Research Article   **Open Access**

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

**Ahamed MEH[1], Marjanovic L[3] and Mbianda XY[1,2]***

[1]Department of Applied Chemistry (Doornfontein Campus), University of Johannesburg, South Africa
[2]Centre for Nanomaterial Science Research, University of Johannesburg, South Africa
[3]Department of Chemistry, Faculty of Science, University of Johannesburg, South Africa

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 $Ag(CN)_2^-$, $Fe(CN)_6^-$, 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 $Au(CN)_2^-$, $Fe(CN)_6^-$, 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 KNO_3 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.
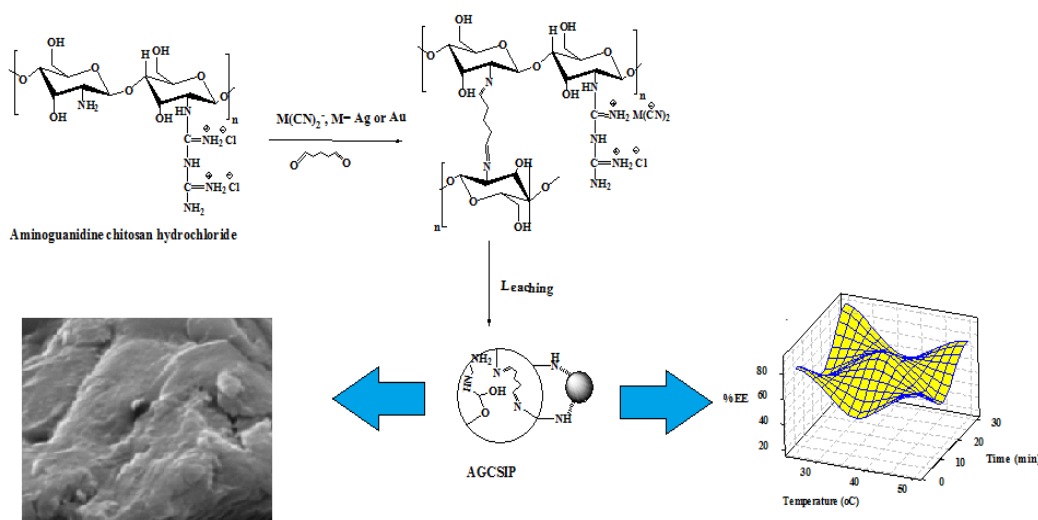
Keywords: Aminoguanidyl-chitosan imprinted polymers; Silver and gold cyanocomplexes; Selective adsorption; Experimental design; Equilibrium isotherm; Kinetics

Introduction

The recovery of precious metals, particularly gold and silver, from their primary and secondary sources has always attracts 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 extensive 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_a 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 ions 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 AGCSIPs materials were also investigated.

Experimental

Chemicals and solutions

Chitosan (medium M_n ~ 9000, N- deacetylation degree > 75%) and glutaraldehyde (50%) were obtained from Sigma -Aldrich Chemicals, Saint Louis, Mo, USA. Potassium dicyanoargentate and potassium aurocyanide were supplied by South Africa Precious Metal, Ltd, South Africa. 1-Cyanoguanidine and hydrochloric acid were purchased from Riedel-de Haën (Germany). Acetic acid (97%), ethanol, acetone, sodium hydroxide, thiourea, sodium nitrate, sulphuric acid, metal salts of $Hg(CN)_2$ and $K_3Fe(CN)_6$ 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 $\mu\Omega$ cm^{-1} at 25°C) was obtained from an Elix/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. ^{13}C 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 K_a radiation of wavelength 1.54. Nitrogen adsorption/desorption experiments were carried out using Micrometric ASAI 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 NH_2) 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.
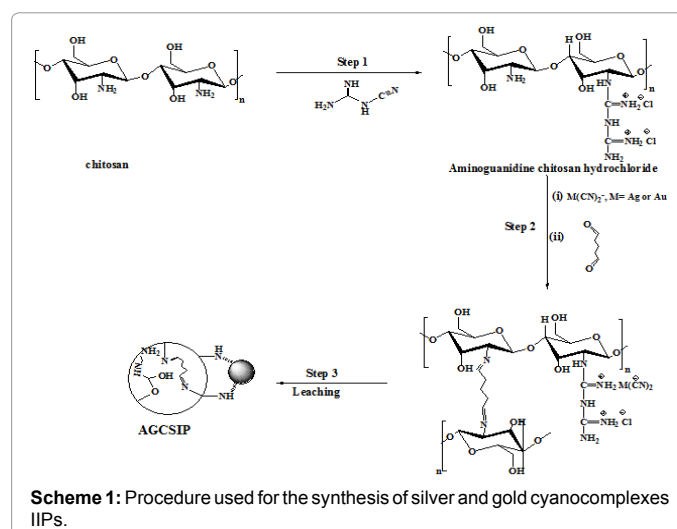
Synthesis of aminoguanidyl-chitosan imprinted polymer (AGCIP) and control polymers (CP): The aminoguanidyl chitosan hydrochloride (3.00 g) was dissolved with constant sonication in 50 mL acetic acid solution (2%V/V) and then transferred into a 250 mL round bottom flask containing 50 mL of potassium dicyanoargentate 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 NaNO$_3$ at pH 10.5, to strip the template anion. This stage was monitored with an ICP-OES spectrophotometer. The residue was subsequently mixed with a 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 grounded 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 2^5 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.

