

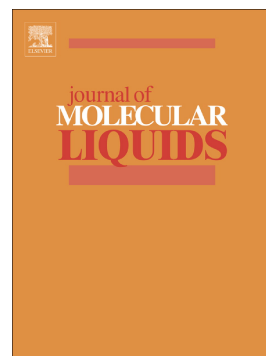
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Gold recovery from very dilute solutions from a mine in closing process: Adsorption-desorption onto carbon materials

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Abstract

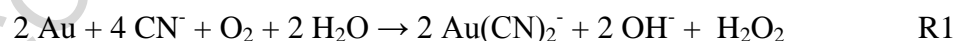
The aurocyanide complex recovery by precipitation with zinc decreases when gold concentration drops to less than $20 \mu\text{g L}^{-1}$. Therefore, a technology capable of recovering gold from very diluted solution is necessary. Adsorption and desorption experiments were carried out with real solutions in batch and in continuous processes to determine the gold adsorption capacity and rate onto two activated carbons (AC). The results showed that AC F400 and CSC removed 86 and $81 \mu\text{g g}^{-1}$, respectively, at pH 11 and C_e of $10 \mu\text{g L}^{-1}$ in about 4 h. Whereas desorption test by NaOH and CN^- showed a gold recovery of up to

86%. These experiments were correlated to the textural and chemical properties of adsorbents and to the chemical composition of samples from a heap leach process. AC is a highly efficient and selective adsorbent for gold cyanide solutions when gold is present in very low concentration ($<12 \mu\text{g L}^{-1}$).

Keywords: Gold Cyanide, Activate Carbons, Adsorption, Desorption, Packed Bed Column

Introduction

Heap leaching is a well-known process for gold beneficiation, being cyanide the most implemented lixiviant. Cyanide is preferred over other alternatives because of its higher chemical stability, low cost, and better chemical understanding [1]. In brief, cyanide heap leaching process initiates with ore extraction and a combination with lime to maintain a high pH of the ore. The basified ore is placed over an impervious pad and it is rinsed with a cyanide solution. Cyanide flows down through the heap and reacts with gold (and silver) to form a complex of cyanide according with the following expressions [2,3]:



Thereafter, gold cyanide complexes in solution are recovered at the bottom of the heap and directed towards a process for metallic gold extraction. One of the most used processes for this last step is the Merrill-Crowe process, where gold is cemented onto zinc powder, and it is specially used when the silver/gold molar ratio exceeds two [4,5]. However, this process

decreases its efficiency at very low gold concentrations [6]. This fact becomes more relevant as the closure of a mining site is approached, when gold concentrations drop to less than $20 \mu\text{g L}^{-1}$, and therefore it is necessary a technology capable of recovering these residual values.

In this work, the use of commercially-available activated carbon was proposed as an alternative to solve the aforementioned problem. This kind of material is already used in hydrometallurgical operations for the recovery of gold and silver from cyanide solutions. However, its implementation for extremely low gold concentrations ($<12 \mu\text{g L}^{-1}$) to the best of our knowledge, has not been reported. Although, it is known there have been attempts for recovering gold(III) from acid media solutions, using carbon-coated cobalt nanoparticles and concentrations of gold as low as $1 \mu\text{g L}^{-1}$. [7]

Thus, the aim of this work was to evaluate the use of commercial activated carbon as an alternative for gold recovery from extremely diluted solutions. In specific, the adsorption capacity of bituminous and coconut shell carbons was evaluated using solutions that were obtained from column cyanide leaching experiments carried out under conditions that emulate the stage of mining closure. The solutions contained a very low concentration of gold (concentration of approximately $10 \mu\text{g L}^{-1}$), in presence of many other ions and organic matter, generated during the closure of a mining site.

2. Materials and methods

2.1. Materials

The activated carbons used in this study were a bituminous material called Filtrasorb 400 (F400), manufactured by Calgon (Calgon Carbon Corporation 3000 GSK Drive Moon Township, United States), and a coconut shell adsorbent, manufactured by Clarimex (Tlalnepantla, Estado de Mexico, Mexico). The chemicals used in this study were reactive grade: NaOH, Au standard, and NaCN.

2.2. Materials characterization

Surface Area and pore Volume: Surface area and pore size distribution of materials were calculated from the corresponding nitrogen adsorption-desorption isotherm at 77 K using a Micrometrics Accelerated Surface Area and Porosimetry (ASAP) analyzer 2020. The specific surface area was calculated using the BET isotherms, and the pore size distribution was determined by using the density functional theory (DFT).

Surface Charge Distribution and Point of Zero Charge: The surface charge distribution and point of zero charge (pH_{PZC}) of each adsorbent were obtained by an automatic titrator (Mettler-Toledo T70). A sample of 0.1 g was dispersed in 50 mL of 0.1M NaCl as background electrolyte and was stirred for 12 h, in order to guarantee that equilibrium was reached. Then, a titration with 0.1 N NaOH was carried out under a nitrogen atmosphere to avoid CO_2 interferences. The pK_a distribution was obtained with the SAEIUS-pK-Dist© (1994) program.

2.3. Gold adsorption experiments on carbonaceous materials

Batch experiments were conducted to determine the adsorption kinetics, the adsorption capacity and the effect of solution pH on gold adsorption. Solution with a gold concentration of 10 to 12 $\mu\text{g L}^{-1}$ was used to perform the adsorption experiments: the physicochemical characterization of this solution is reported in Table 1S in supplementary information. The adsorption capacity of the activated carbons was determined as follows:

$$q = \frac{V(C_0 - C_e)}{w} \quad \text{Eq. 1}$$

Where V is the total volume, w is the mass of adsorbent, C_0 and C_e are the initial and final (or equilibrium) gold cyanide concentration, respectively.

Adsorption isotherms of both activated carbons F400 and coconuts shell from the gold cyanide solution were determined by using 0.025 g activated carbon in 150 mL gold cyanide solutions at different concentrations (10 to 100 $\mu\text{g L}^{-1}$): it has important to notice that the solution samples were spiked with gold in order to attain these concentrations. The reactants were placed in a glass vessel and stirred continuously to ensure a better contact between the activated carbons and gold solution at 25 °C and pH 11±0.2. The solution and activated carbon were left in contact during 5 days. Later the residual gold concentration was analyzed by Atomic Absorption Spectrophotometer (AAS) at a wavelength of 242 nm.

The adsorption kinetics experiments were conducted as follows: 50 mL of gold solution with a gold concentration of 12 $\mu\text{g L}^{-1}$ at pH 11 were placed in 50 mL conical bottom polypropylene tubes. After, 0.08 g of adsorbent were added, the tubes were shaken at 130 rpm in a thermostatic shaker at 25 °C. A 30 mL aliquot was taken at different times after

each sacrificial experiment was initiated. In addition, the pseudo-first-order, pseudo-second-order and Weber-Morris kinetic models were used to simulate the Au adsorption kinetics on F400 and CSC. The mathematical representation of the models are given in Eq. 2, 3 and 4, respectively.

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad \text{Eq. 2}$$

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad \text{Eq. 3}$$

$$q_t = K_{int}t^{1/2} \quad \text{Eq. 4}$$

The effect of solution pH was conducted for both activated carbons, F400 and CSC, as follows: 150 mL gold cyanide solution at $11 \mu\text{g L}^{-1}$ were added to 0.025 g of adsorbent at initial pH values of 9, 10 and 11, at a temperature of $25 \text{ }^\circ\text{C}$ during 5 days. The residual gold concentration of each experiment was analyzed by AAS.

2.4. Desorption test

A stock elution solution was prepared from NaCN (CN^- 1%) and NaOH 3%. Desorption experiments were carried out in 120 mL serological bottles, in which 0.025 g of each gold dicyanide-loaded activated carbon were contacted with 10 mL of stock elution solution at 50, 80 and $100 \text{ }^\circ\text{C}$ for 24 h. After, the solution was decanted and analyzed by AAS.

2.5 Gold cyanide adsorption in a packed bed column

Gold cyanide adsorption was performed in a 10 cm high glass column with 1 cm of internal diameter. The column was packed with 2 cm^3 of activated carbon F400 (1 g). The solution that passed through the adsorption column (0.15 mL min^{-1}) was obtained from

column cyanide leach experiments with a gold concentration between 10 and 12 $\mu\text{g L}^{-1}$. The effluent was sampled every 100 minutes and analyzed by AAS to determine the gold concentration, and inductively coupled plasma-optical emission spectroscopy (ICP-OES), with a Varian 730-ES spectrophotometer, was used to determine the concentration of other metals.

