0.977        | 0.584  | 0.962 | 0.986            | 0.985  | 0.436 | 0.860 | 0.437 |
| F_exp   | 0.061        | 0.134  | 0.043 | 0.066            | 0.060  | 0.083 | 0.047 | 0.053 |

Table 3: Fitting parameters for the Langmuir and Freundlich to experimental adsorption isotherm of AGCSIPs and CPs.
This work >40

Reference [31]

Table 4: Maximum adsorption capacities for the adsorption of silver cyanide ions onto various adsorbents.

| Adsorbents                        | pH  | qe (mg Ag/g) | Reference |
|----------------------------------|-----|--------------|-----------|
| Conventional anion exchangers with modified amino alkyl group and S or S,N-modified polystyrene | 9.0 | 50.0 -117.0 | [30]      |
| Weak base resin Wofatat AD-4     | 10.4| 36.7         | [31]      |
| Weak base resin (Wofatat AD-42)  | 10.4| 28.0         | [31]      |
| Weak base resin (Lewatit MP-64)  | 10.4| 2.3          | [31]      |
| Weak base resin (Amberlite IRA-93)| 10.4| 25.9         | [31]      |
| Strong base resin (Wofatat RO)   | 10.4| 83.1         | [31]      |
| Strong base resin (Wofatat SBW)  | 10.4| 107.9        | [31]      |
| Strong base resin (Lewatit M 500) | 10.4| 129.4        | [31]      |
| AGCIP                           | 6.9 | 429.2 | This work |
| AGCSIP                          | 10.0| 321.5        | This work |

Table 5: Maximum adsorption capacities for the adsorption of gold cyanide ions onto various adsorbents.

| Adsorbents                        | pH  | qe (mg Au/g) | Reference |
|----------------------------------|-----|--------------|-----------|
| Minex resin                      | 9.0 | 26.0         | [32]      |
| Aminoguanidine of acrylonitrile/vinyl acetate/divinylbenzene | 9.0 | 49.3 | [9] |
| Aminoguanidine of vinyl benzyl chloride/methyl methacrylate/divinylbenzene resin | 9.5 | 30.0 | [8] |
| Aminoguanidine of poly(acrylonitril-co-vinyl acetat-co-divinyl benzene) polymer | 9.6 | 2.3 | [14] |
| Aminoguanidine of poly(vinylbenzyl chloride-co-divinylbenzene) polymer | 9.6 | 23 | [14] |
| Hypersol Macronet resin MN300    | 8.5 | >40          | [1]       |
| Amberjet™ 4400                   | 3.0 | 427.8        | [25]      |
| activated carbon                 | 3.0 | 170.6        | [25]      |
| polyethylenimine modified biomass| 3.0 | 361.8        | [25]      |
| AGCIPs                           | 6.9 | 319.5        | This work |
| AGCSIPs                          | 10.0| 312.5        | This work |

Selectivity studies

AGCIPs and CP particles were tested for the separation of silver or gold cyanocomplexes from mixtures containing hexacyanoferrate(III) and mercuric cyanide. The distribution coefficient (Kd), the selectivity coefficient (β), and the relative selectivity coefficient (kR) values of the competing ions with respect to the target ions, silver and gold cyanocomplexes are summarized in Table 6. The data obtained clearly indicated that the distribution coefficient increased for target anion, silver and gold cyanocomplexes and decreased for other coexisting ions. AGCIPs showed maximum selectivity for the template anions over others anions. The relative selectivity order of AGCIPs silver and gold cyanocomplexes increased from Ag(CN)2− > Au(CN)3− > Fe(CN)63− >> Hg(CN)2− and Au(CN)3− > Ag(CN)2− > Fe(CN)63− >> Hg(CN)2−, respectively, indicating quantitative separation of target template anions when it is present together with other anions. Though the silver and gold cyanocomplexes resemble each other in terms of (i) the weak hydration state compared with other cyanide-complexes anions; (ii) the large ion size (Ag 12.6 nm; Au 13.7 nm) and (iii) their single anions charged [28], the IIP synthesized in this study has a higher selectivity for the specific targeted precious metal anion since, it perfectly fitted the fabricated recognition sites on the polymers.