Experiment	Time (min) B	pH D	X E or C	%EE Ag(CN)$_2^-$	Au(CN)$_2^-$
1	0	-1	-1	85.126	87.042
2	+1	-1	0	85.175	93.244
3	0	0	0	84.370	89.230
4	-1	0	+1	76.9616	54.988
5	0	+1	+1	20.228	49.702
6	0	+1	-1	23.575	64.787
7	+1	0	-1	89.820	90.126
8	-1	+1	0	19.128	44.056
9	0	0	0	81.103	89.541
10	0	-1	+1	78.425	82.899
11	-1	-1	0	81.358	69.012
12	+1	0	+1	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		-1	0	+1	
Time (min) B		10 (2)*	50 (16)*	90 (30)*	
pH D		6	8	10	
X (mg L^{-1}) C		105	157.5	210	
or X: (°C) E		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.
Table 1: Optimization of silver and gold cyanocomplexes adsorption AGCSIPs using Box- Behnken design with five-central points.

Further, experiment were also performed at pH 10 (typical pH of mining operating of gold and precious metal cyanides leach liquor). Sorption kinetic experiments of silver or gold cyanocomplex were performed with 10 mg adsorbent and an initial concentration (100 mg L^{-1}) of metal ions. For the evaluation of the thermodynamic parameters, the experiment was carried out under similar mentioned condition at 25, 35 and 50°C for 30 min. After filtration, the residual silver or gold concentrations were analyzed by ICP-OES

Calculation of extraction efficiency and other constants

The extraction efficiency (%EE) was calculated by relating the obtained concentration (C$_f$) of the analyte to the original concentration (C$_i$) of the metal ion in the model solution (Equation 1)

$$\%EE = \frac{C_i - C_f}{C_i} \text{ x } 100 \qquad (1)$$

The amount adsorbed per unit mass of polymer (q, mg g^{-1}) was calculated by mass balance equation.

$$q = \frac{C_i - C_f}{m} \text{ x } V \qquad (2)$$

where m (g) and V (L) is the mass of the polymer and solution volume, respectively.

The competitive sorption experiments were conducted by preparing binary-mixture of Ag(CN)$_2^-$/Au(CN)$_2^-$, Ag(CN)$_2^-$ or Au(CN)$_2^-$/Fe(CN)$_6^{-3}$ and Ag(CN)$_2^-$ or Au(CN)$_2^-$/Hg(CN)$_2$. Ag(CN)$_2^-$, Au(CN)$_2^-$ and the two competitors had an initial metal concentration of 100 mg L^{-1} The pHs of the solutions were then adjusted accordingly to pH 6.9. These were placed in sealed containers and mechanically stirred for 30 min. The experiments were performed in triplicates.

The effect of imprinting on selectivity was defined by:

$$k_d = \frac{C_i - C_f}{C_f} \times \frac{V}{m} \qquad (3)$$

where K_d 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 (β), for the binding of a particular metal ion in the presence of a competing ion can be obtained by;

$$\beta_{Ag(CN)_2^- \text{ or } Au(CN)_2^-} = \frac{k_{Ag(CN)_2^- \text{ or } Au(CN)_2^-}}{k_{\text{competing ion}}} \qquad (4)$$

The relative selectivity coefficient k`;

$$k` = \frac{k_{Ag(CN)_2^- \text{ or } Au(CN)_2^-}}{k_{\text{non-imprinted}}} \qquad (5)$$

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 $NaNO_3$ (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:

$$\text{Desorption ratio} = \frac{\text{amount of ions desorbed to the elution medium}}{\text{amount of ions adsorbed onto the sorbent}} \times 100 \quad (6)$$

Results and Discussion

Synthesis and characterization of the polymers

Synthesis and characterization of the aminoguanidyl-chitosan hydrochloride: In this work, aminoguanidyl-chitosan hydrochloride was successfully synthesized by condensation of chitosan with 1-cyano guanidine in acidic media (Scheme 1 step 1). The reaction is believed to follow the addition mechanism, where the primary amino groups on chitosan backbone can undertake direct addition to C≡N bond. The reaction requires acid catalysis in order to proceed at a practical rate [17]. Evidence of the successful grafting of the aminoguanidyl groups on the chitosan molecules was provided by ^{13}C NMR spectrum, where the appearance of a signal at 165 ppm is assigned to the carbon attached to active hydrogen atom of guanidium salt groups (Figure S1, Supplementary data). This signal does not exist in the spectral data of native chitosan [18]. Additional confirmation of the chemical modification of chitosan was provided by the Fourier transform infrared (FT-IR) spectra, where new peaks characteristics of guanidyl groups are observed. These new features include: a strong peak at 1653 cm^{-1} associated to the stretching vibration of C=N of guanidyl group; and two peaks at 1358 cm^{-1} and 1590 cm^{-1} which are assigned to the stretching vibration of C–N and the scissoring bending of N-H, respectively [19].