3. Results and Discussion

3.1. Materials characterization

3.1.1. Textural properties

The surface area and pore size distribution of the adsorbent materials were determined by nitrogen adsorption-desorption isotherm at 77 K by using the BET equation and the Density Functional Theory (DFT), respectively. Table 2S (supplementary information) summarizes the results obtained from physisorption analysis, where it can be observed that the activated carbons studied in this work are highly microporous (diameter < 2 nm). Activated carbon F400 showed higher micropores and mesopores volume than CSC; therefore, F400 reported a BET surface area of $905 \text{ m}^2 \text{ g}^{-1}$, which is 53% higher than that of CSC, $591 \text{ m}^2 \text{ g}^{-1}$.

3.1.2. Surface charge and pK_a distribution

In order to have an efficient carbonaceous material on removing anions such as $\text{Au}(\text{CN})_2^-$, it is important to promote or include positive active sites on the adsorbent material. Fig. 1, shows that the pH_{PZC} of activated carbons F400 and CSC are 9.5 and 9.0, respectively. Although, the pH_{PZC} is similar for both activated carbons, the concentration of positive active sites is much higher in F400 ($0.288 \text{ mmol g}^{-1}$) than in CSC ($0.164 \text{ mmol g}^{-1}$).

¹). When both activated carbons were loaded with gold cyanide, the PZC was shifted to the left, which suggests that the positive surface groups interacted with gold cyanide complexes.

The pK_a intensity and distribution are presented in Fig. 2, where chemical changes, caused by loading gold cyanide on activated carbons, are illustrated. Activated carbon F400 showed a higher intensity for the peaks associated to carboxylic ($3 < pK_a < 6$) and phenolic ($8 < pK_a < 11$) groups compared with CSC (Fig. 2A). Fig. 2B and 2C show a decrease and displacement of both peaks associated to carboxylic and phenolic groups when the gold cyanide complex was loaded in the F400 and CSC surface. This suggests gold cyanide complex interacts with phenolic and carboxylic groups, probably by anion exchange between OH^- and $Au(CN)_2^-$. It was also possible to appreciate the presence of a new peak in the pK_a interval between 7.2 and 8.9, indicating the presence of lactonic groups ($7 < pK_a < 9$) and/or the interaction between the surface of activated carbon and free CN^- ($pK_a = 9.4$).

3.2. Gold adsorption experiments

3.2.1 Adsorption isotherms

Gold cyanide adsorption isotherms were conducted at $pH > 11$ and $25^\circ C$ (Fig. 3). Activated carbon F400 showed a gold adsorption capacity of $330.54 \mu g g^{-1}$ at a gold concentration in the equilibrium (C_e) of $40 \mu g L^{-1}$, while the CSC showed a gold adsorption capacity of $224.37 \mu g g^{-1}$ at the same conditions. Therefore, F400 removes 32.12% more gold cyanide complexes than CSC that can be associated with the larger surface area of F400, 53% more than that of CSC, and also to the 42.85 % higher concentration of positive

surface active groups (0.28 mmol g^{-1} compared to 0.16 mmol g^{-1} for CSC) as shown in Fig. 1.

The porosity of activated carbon is a very important property since it greatly influences the aurocyanide adsorption. Adams (1993) [8] and Newcombe et al., (1996) [9] presented a compelling evidence that small ions or molecules, such as gold cyanide (0.19 nm), adsorb mainly in the micropore volume as an ion-pair $\text{M}^{n+}\text{Au}(\text{CN})_2^-$, which is in agreement with other studies related to gold recovery [10,11]. From the results reported herein, it is interesting to highlight that activated carbon F400 contains 36% more micropores, i.e. higher surface area, than CSC, which shows a close correlation with its 32.12% higher adsorption capacity at the maximum equilibrium concentration studied, $40 \mu\text{g L}^{-1}$, as mentioned above. These findings are consistent with the explanation given by Adams (1993), about the markedly correlation between gold cyanide adsorption and micropore volume on the basis of the dimension of micropores ($<2 \text{ nm}$) and the gold cyanide ion (0.19 nm). In other words, the small gold aurocyanide ions do not have restriction to diffuse and adsorb onto the carbon's microporous structure.

3.2.2. Gold adsorption kinetics

Adsorption kinetics were performed to evaluate the gold cyanide adsorption rate for both activated carbons F400 and CSC as well as to determine the time needed to reach equilibrium (Fig. 1S-A and 1S-B). In this study, two granular sizes were used for each activated carbon. The mesh size of F400-A and CSC-A was 13X35 ($1.77\text{-}0.5 \text{ mm}$) and that for F400-B and CSC-B was 60X170 ($0.25\text{-}0.09 \text{ mm}$).

The F400-A carbon removed 33% of the gold initial concentration ($12 \mu\text{g L}^{-1}$) within the first hour and 85% in 12 hours, while the CSC-A removed 40% of the gold initial concentration within the first hour and 71% in 12 hours. In this case both carbons needed 12 hours to reach equilibrium. When the granular activated carbons were reduced to a particle size between 0.25 and 0.09 mm, the time needed to reach equilibrium was lower; The F400-B removed 85% of the initial gold concentration in the first hour and 93% in 4 hours, while CSC-B removed 30 % in the first hour and 67% in 4 hours. These results indicated that the size reduction shorten the distance to reach the positive sites. It is reported that gold cyanide adsorption occurs at the most accessible sites in the macropores and mesopores, and with time the diffusion rate decreases as equilibrium is approached. Once the maximum adsorption capacity has been achieved in the macropores and mesopores, a pseudo-equilibrium is established beyond which adsorption must take place in the micropores [11,12]. The diffusion of gold cyanide species into the microporous structure is a slower process, because the diffusion process is complicated by the length and tortuosity of the porous structure, this effect decreases when the adsorbent is reduced in size [11,13]. Therefore, F400-B and SCC-B showed a higher adsorption capacity in a shorter time.

The pseudo-first-order, pseudo-second-order and Weber-Morris kinetic models were used to simulate the Au adsorption kinetics on F400 and CSC. The kinetics parameters were obtained by fitting the experimental data with the mentioned models and are summarized in Table 1. The pseudo-second-order model fitted better than the pseudo-first-order model based on the values of regression coefficients (R^2) [14]. On the other hand, for Weber-Morris, it is essential for the $q_t \sim t^{1/2}$ plot to go through the origin if the intraparticle diffusion

is the sole rate-limiting step. However, for this work the slope is not equal to zero, thus, adsorption kinetics may be controlled by film diffusion and intraparticle diffusion simultaneously [15].

Additionally, adsorption kinetics also allowed to evaluate the effect of As, $\text{Ag}(\text{CN})_2^-$, and other cations such as Na^+ , K^+ , Ca^{2+} , Si^{4+} , and Zn^{2+} , present in the solution, in the gold adsorption capacity. Fig. 4A and 4B show that ions As(V), Na^+ , Si^{4+} , Ca^{2+} , and K^+ , were not adsorbed onto the activated carbons studied, even when the active sites on their surfaces were predominantly negative. However, a 20% slight decrease of Zn^{2+} concentration can be appreciated, which may be adsorbed as Zn^{2+} or as ZnCN^+ . It is noteworthy that, in the first case, adsorption could occur because the pH was higher than the point of zero charge of activated carbon, and under such condition, the carboxylic groups deprotonate acquiring a negative charge that interacts with cations; this phenomenon could play an important role in the metallic ion adsorption [16]. Sheya and Palmer (1989) [17] reported that in the pH range between 9.5 and 12, the adsorption of zinc cyanide complex increases in presence of gold.

Fig. 4 shows a removal efficiencies of above 60% and 33% for Ag (as $\text{Ag}(\text{CN})_2^-$) on activated carbon F400 and CSC, respectively, after 12 hours. Such removal capacity can be associated with the higher initial concentration of silver cyanide complexes in comparison with the initial concentration of the gold cyanide complexes (179.9 and 12.57 $\mu\text{g L}^{-1}$, respectively). Nevertheless, although the Ag concentration (as $\text{Ag}(\text{CN})_2^-$) at the beginning of the experiment was 14.3 times higher than that of Au concentration, the removal efficiency of Ag was consistently lower than the Au removal (80-100 %). These results

contrast with those observed at higher concentrations where a detrimental effect on Au adsorption was observed for tests with a Ag/Au molar ratio higher than two [4,17]. Thus it can be stated that the activated carbons studied here were highly selective for $\text{Au}(\text{CN})_2^-$ complexes.