Desorption and reusability studies

In order to reduce the cost of the extraction process, the reusability of polymer is a crucial factor for the adsorbent. Table 5 (Supplementary data) demonstrates the results of three different eluents used for the extraction of silver and gold cyanocomplexes from the metal anion adsorbed resin. It was observed that silver and gold cyanocomplexes could be quantitatively desorbed with 10 ml of 2M KNO3 at pH 10.5 with extraction above 95% in the first elution cycle. The probable mechanism of the regeneration might be that the aminoguanidyl functional groups are deprotonated causing release of the precious metal cyanide anions [1,29]. The reason for using relatively high concentrations of nitrate counter ions is to replace the loaded silver and gold cyanocomplexes in the loaded resin. This synergic effect is required to establish a driving force for the elution of the cyanocomplexes in aqueous media. To assess the regeneration of the adsorbent, five consecutive adsorption-desorptions cycles were conducted using 2M KNO3 at pH 10.5 as desorbing agent. It is shown (Figure S3, Supplementary data) that the uptake capacity of Ag(CN)2− and Au(CN)3− on the adsorbents decreased slowly with increasing number of cycles. At the fifth regeneration cycle, the adsorption remained above 85%. These results show that the adsorbents could be effectively recycled and reused for silver and gold cyanocomplexes adsorption with 2M KNO3 at pH 10.5, and the adsorbents. And it can be concluded that silver and gold cyanocomplexes imprinted polymers could be used several times without significantly diminishing their adsorption capacity.

Conclusion

In summary, two aminoguanidyl-chitosan ion imprinted polymers have been successfully prepared and tested for the extraction of gold and silver cyanides ions in aqueous solution. High adsorption rates, high adsorption capacity and high selectivity have been observed for the two polymers. The optimum adsorption conditions were established at 72 min, 6.9 and 142.1 mg L−1 for time, pH and initial concentration respectively. AGCIPs also exhibit excellent stability and reusability (up to five cycles). When compared to the existing gold and silver cyanides adsorbents, these polymers were faster and presented good adsorption capability even at typical mining operation pH (pH=10).
Thus suggesting that these new aminoaguindyl-chitosan imprinted polymers could be used effectively in practical applications for the selective recovery of silver and gold cyanide ions in aqueous solutions.

**Acknowledgements**

The authors acknowledge the Centre for Nanomaterial Science Research (CNSR), the Department of Applied Chemistry, and the University of Johannesburg (UJ) for their financial support.

**References**

1. Cortina JL, Kautzmann RM, Gliese R, Sampaio CH (2004) Extraction studies of cyanocyanide using macropet adsorbents: Physico-chemical characterization. Reactiv & Functional Polymers 60: 97-107.

2. Xie F, Lu D, Yang H, Dreisinger D (2014) Solvent extraction of silver and gold from alkaline cyanide solution using anion exchange resins. Journal of Water, Air and soil Pollution 223: 6069-6081.

3. Syed S (2012) Recovery of gold from secondary sources—a review. Hydrometallurgy 115: 30-51.

4. Soleymani M, Kaghazchi T (2008) The investigation of the potential of activated hard shell of apricot stones as gold adsorbents. Journal of Industrial and Engineering Chemistry 14: 28-37.

5. Fleming C, Cromberge G (1984) The extraction of gold from cyanide solutions by strong- and weak-base anion-exchange resins. J S Afr Inst Min Metall 84: 125-137.

6. Ahamed MEH, Mbianda XY, Mulaba-Bafubiandi AF, Marjanovic L (2013) Selective extraction of gold(ii) from metal chloride mixtures using ethylenediamine n-(2-(1-imidazolyl)ethyl) chitosan ion-imprinted polymer. Hydrometallurgy 140: 1-13.

7. Xie Y, Li S, Liu G, Wang J, Wu K (2012) Equilibrium, kinetic and thermodynamic studies on perchlorate adsorption by cross-linked quaternary chitosan. Chemical Engineering Journal 192: 269-275.

8. Bozena NK, Dorota JB, Bulina J, Wieslaw A, Barbara P (1998) New selective resins with guanidyl groups. Reactive & Functional Polymers 42: 213-222.

9. Bozena NK, Dorota B, Andrzej WT, Wieslaw A, Barbara P (1998) New selective resins with guanidyl groups. Reactive and Functional Polymers 36: 185-195.

10. Pan L, Wang F, Bao X (2013) Selective extraction of gold(ii) from alkaline cyanide solution with surfuryl thiolalcohol. Separation Science and Technology 48: 2007-2012.

11. Yan H, Row KH (2006) Characteristic and synthetic approach of molecularly imprinted polymer. International journal of molecular Sciences 7: 155-176.

12. Nishad PA, Bhaskarapillai A, Velmunugan S, Narasimhan SV (2012) Cobalt (ii) imprinted chitosan for selective removal of cobalt during nuclear reactor decontamination. Carbohydrate Polymers 87: 2690-2696.