Synthesis and characterization of the AGCIPs: For the synthesis of AGCSIPs, 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 1655 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 aminguanidyl 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 cyanide 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
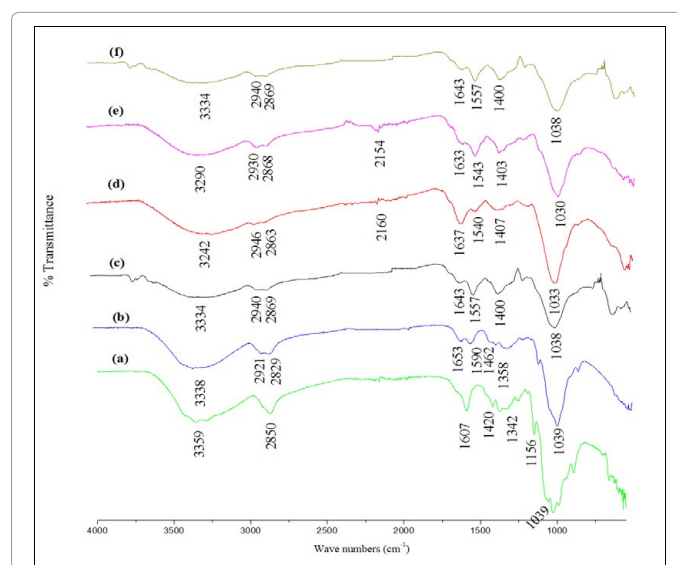

Figure 1: FTIR spectra of native chitosan (a), aminoguanidine chitosan hydrochloride (b), CP (c), silver cyanide AGCIP before leaching (d) gold cyanide AGCIP before leaching (e) and silver cyanide/gold cyanide AGCIPs (f) after leaching.
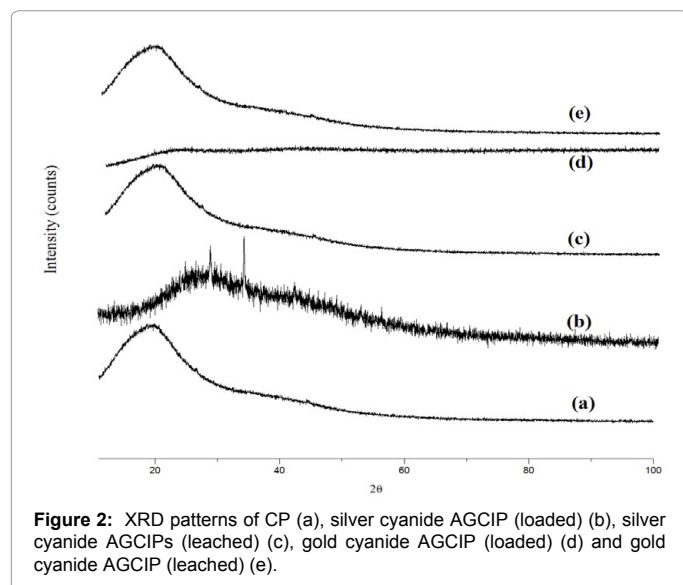
Figure 2: XRD patterns of CP (a), silver cyanide AGCIP (loaded) (b), silver cyanide AGCIPs (leached) (c), gold cyanide AGCIP (loaded) (d) and gold cyanide AGCIP (leached) (e).

silver cyanide AGCIP particles (pattern 3b), the peaks at $2\theta = 38.5°$ (1 1 1) and $59.2°$ (2 2 0) is assigned to silver metal which may be formed due to the reduction of silver cyanide to crystalline metallic silver [20]. In contrast, the diffractogram of unleached gold cyanide AGCIP (pattern d) show a significant decrease in the crystallinity at $2\theta = 20.42$ without indication of the reduction to Au metal, thus suggesting that gold cyanide disturb the inter-polymer bond and form stable complex with functional groups on the polymer. After leaching, the peaks related to silver cyanide (in pattern 3b) were absent in pattern (3c), while for leached gold cyanide AGCIP particles, the polymer retains its crystallinity (in pattern 3e). This indicates that the template anions were completely removed during leaching. The XRD pattern of leached AGCIP was found to be similar to that of the CP particles. Thus confirming the results obtained in the FTIR analysis.

Surface morphology, surface area and zeta potential measurements of the AGCSIPs and CPs

The surface morphology of the AGCIPs and CPs were studied using scanning electron microscopy (Figure 3a-c). The micrographs reveal that the leached imprinted polymers exhibit a rougher and porous surface which may be due to the imprinting of template anions on the polymer matrices.

The specific surface area of the particles were determined using BET method and were found to be 0.320 m^2 g^{-1}, 0.372 m^2 g^{-1} and 0.001 m^2 g^{-1} for the leached silver cyanide AGCIP, the leached gold cyanide AGCIPs, and CP, respectively. Furthermore, the pore sizes for leached silver and gold cyanocomplexes AGCIPs were also found to 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 for template anions-AGCIPs with a porous patterned surface due to imprinting effect. This result is consistent with the conclusion obtained from SEM and again confirms that the porous texture observed in SEM images of IIPs is due to the template anions imprinting.