3.2.3. Effect of pH in the $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$ adsorption capacity

Fig. 5 shows the effect of pH on the $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$ adsorption capacity on activated carbons F400 and CSC. Fig. 5A shows that pH values of 10 and 11, favored a higher adsorption capacity of $\text{Au}(\text{CN})_2^-$ complexes (121 and 116 $\mu\text{g g}^{-1}$, respectively) on F400 in comparison with CSC (100 $\mu\text{g g}^{-1}$). On the other hand, CSC showed a 20 % difference in adsorption capacity between pH 9 and 11. Likewise, both activated carbons did not show significant differences in $\text{Ag}(\text{CN})_2^-$ adsorption capacity in the pH range studied. It has already been demonstrated that aurocyanide is adsorbed onto activated carbon mainly as $\text{Au}(\text{CN})_2^-$ at all pH values between 1 and 10. Also, it has been shown by Mössbauer spectroscopy that $\text{Au}(\text{CN})_2^-$ is adsorbed onto activated carbon without significant changes in the entire pH range [18,19]. This can be attributed to the strong interaction between gold cyanide and activated carbon by a partial donation of the delocalized π -electrons from activated carbon towards gold. Jones et al. (1989) proposed that $\text{Au}(\text{CN})_2^-$ adsorbs onto the basal plane of the graphite crystallites of activated carbon. They also showed that the linear dicyanoaurate complex (NC-Au-CN) fits very well with the hexagonal ring structure of graphite. Therefore, a graphitic structure is essential for a

carbon material to be a good adsorbent for gold cyanide complexes [20]. On the other hand, according to the work carried out by Stavropoulos et al. (2015) [21], an important factor in cyanide adsorption capacity is the CN^- dissociation constant given by hydrocyanic acid. Considering that the pK_a of hydrocyanic acid is 9.4, then, at pH lower than this, cyanide is present as hydrocyanic acid (HCN), but at pH greater than the pK_a value of HCN, cyanide ions (CN^-) prevail in solution. Also considering that the pH_{PZC} of activated carbons are 9.5 and 10.2 for F400 and CSC, respectively, then at pH values lower than the pH_{PZC} , the activated carbons surface is positively charged, while the dissociation degree of HCN is small and hence the concentration of $\text{Au}(\text{CN})_2^-$ is low thus affecting the gold adsorption. According to the results obtained, the optimum pH values for cyanide adsorption are between 9 and 11.5 where the dicyanoaurate complex is formed. Fig. 5B shows that both carbons, F400 and CSC, have the maximum $\text{Ag}(\text{CN})_2^-$ adsorption capacity of 2.07 y 2.04 mg g^{-1} , respectively, at pH between 9 and 11.

The cyanide solution in addition to containing gold and silver (as gold and silver cyanide complexes), also contains cations such as Ca^{2+} , K^+ and Na^+ . The presence of these cations may positively influence the anions adsorption ability. This is because the cations mutually interact with the negative centers (CO^- and COO^-) of the activated carbon surface. Kongolo et al., (1997)[19], suggested that regardless of the composition and the pH of the solution, the cations and anions adsorbed on activated carbon should occur as ion pairs, $\text{M}^{n+}[\text{Ag}(\text{CN})_2^-]_n$, where M^{n+} represents H^+ , K^+ or Ca^{2+} , and where the centers of adsorption on the surface of activated carbon and equivalent mole ratios may be different. This can also explain the adsorption of $\text{Au}(\text{CN})_2^-$ and $\text{Ag}(\text{CN})_2^-$ onto activated carbon.

3.2.4. Desorption of gold and silver from activated carbon.

Fig. 6A shows that gold desorption is most efficient when the solution temperature increases. Gold desorption at 25 °C was not detected, however, by increasing the temperature to 50 °C gold lightly desorbs up to approximately 7 and 26 % from CSC and F400, respectively. At 80 °C a gold desorption of 56 ± 11 % was achieved for F400 and 68 ± 8 % for CSC. Meanwhile, at 100 °C the gold elution reached 87 ± 9 and 82 ± 9 % for F400 and CSC, respectively. This is because, the adsorption of gold onto activated carbon is an exothermic reaction and an increase in temperature will shift the equilibrium in favor of desorption. However, the presence of cyanide in this process is necessary to prevent the formation of AuCN, which is difficult to desorb [22].

On the other hand, silver desorption is low compared to the gold desorption (see Fig. 6B), 12 ± 1 % of silver was desorbed at 25 °C for activated carbon F400 and 10 ± 2 % for CSC. Silver desorption at 50 °C showed an increase of 20 ± 2 % of desorption for both activated carbons. When the temperature was increased to 80 °C, it was observed that the Ag desorbed more than double in comparison with desorption at 50 °C (44 ± 6 and 32 ± 4 % for F400 and CSC, respectively). However, no increase on silver desorption was detected when the temperature increased from 80 to 100°C. Desorption increasing rates of Au and Ag as the temperature rises is also associated with the higher vibration energy of the adsorbed molecules in the system [23].

3.3. Gold and silver adsorption in a continuous process

The breakthrough curves show the adsorption profiles for valuable metals and other ions, such as Na^+ , Si^{4+} , K^+ , Zn^{2+} and As(V) present in the leach solution studied (Fig. 7). It

was noted that the silver concentration in the effluent was maintained at a constant value in the first 2.7 bed volumes. This corresponds to a silver adsorption efficiency of approximately 95%. After treating 2.7 bed volumes, the silver concentration in the effluent began to gradually rise at a rate of 0.1486 g L^{-1} every hour, reaching the saturation point of the column after 13 bed volumes. Moreover, it was observed that the breakthrough point for gold occurred after processing 15 bed volumes which coincided with the maximum uptake of silver. In addition, it can be seen that the concentration of cations such as sodium, potassium, silicon and zinc begins to decay just after the breakthrough of gold. Therefore, the adsorption mechanism is related to interactions between the activated carbon, the cations present in the solution and the gold cyanide complexes.

The packed bed column results showed an Au adsorption capacity of 250 mg g^{-1} , this being 2.9 times the adsorption capacity obtained in batch experiments ($q_{\text{Au}} = 86 \text{ } \mu\text{g g}^{-1}$). This may be related to the presence of organic matter that accumulates in the continuous system. It is known that organic matter can contribute in adsorbing inorganic compounds due to its variety of active groups. Additionally, a higher affinity of activated carbon for cations such as sodium, potassium and silicon was observed. The presence of these cations is not necessarily a disadvantage in the adsorption process, as they can improve the adsorption of cyanide complexes of gold and silver [16]. This effect is particularly important when working at pH values above the pH_{PZC} of the activated carbon (9.5), where its surface is negatively charged. Furthermore, it was observed that the adsorption of As was 2% of the initial concentration, which could be attributed to inorganic impurities in activated carbon F400 that include Al, Ca, Fe and Na [24]. Iron oxides have shown a high

affinity for arsenate [25–27], thus arsenic adsorption could be attributed to the presence of iron in activated carbon.

Additionally, saturated activated carbon from the packed column was treated with a solution of NaOH-CN⁻ (3 and 1%) at 100 °C for 24 hours in batch. The gold and silver rich solution was analyzed by AAS and ICP-OES. A mass balance revealed a recovery of 82 and 95 % of Au and Ag, respectively (Fig. 8). Also, the desorption of other cations such as K, Na and Zn (6, 0.86 and 3.5% respectively) was observed. Finally, As and Si did not desorb.

4. Conclusions

This study demonstrated that activated carbon can be used to recover Au and Ag from extremely diluted solutions. Specifically, activated carbons F400 and CSC have a gold cyanide adsorption capacity of 86 and 81 $\mu\text{g g}^{-1}$, respectively, at an equilibrium concentration of gold of 10 $\mu\text{g L}^{-1}$. According to adsorption kinetics, the gold initial concentration decreased 93 and 83 % in the first 4 hours using a particle size between 0.25 and 0.09 mm of F400 and CSC, respectively. On the other hand, with a particle size of 1.7-0.5 mm, the gold initial concentration decreased 85 % and 75% in the first 12 hours, for F400 and CSC, respectively. The desorption batch experiments showed that 86 and 82 % of Au can be recovered from activated carbons F400 and CSC, respectively. Likely, activated carbon can recover 95% of the silver concentration from solution in the first 2.7 bed volumes. It is important to note that after the breakthrough of gold, the cations present in solution begin to adsorb in the activated carbon, suggesting adsorption of gold cyanide

complexes as ion pairs of the form $Mn^+[Ag(CN)_2]_n$. Finally, 100% of gold is recovered in the first 14.5 bed volumes