13. Cortina JL, Meinhardt E, Roijals M, Martí V (1998) Modification and preparation of polymeric adsorbents for precious-metal extraction in hydrometallurgical processes. Reactive & Functional Polymers 36: 149-165.

14. Dorota JB, Bozena NK (2002) Gold sorption on weak base anion exchangers with aminoaguanidyl groups. European Polymer Journal 38: 2239-2246.

15. Umesh KG, Kaur MP, Garg VK, Dhiraj S (2008) Removal of nickel(ii) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach. Bioresource Technology 99: 1325-1331.

16. Zare F, Ghaderi M, Daneshfar A, Agarwal S, Tyagi I, et al. (2015) Efficient removal of radioactive uranium from solvent phase using ag-mowts nanoparticles. Kinetic and thermodynamic study. Chemical Engineering Journal 273: 296-306.

17. Yongbo S, Guixiao L, Yunling L (2012) Self-aggregation and antimicrobial activity of alkylguanidinium salts. Colloids and Surfaces A: Physicochem Eng Aspects 393: 11-16.

18. Liu M, Zhou Y, Zhang Y, Yu C, Cao S (2013) Preparation and structural analysis of chitosan films with and without sorbitol. Food Hydrocolloids 33: 186-191.

19. Bozena NK, Dorota JB, Julia J, Wieslaw A (2001) Anion exchangers with alkyl substituted guanidyl groups gold sorption and cu(ii) coordination. Reactive & Functional Polymers 48: 169-179.

20. Liang Z, Shuaiwei Y, Tong H, Lving Z, Cailian M, et al. (2012) Improvement of ag(i) adsorption onto chitosan/triethanolamine composite sorbent by an ion-imprinted technology. Applied Surface Science 263: 696-703.

21. Joglekar AM, May AT (1987) Product excellent through experimental design. General Food World 32: 857-866.

22. Camilla GP, Fernanda SR, Nathalía MS, Araci ASJ, Júlio CPV, et al. (2006) Use of statistical design of experiments to evaluate the sorption capacity of 7-amino-4-azahexyladyl and 10-amino-4-azadecyladyl for cu(ii), pb(ii), and fe(ii) adsorption. Journal of Colloid and Interface Science 302: 396-407.

23. Somera BF, Corazza MZ, Yabe MMJS, Segatelli MG, Galunin E, et al. (2012) 3-mercaptopropyltrimethoxysilane-modified multi-walled carbon nanotubes as a new functional adsorbent for flow injection extraction of pb(ii) from water and sediment samples. J Water, Air and soil Pollution 223: 6069-6081.

24. Jorge LB, Ricardo RE, Caroline DM, Lucas CM, Flavio AP, et al. (2006) Statistical design of experiments as a tool for optimizing the batch conditions to cr(vi) biosorption on araucaria angustifolia wasls. Journal of Hazardous Materials B 133: 143-153.

25. In Seob K, Min AB, Sung WW, Juan Maob KS, Jieyong P, et al. (2010) Sequential processes of sorption and incineration for recovery of gold from cyanide solutions: Comparison of ion exchange resin, activated carbon and biosorbent. Chemical Engineering Journal 165: 440-446.

26. Jayakumar R, Rajasimman M, Karthikeyan C (2015) Optimization, equilibrium, kinetic, thermodynamic and desorption studies on the sorption of cu (ii) from an aqueous solution using marine green algae: Halimeda gracilis. Ecotoxicology and environmental safety 121: 199-210.

27. Zhou L, Shang C, Liu Z, Huang G, Adesina AA (2012) Selective adsorption of uranium (vi) from aqueous solutions using the iron-imprinted magnetic chitosan resins. Journal of Colloid and Interface Science 366: 165-172.

28. Xihui Y, Aleksandra O, Hao D, Jian DM (2011) Molecular dynamics simulations of metal-cyanide complexes: Fundamental considerations in gold hydrometallurgy. Hydrometallurgy 106: 64-70.

29. Adelia MO, Versiane AL, Carlos AS (2008) A proposed mechanism for nitrile and thioacrylate elution of strong-base ion exchange resins loaded with copper and gold cyanocomplexes. Reactive & Functional Polymers 68: 141-152.

30. Knothe M, Feistel L, Hauptmann R, Schwachula G, Schwachula Chemie H (2012) Competitive adsorption properties of AGCISPs (mixture: Ag(CN)2-/Fe(CN)63-/Hg(CN)2-). T 25 ± 1°C, time 30 min and pH 6.9 ± 0.1)