Zero point charge (pH_{zpc}) for the polymers was determined to get a better understanding of the adsorption mechanism for adsorbing silver and gold cyanocomplexes on the sorbent. The pH_{zpc} for all AGCIPs and their CPs were found to be at 8.8. From the electrostatic interaction point of view, we expected that guanidyl groups in the polymer will be protonated at $pH < pH_{zpc}$ (10.5) to afford positively charged sorbent,

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. 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. 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 statically 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 2^5 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
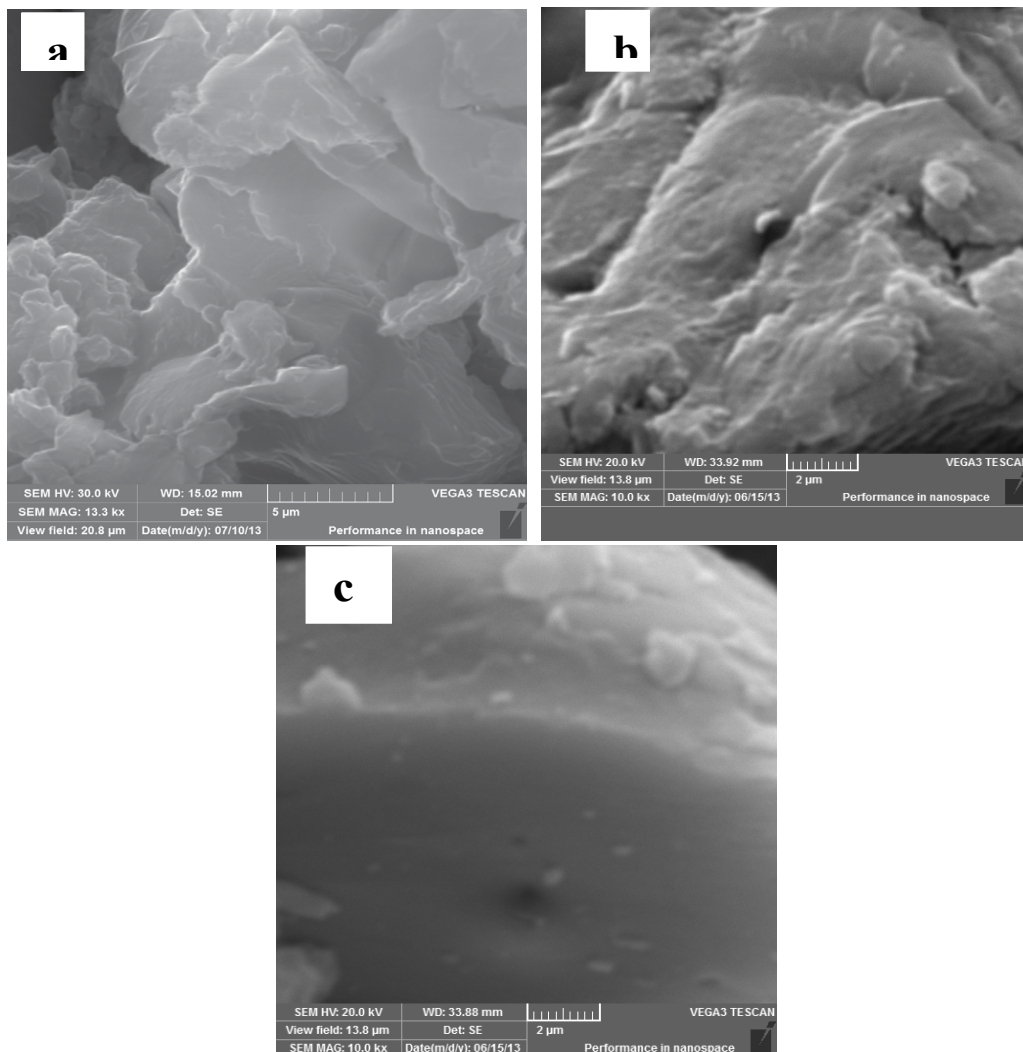
Figure 3: Scanning electron micrographs of silver cyanide AGCIP (a), gold cyanide AGCIP (b) and CP (c), magnification × 10000.
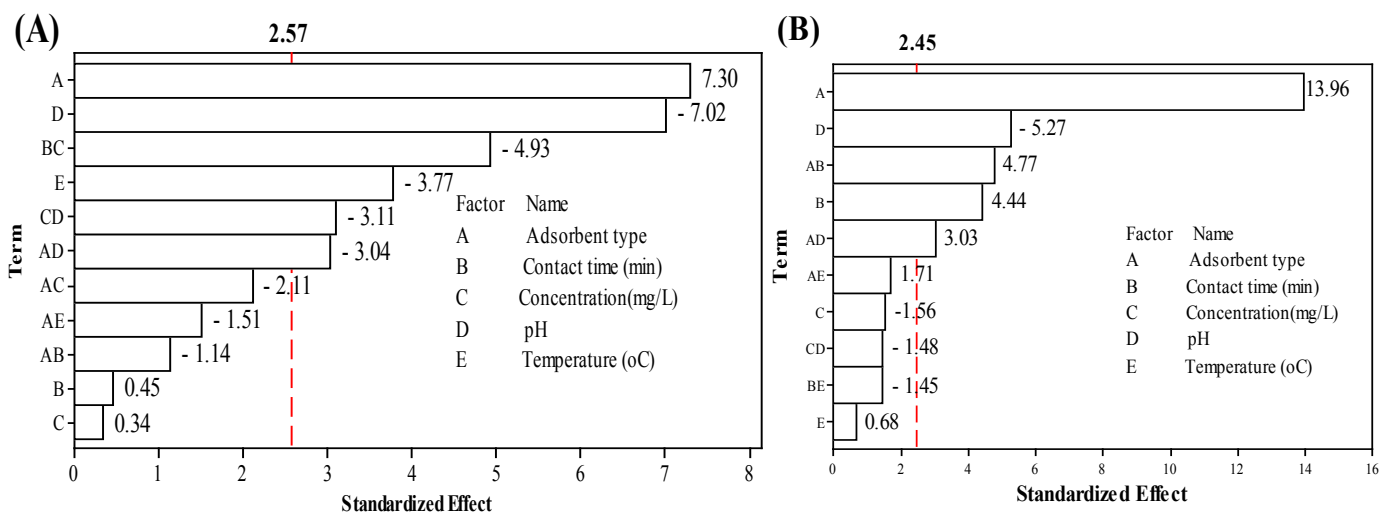