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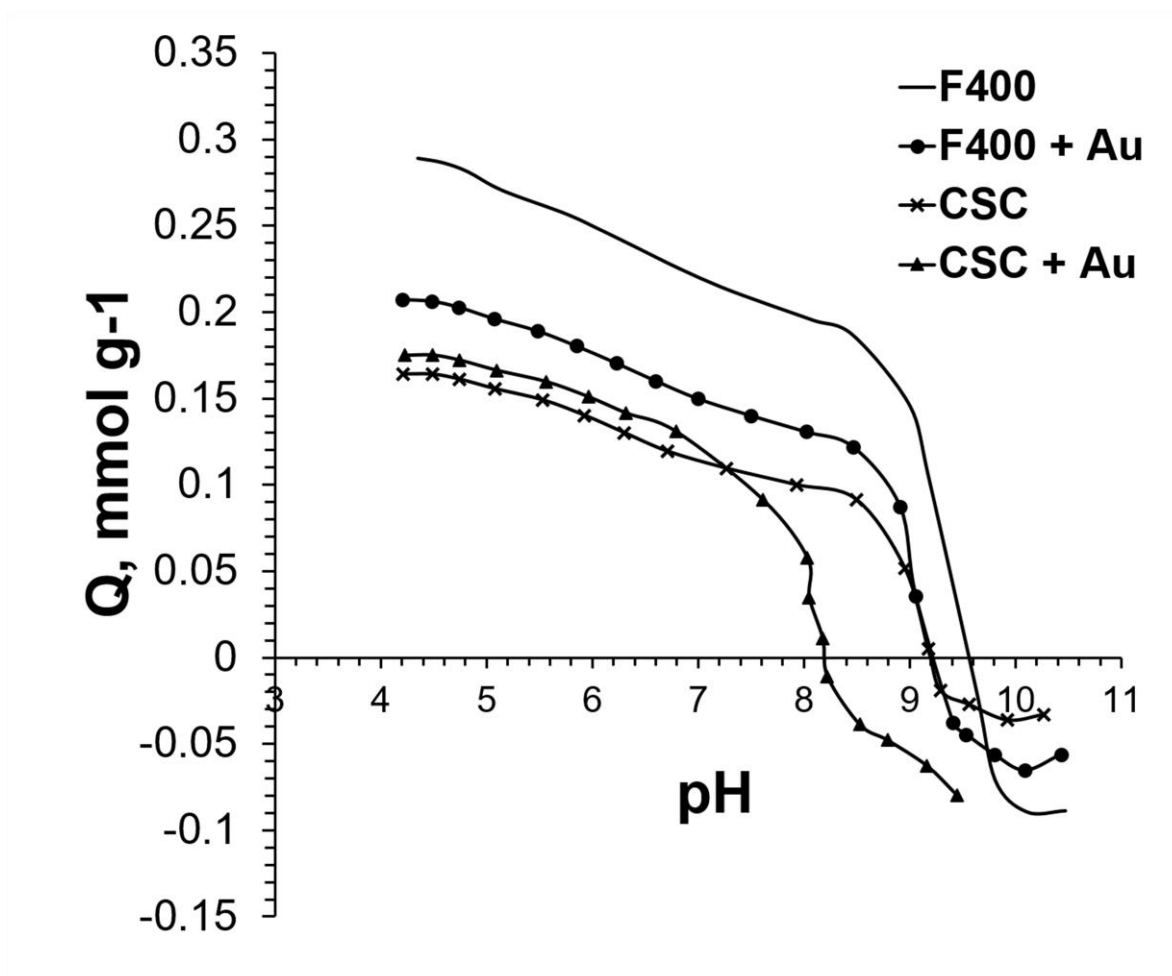
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Table

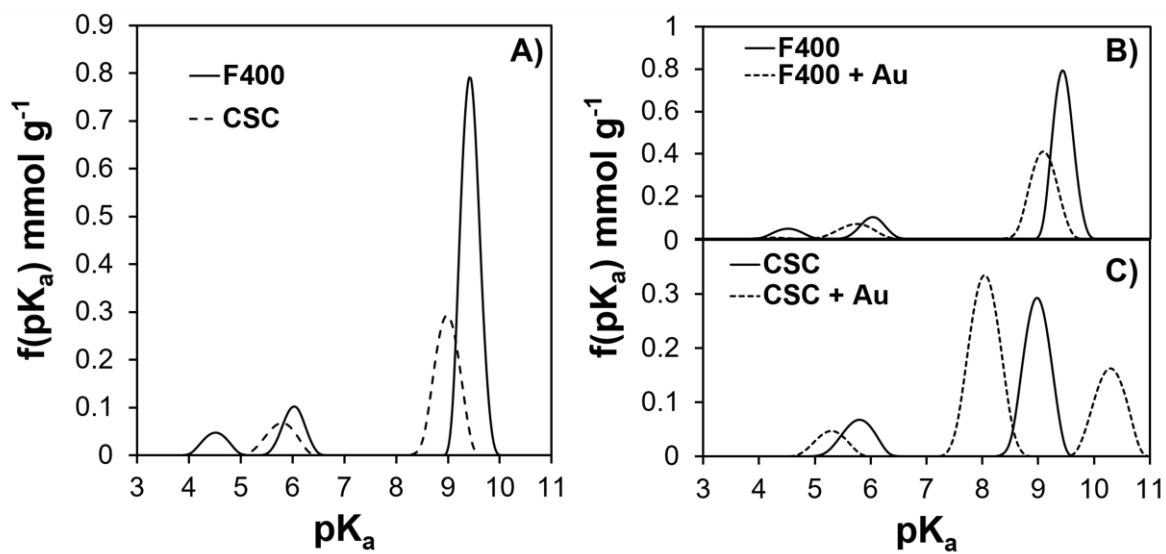
Table 1 Pseudo-first-order, pseudo-second-order and Weber-Morris kinetic parameters

| Material | Pseudo first order | | | Pseudo second order | | | Weber-Morris | |
|----------|--------------------------------|-------------------------------|-------|--------------------------------|-------------------------------|-------|--------------------------------|-------|
| | K_1 (min^{-1}) | q (mg g^{-1}) | R^2 | K_2 (min^{-1}) | q (mg g^{-1}) | R^2 | K_1 (min^{-1}) | R^2 |
| F400-A | 0.069 | 87.55 | 0.91 | 0.002 | 126.4 | 0.98 | 15.9 | 0.86 |
| F400-B | 0.091 | 27.26 | 0.79 | 0.016 | 124.76 | 0.99 | 9.7 | 0.46 |
| CSC-A | 0.051 | 82.78 | 0.75 | 0.005 | 105.41 | 0.97 | 10.9 | 0.83 |
| CSC-B | 0.062 | 64.00 | 0.85 | 0.006 | 116.15 | 0.99 | 25.4 | 0.98 |

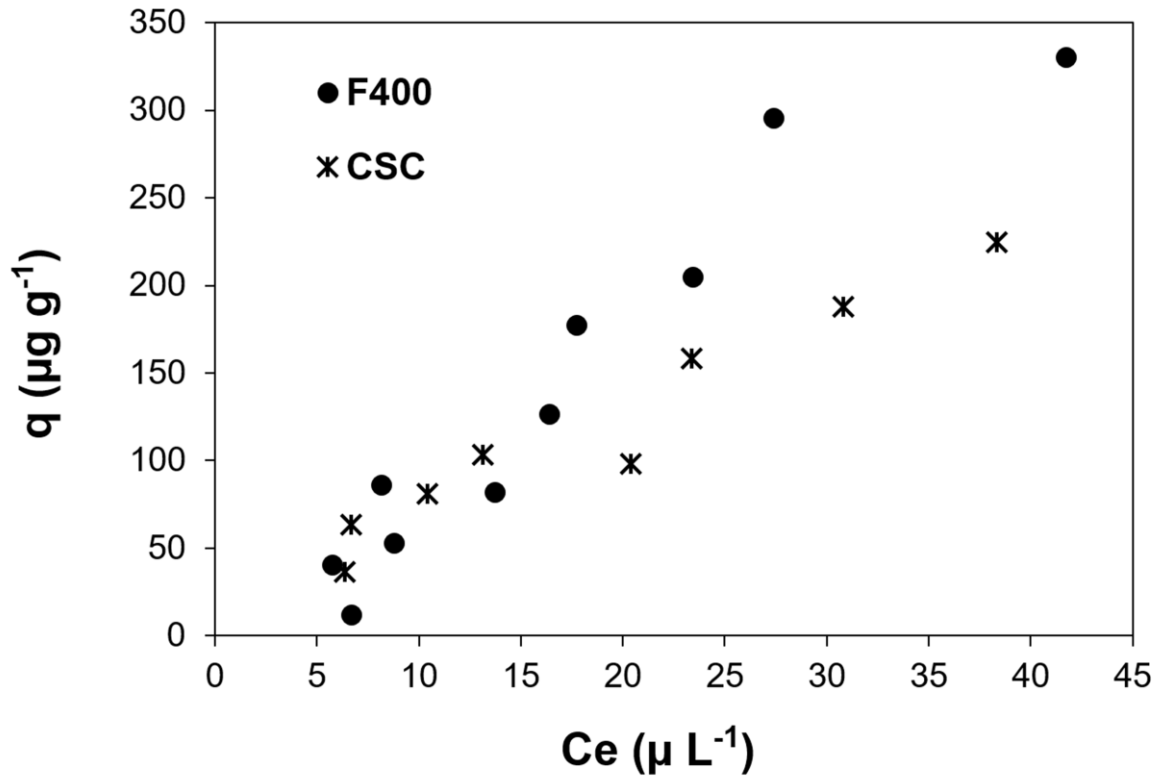
Labels A and B indicate the adsorbent particle size: A) 1.7-0.5 mm and B) 0.25-0.09 mm