Figure 4: Pareto chart of standardized effects for variables related to the extraction of silver cyanide (A) and gold cyanide (B).

as designed by RSM and the values of the response (% EE) for each metallic cyanide anion obtained are given in Table 1. The regression analysis was carried out to fit the response. The final regression function of the extraction response (extraction efficiency, %EE) of silver and gold cyanocomplexes on imprinted polymers were expressed in terms of actual factors.

$$\%EE \text{ (silver cyanide)} = -251.71 + 0.39B + 100.38D - 0.37E - 7.32D^2 + 0.02BD - 0.01BE + 0.03DE \quad (7)$$

$$\%EE \text{ (gold cyanide)} = -106.15 + 1.19B + 1.01C + 25.74D - 0.01B^2 - 2.75 \times 10^{-3}C^2 - 1.65D^2 - 1.20 \times 10^{-3}BC - 0.02CD \quad (8)$$

The significance of each coefficient present in Equations (7 and 8), were determined by the student's t-test and p-values. The results of the quadratic model for % extraction efficiency in the form of analysis of variance (ANOVA) are given in Table 2. The values of R^2, $R^2_{adjusted}$ and $R^2_{predicted}$, for the extraction of both metallic cyanide anions were close to 1, thus demonstrating a qualitative agreement between the experimental values and the predicted values obtained for the three variables under study [15]. It also means that most of the data variations were explained by the regression model. In addition, the model is considered to be statistically significant because the associated Probability (p value) for the model is lower than 0.05, at 95% confidence. Meanwhile, the lack-of-fit for p-values were more than 0.05 (0.142 and 0.954 for recovery silver and gold cyanocomplexes, respectively), and thus statically insignificant at 95% confidence level. These results demonstrate that the quadratic model is statically significant for the response and therefore it will be used for further analysis [15].

Three-dimensional (3D) response surface plots: The three-dimensional (3D) response surface plots of the dependent variable as a function of two independent variables, maintaining all other variables at fixed levels can provide information on their relationships and can be helpful in understanding both the main and the interaction effects of these two independent variables. Therefore, to investigate the interactive effect of two factors on the extraction efficiency of silver and gold cyanocomplexes, the three dimensional response surface plots were constructed based on the quadratic model. The constructed plots under the combined effect of process parameters shown in Figure 5A-5F together with the inferences so obtained are discussed below.

The effect of pH: Figure 5A, 5B, 5D and 5F show the interactive effect of pH with time of contact (Figure 5A and 5D), pH with temperature (Figure 5B) or pH with initial concentration (Figure 5F) for the extraction of silver and gold cyanocomplexes from the aqueous phase. As can be seen, the influence of pH was found to be the highest amongst the studied variables. A major decrease was observed in the extraction efficiency as pH was increased from 6.0 to 10.0 in both figures. Accordingly, when pH was held below 9.0 (preferably at pH ~8.0), 80% and 90% of silver and gold cyanocomplexes were recovered respectively, regardless of contact time, temperature or initial concentration. The results implied that the adsorption capability of the adsorbent was nearly independent of pH in a range from 6.0 to 9.0, which was consistent with the pHzpc discussed above. While the observed reduction in adsorption ability of the adsorbent when the pH further increase (pH > 9) can be explained by the competition between the excessive OH⁻ ions (introduced by base adding) and template metal cyanide for the binding sites. There are also electrostatic repulsion between the negatively charged surface of adsorbent and the anionic metal cyanide. So the optimal pH range of the IIP CUCS-GLA polymer was 6.0–9.0, which was much wider than that of the protonated cross-linked chitosan (4.0-6.0) [7].

The effect of contact time: Figure 5A and 5B reveal that among all the three parameters considered for silver cyanide adsorption, contact time has the minimum impact since two maxima has been found; so from the 3D graphs the optimum value of the contact time was found to be 30 min. On the contrary, the effect of contact time was significant for gold cyanide extraction, and the extraction efficiency increases with increasing contact time between the metal cyanide and adsorbent, within its respective experimental range. The optimum condition of time, pH and initial concentration in the adsorption of gold cyanide were estimated to be 72 min, 8.5 and 170 mg.L⁻¹, respectively.

The effect of temperature and initial concentration: The conjugated effects of temperature with contact time and temperature with pH on the extraction efficiency of silver cyanide under predefined condition are visualized in Figures 5C and 6B, respectively. The solution temperature has no significant effect on the silver cyanide extraction. The extent of extraction was suppressed only by 8% when solution temperature was increased from 25 to 50°C for constant pH and contact time levels. Thus, it may be evident that the adsorption of silver cyanide is an exothermic process which will be verified later in thermodynamic study. An optimum silver cyanide extraction is observed at the lowest solution temperature (25°C) and contact time (30 min) at pH 8. Under these conditions, 80% extraction efficiency recovery for silver cyanide was obtained.

The combined effects of initial concentration and contact time, and initial concentration and pH on the extraction of gold cyanide by the imprinted polymer are visible in Figure 5E and 5F, respectively. As can be seen, the extraction efficiency increases linearly with increasing concentration from 100 to 150 mg L⁻¹; and the trend is reversed at higher concentration (above 150 mg L⁻¹), where the gold cyanide sorption decreases with increasing concentration. This behaviour can be understood as the increase in metal cyanide ions concentration with fixed adsorbent amount results in saturation of the binding sites on the surface of the polymer. The maximum adsorption of gold cyanide by the imprinted polymer was 90% at 150 mg L⁻¹ initial concentration at constant pH (~6.5) and time (72 min), which is accordance with the model.

Confirmation experiments: To check the validity and suitability of the data obtained from the software numerical modelling under optimized condition, confirmatory experiments were conducted with parameters suggested by the model. The optimum values of the independent process variables to achieve the maximum extraction efficiency (94.4%) of the silver cyanide from an aqueous solution of 100 mg L⁻¹ were; contact time 30.0 min; solution pH 6.9 and temperature 25°C. In the case of the gold cyanide, the theoretical maximum extraction efficiency (97.3%) was obtained at 25°C when the independent process variables were set as: contact time 72.2 min; solution pH 6.9 and the initial metal concentration 142.1 mg L⁻¹. The corresponding experimental value of the silver and gold cyanocomplexes adsorption under the optimum condition of the variables were determined respectively as 92.9% ± 1.2 and 95.4% ± 1.3 (mean ± SD of three replicates), which is very close to the theoretical value (error margin of less than 1.5). The good correlation between these two set of results, indicates that the Box-Behnken design coupled with desirability functions could be effectively used to optimize the adsorption parameters for the extraction of silver and gold cyanocomplexes.

Adsorption isotherms

In this study, the adsorption isotherms at two different pHs, 6.9 and 10 were investigated using two equilibrium models, which are Langmuir and Freundlich isotherm models with the quality of the
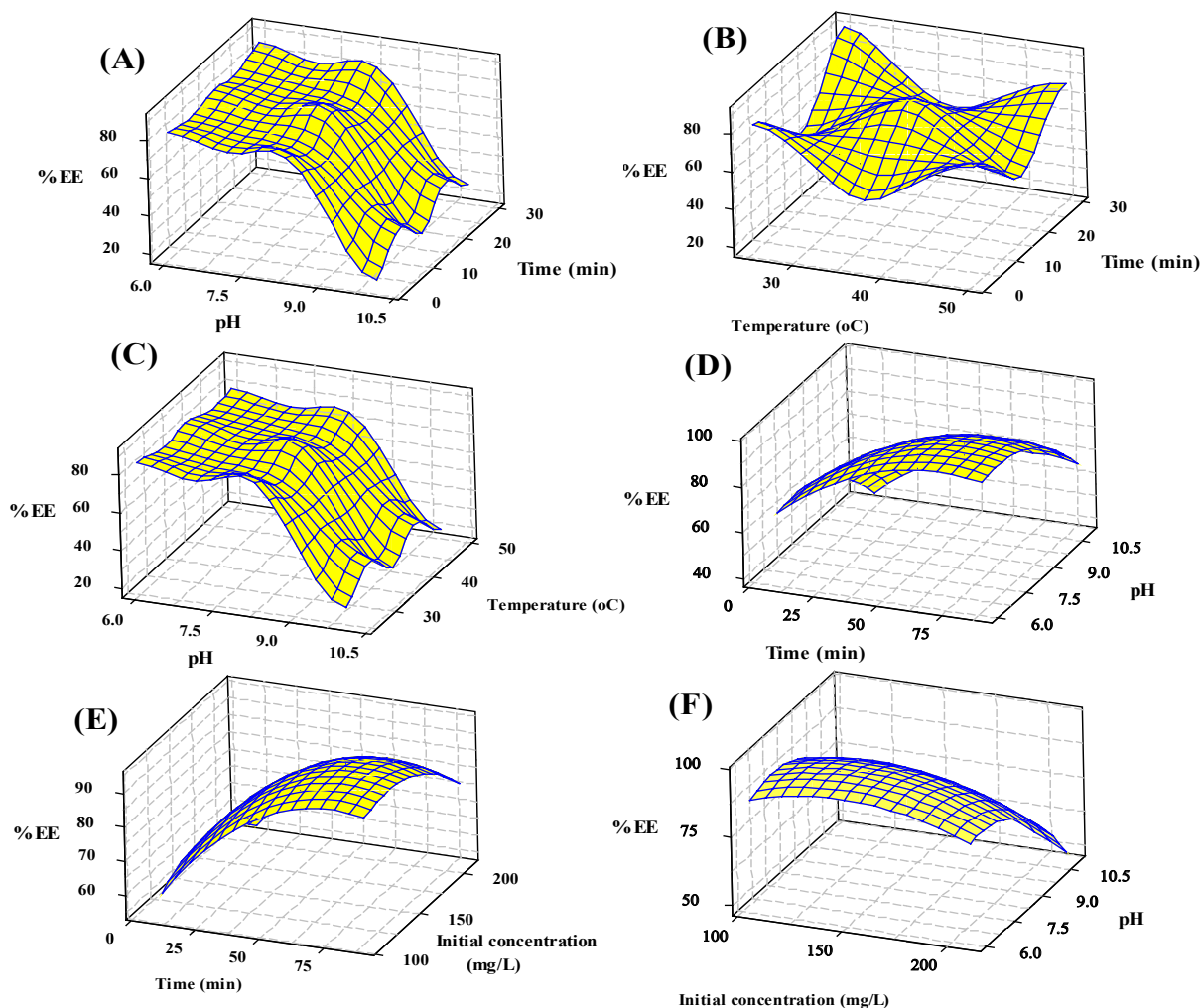
Figure 5: Three-dimensional response surface for extraction efficiency of silver cyanide (A-C) and gold cyanide (D-F) using AGCIPs.