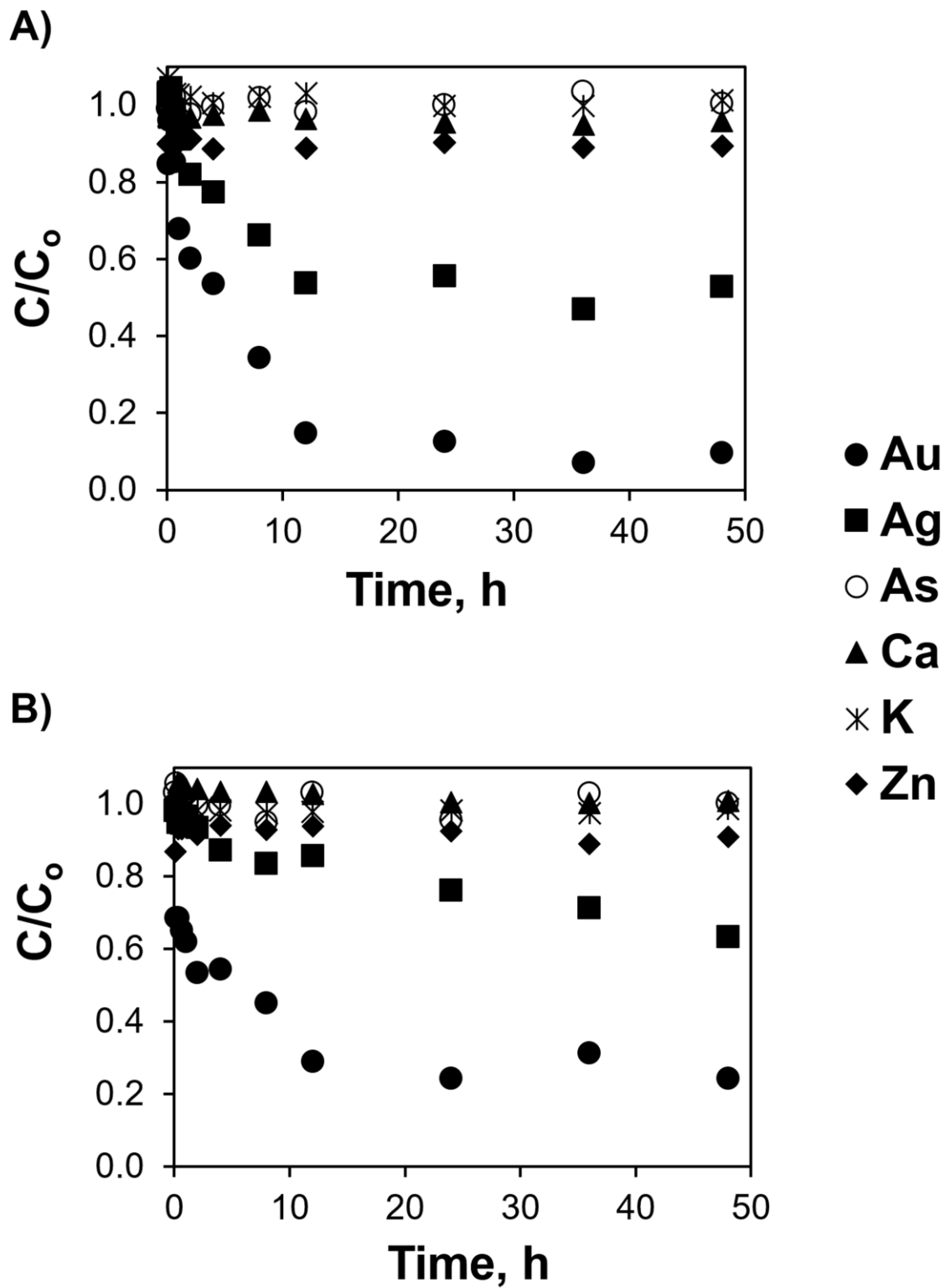


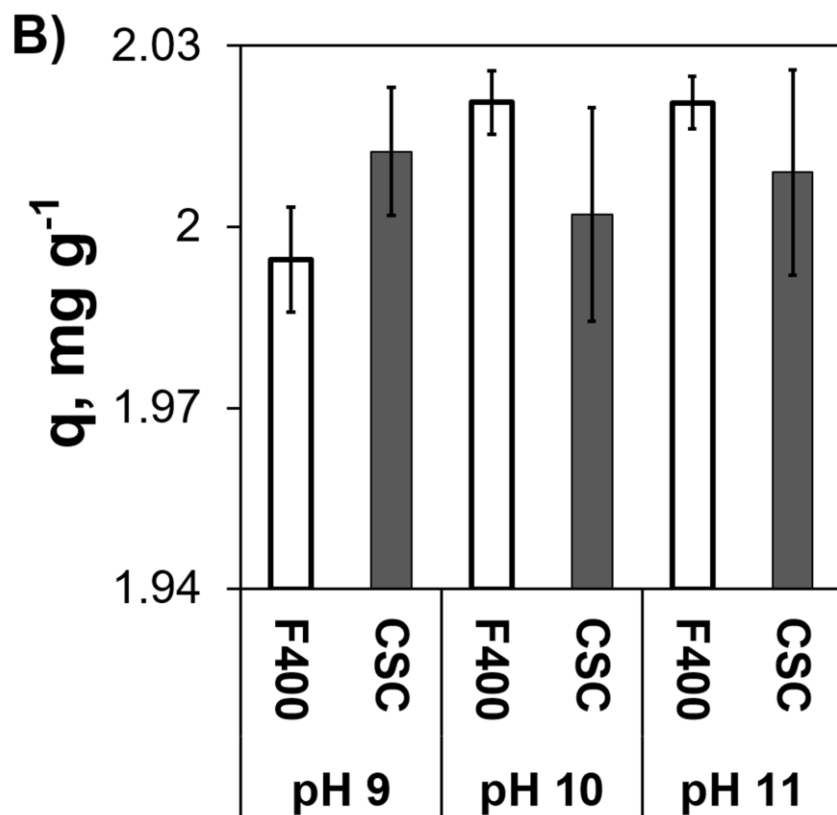
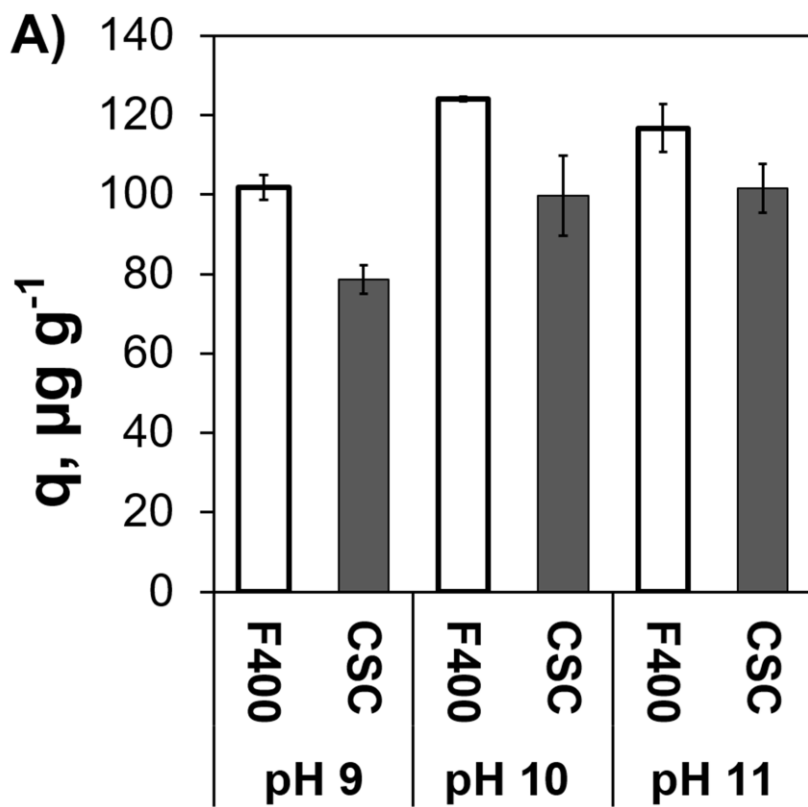
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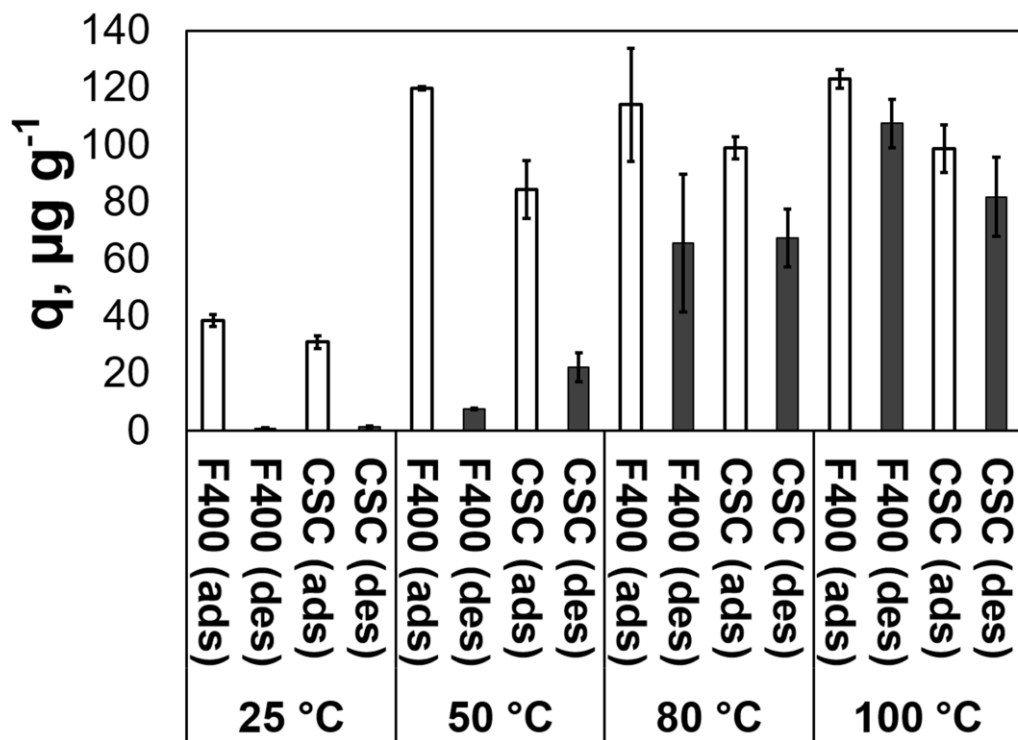