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						
Source		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 (R^2) and relative average error (F_{error}) are listed in Table 3. Inspection of the correlation coefficients (R^2) and relative average errors (F_{error}) 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_{max} 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_{exp}), 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_L, which describes the type of isotherm and it is calculated by the equation $R_L = 1 + (1/K_L C_i)$ where, C_i is the initial concentration of template anions. The values of R_L 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_{max} 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 studies, except for the adsorption of gold cyanide by the Amberjet^{TM}

4400 and the biosorbent reported by In Seob et al. [25]. However, the adsorption pH used in the reported work was not practically feasible since the extraction was conducted in acidic medium and the adsorption time was longer (24 hours). This finding suggests that the adsorption process for the extraction of gold cyanide by the synthesized imprinted polymer presented in this study is economically more viable than the existing ones, since it is faster and presents a good adsorption capability even at typical mining operating pH (pH =10).

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 (R^2) and relative average error (F_{error}) 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 R^2 value of 0.9775 to 0.9999, as well as better predicted the value for q_e 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_t vs. $t^{0.5}$ (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				$Au(CN)_2^-$ AGCAGC			
	pH 6.9		pH 10		pH 6.9		pH 10	
	IIP	CP	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
q_m (mg g^{-1})	429.185	150.830	321.543	104.822	319.489	52.826	312.500	35.199
K_L (L mg^{-1})	0.041	0.008	0.062	0.028	0.0914	0.079	0.084	0.024
R^2	0.999	0.887	0.998	0.990	0.999	0.998	0.999	0.909
F_{error}	0.041	0.158	0.042	0.058	0.026	0.084	0.041	0.163
Freundlich								
K_F ((mg.g^{-1}.(mg L^{-1})$^{1/n}$)	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
R^2	0.977	0.584	0.962	0.986	0.985	0.436	0.860	0.437
F_{error}	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.

Adsorbents	pH	q_e (mg Ag/g^{-1})	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 Wofatit AD-4	10.4	36.7	[31]
Weak base resin (Wofatit 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 (Wofatit RO)	10.4	83.1	[31]
Strong base resin (Wofatit 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 4: Maximum adsorption capacities for the adsorption of silver cyanide ions onto various adsorbents.

Adsorbents	pH	q_e (mg Au/g^{-1})	Reference
Minix resin	9.0	26.0	[32]
Aminoguanidine of acrylonitrile/vinyl acetate/divinylbenzene	9.0	49.3	[9]
Aminoguanidine of vinyl benzyl chloride/ methyl methacrylat/ 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

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

Adsorption thermodynamic

Thermodynamic parameters were evaluated to confirm the nature of the adsorption process. The thermodynamic parameters, Gibbs free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$), were calculated according to the equations given in Table S2 (Supplementary data) and the results are reported in Table S4 (Supplementary data). The negative value of $\Delta H°$ indicates the exothermic nature of the adsorption reaction, while the negative values of entropy change ($\Delta S°$) reflect a decreased in randomness at the solid–solution interface due to the electrostatic attraction between the template anions and the active sites of the resins to form stable structure [26]. The negative values of $\Delta G°$ (except for the adsorption of gold cyanide anions by CP) confirm the favourability of the process and the spontaneous nature of adsorption with a high preference for silver and gold cyanocomplexes onto the resins. This means that the energy input from outside is not necessary. The data given in Table S4 (Supplementary data) also show a slight change in the value of $T\Delta S°$ at all temperatures and all $|\Delta H°| > |T\Delta S°|$. This indicates that the adsorption process is dominated by enthalpic rather than entropic changes. However, the adsorption of gold cyanide onto CP is an exceptional case since $|T\Delta S°| > |\Delta H°|$, meaning that the former process is dominated by entropic change [27].

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 (K_d), the selectivity coefficient (β) and the relative selectivity coefficient (k') 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 other anions. The relative selectivity order of AGCSIPs silver and gold cyanocomplexes increased from $Ag(CN)_2^->Au(CN)_2^->> Fe(CN)_6^{3-} >>>> Hg(CN)_2$ and $Au(CN)_2^-> Ag(CN)_2^->> Fe(CN)_6^{3-} >>>> Hg(CN)_2$, 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 ionic 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 S5 (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 KNO_3 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 KNO_3 at pH 10.5 as desorbing agent. It is shown (Figure S3, Supplementary data) that the uptake capacity of $Ag(CN)_2^-$ and $Au(CN)_2^-$ 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 KNO_3 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 cyanide 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 mn, 6.9 and 142.1 mg L^{-1} for time, pH and initial concentration respectively. AGCSIPs also exhibit excellent stability and reusability (up to five cycles). When compare 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).

$Ag(CN)_2^-$ AGCIP						
Couple mixture	K_D $Ag(CN)_2^-$ (ml/g)		K_D $M(CN)_x^{-n}$ (ml/g)		B $Ag(CN)_2^-/M(CN)_x^{-n}$		k`
	IIP	CP	IIP	CP	IIP	CP	
$Ag(CN)_2^-$/ $Au(CN)_2^-$	5.856	0.361	1.941	0.592	3.017	0.610	4.946
$Ag(CN)_2^-$/$Fe(CN)_6^{3-}$	21.813	0.039	0.289	0.0294	75.478	1.327	56.878
$Ag(CN)_2^-$/ $Hg(CN)_2$	∞	0.059	0	0	∞	∞	∞
$Au(CN)_2^-$ AGCIPs							
Couple mixture	K_D $Au(CN)_2^-$ (ml/g)		K_D $M(CN)_x^{-n}$ (ml/g)		β $Au(CN)_2^-/M(CN)_x^{-n}$		k`
	IIP	CP	IIP	CP	IIP	CP	
$Au(CN)_2^-$/ $Ag(CN)_2^-$	4.693	0.999	0.541	1.561	8.675	0.128	67.773
$Au(CN)_2^-$/$Fe(CN)_6^{3-}$	10.376	0.050	0.399	0.281	26.005	0.177	146.921
$Au(CN)_2^-$/ $Hg(CN)_2$	205.008	0.910	0.036	0.163	5694.667	5.583	1020.001

Table 6: Competitive adsorption properties of AGCSIPs (mixture: $Ag(CN)_2^-/Au(CN)_2^-/Fe(CN)_6^{3-}/Hg(CN)_2$), T 25 ± 1°C, time 30 min and pH 6.9 ± 0.1)

Thus suggesting that these new aminoguanidyl-chitosan imprinted polymers could be used effectively in practical applications for the selective recovery of silver and gold cyanide ions in aqueous solutions.

Acknowledgements

References

1. Cortina JL, Kautzmann RM, Gliese R, Sampaio CH (2004) Extraction studies of aurocyanide using macronet adsorbents: Physico-chemical characterization. Reactive & 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 with lix 7950. Mineral Processing & Extractive Metall Rev 35: 229-238.

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

4. Soleimani 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(iii) 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, Andrzej WT, Wieslaw A (1999) Influence of the structure of chelating resins with guanidyl groups on gold sorption. Reactive and Functional Polymers 42: 213-222.

9. Boiena 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) Solvent extraction of gold(i) from alkaline cyanide solution with furfuryl thioalcohol. 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: 155-178.

12. Nishad PA, Bhaskarapillai A, Velmurugan 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, Marti 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 aminoguanidyl 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, Ghaedi M, Daneshfar A, Agarwal S, Tyagi I, et al. (2015) Efficient removal of radioactive uranium from solvent phase using agoh–mwcnts nanoparticles: Kinetic and thermodynamic study. Chemical Engineering Journal 273: 296-306.

17. Yongbo S, Qiuxiao L, Yunling L (2012) Self-aggregation and antimicrobial activity of alkylguanidium 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, Shuwei Y, Tong H, Lvling 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: 857-868.

22. Camila GP, Fernanda SR, Nathália MS, Araci ASJ, Júlio CPV, et al. (2006) Use of statistical design of experiments to evaluate the sorption capacity of 7-amine-4-azaheptylsilica and 10-amine- 4-azadecylsilica for cu(ii), pb(ii), and fe(iii) 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 wastes. Journal of Hazardous Materials B 133: 143-153.

25. In Seob K, Min AB, Sung WW, Juan Maob KS, Jiyeong P, et al. (2010) Sequential process 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 ion-imprinted magnetic chitosan resins. Journal of Colloid and Interface Science 366: 165-172.

28. Xihui Y, Aleksandra O, Hao D, Jan 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 nitrate and thiocyanate 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 (1991) Studies on the adsorption of silver from cyanide solutions by fuctional polymers. Solvent Extraction and Ion Exchange 9: 677-696.

31. Slavica P, Ivan P (1998) Electrolytic desorption of silver from ion-exhange resins. Wat Res 32: 2913-2920.

32. Conradie PJ, Johns MW, Fowles RJ (1995) Elution and electrowinning of gold from gold-selective strong-base resins. Hydrometallurgy 37: 349-366.