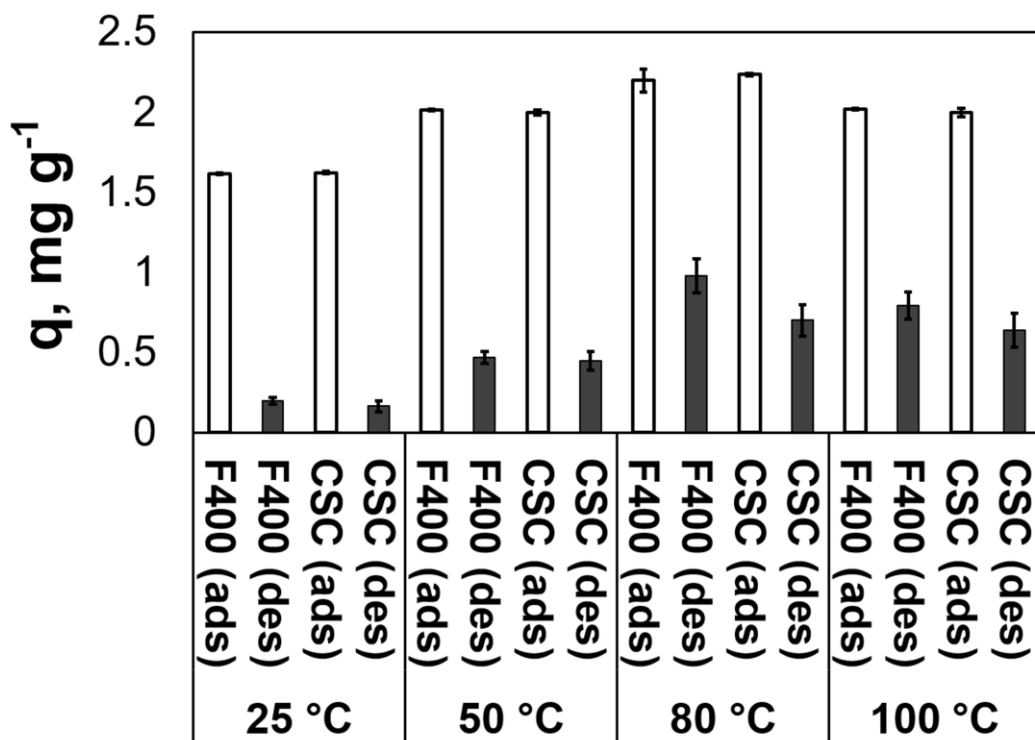


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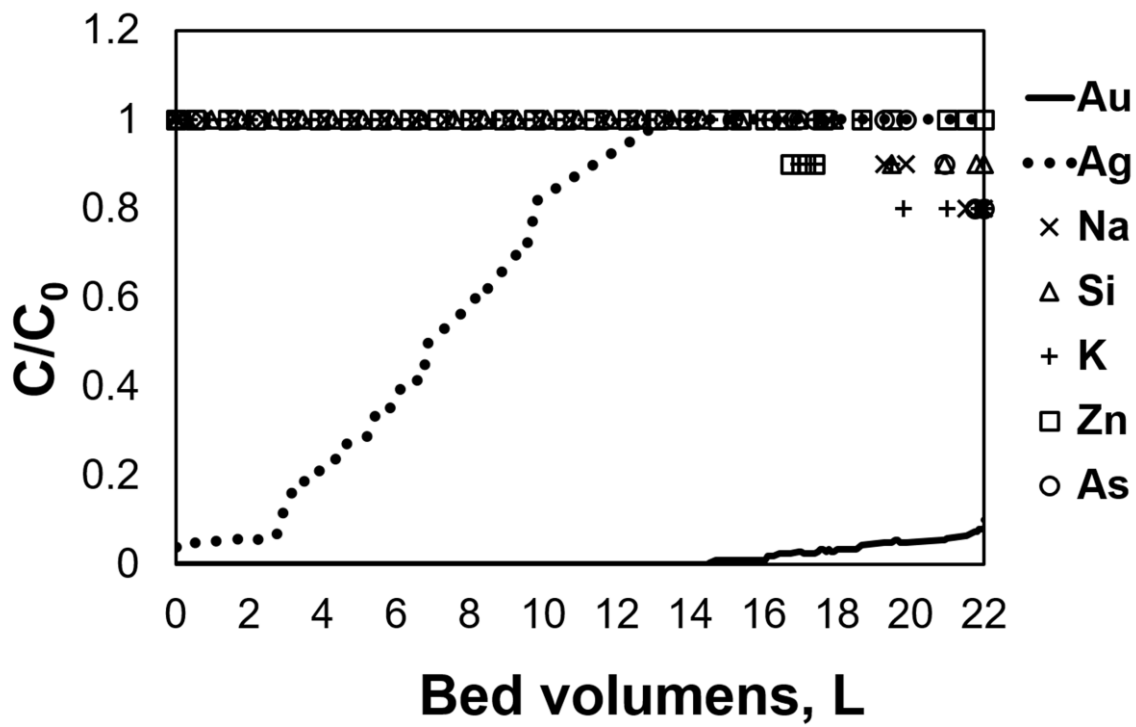
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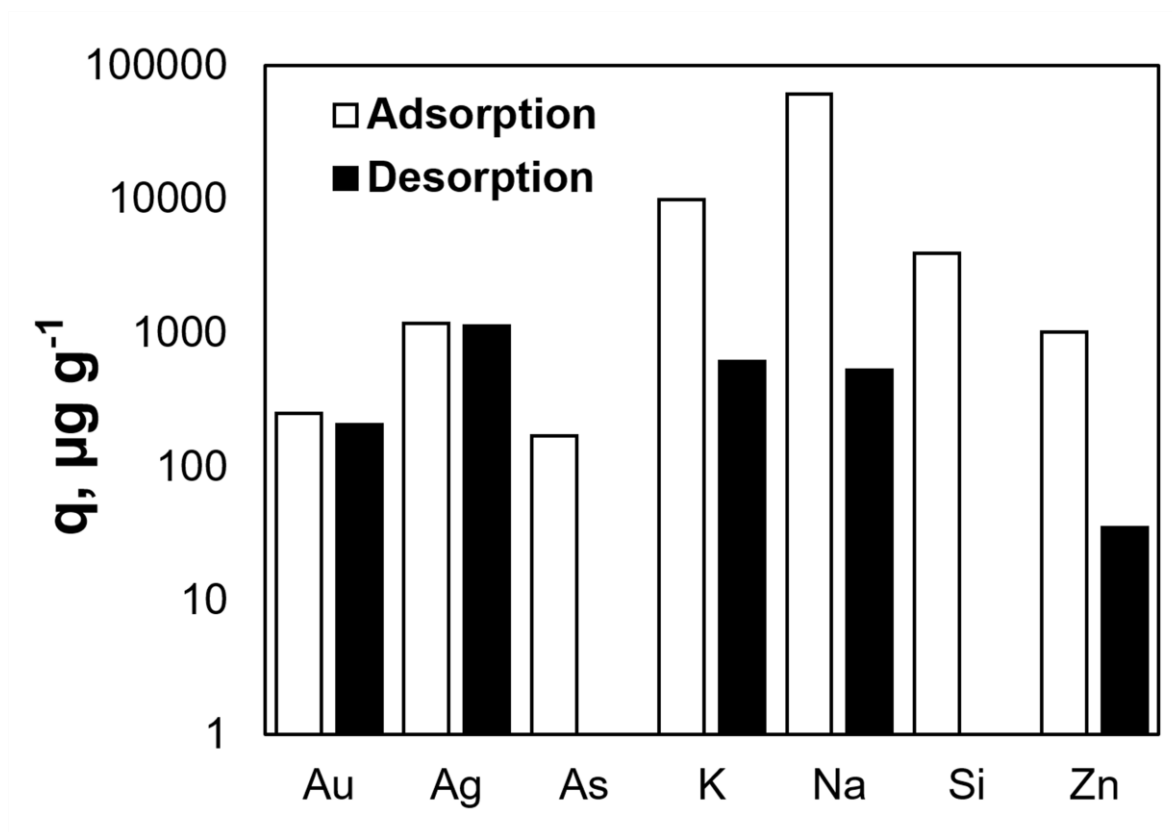


B)



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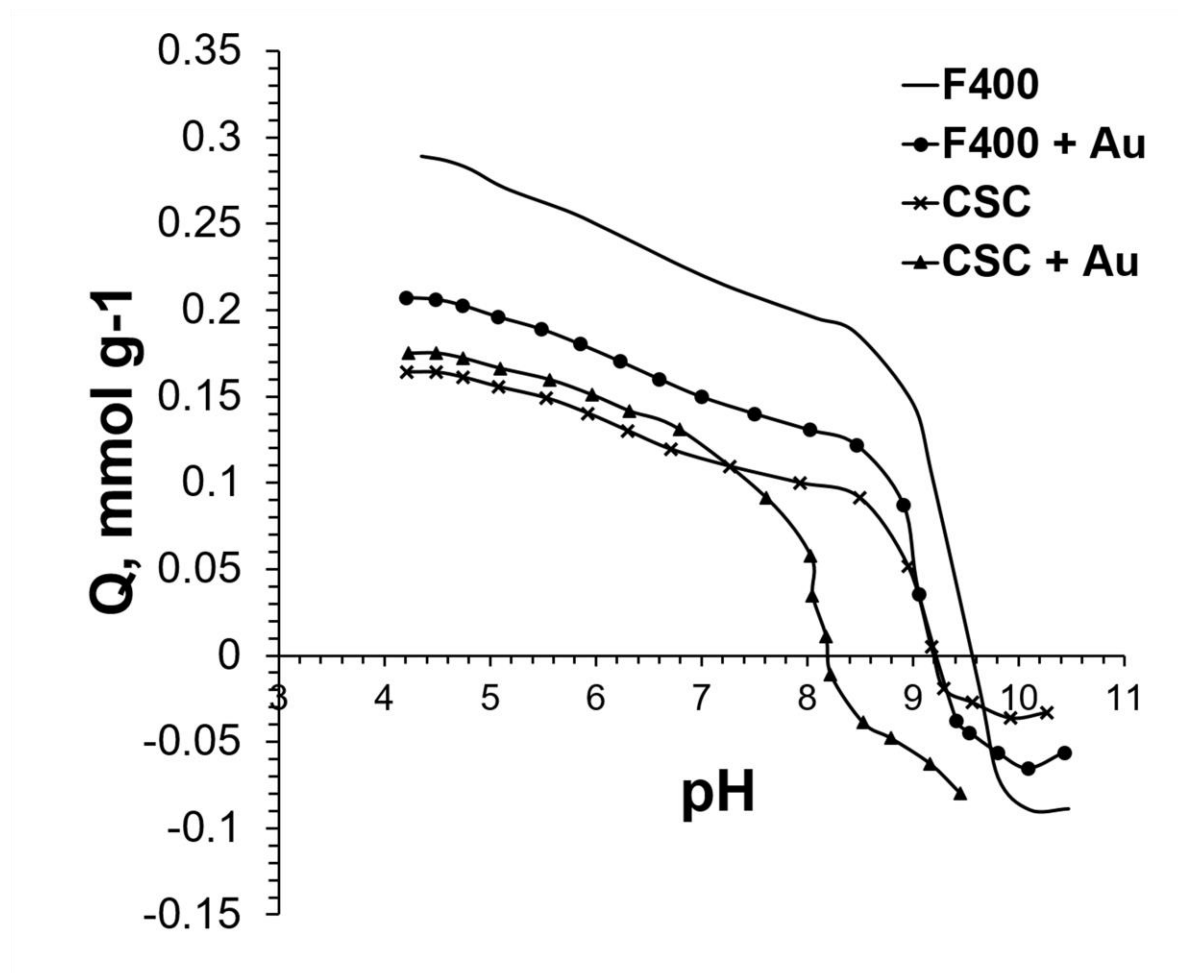




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Figure Captions

Fig. 1. Point of Zero Charge of the activated carbon F400 and coconut shell carbon (CSC), before and after adsorbing gold cyanide complexes.



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Fig. 2. pK_a distribution for: **A)** Activated carbon F400 and coconut shell carbon (CSC), **B)** F400 loaded with gold cyanide and, **C)** CSC loaded with gold cyanide at pH 11 and 25 °C.

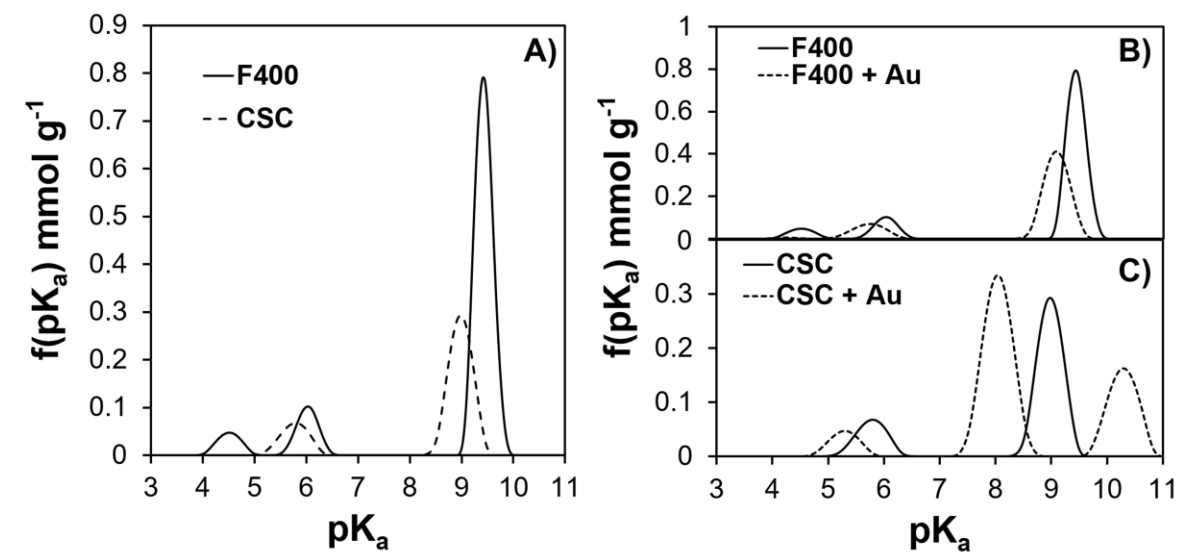
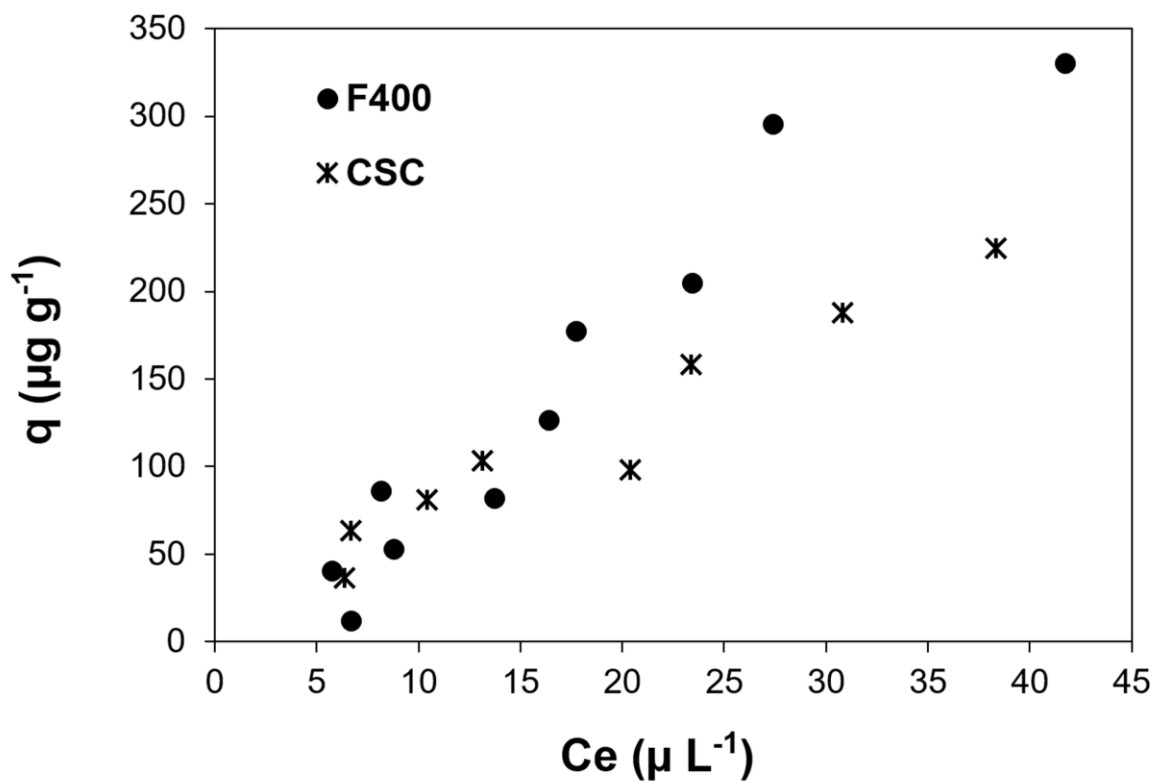


Fig. 3. Adsorption isotherms of gold on activated carbon F400 and coconut shell carbon (CSC) at pH 11 and 25 °C.



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Fig. 4. Effect of cations and arsenic in the gold adsorption on activated carbons F400 (A) and CSC (B).

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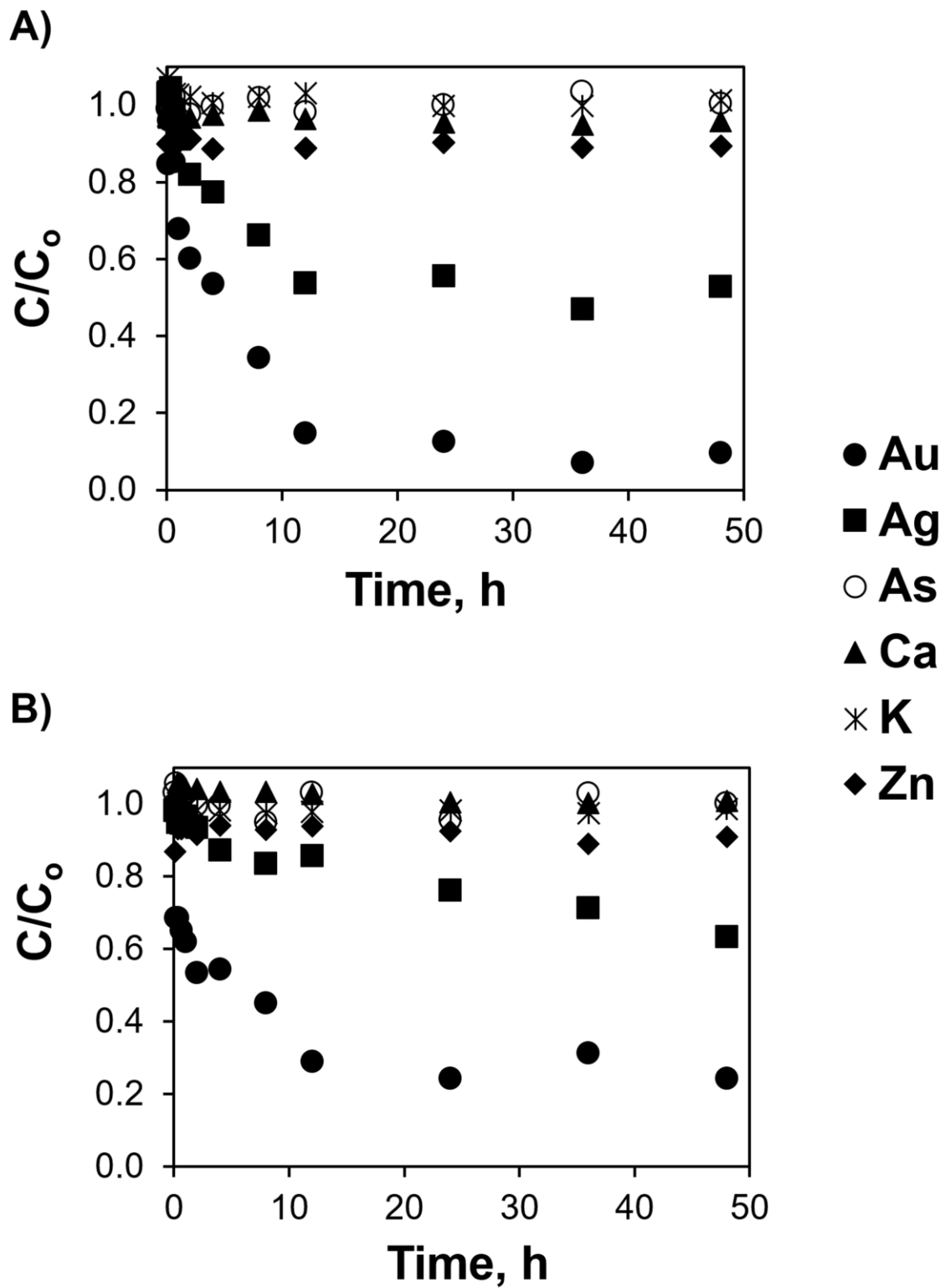


Fig. 5. Effect of pH on the adsorption capacity of **A)** gold cyanide and **B)** silver cyanide on activated carbon F400 and coconuts shell carbon (CSC), at Au and Ag initial concentrations of 30 and 365 $\mu\text{g L}^{-1}$, respectively.

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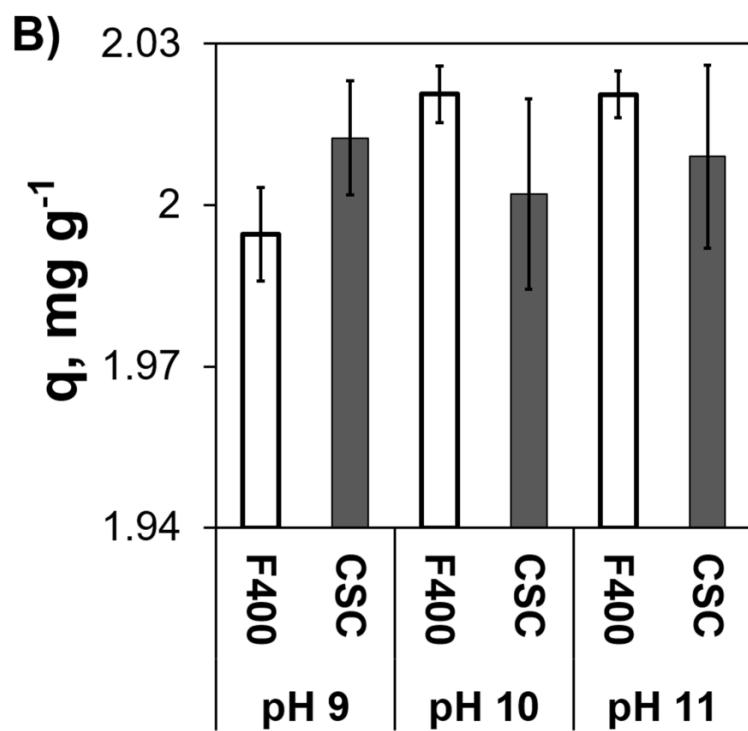
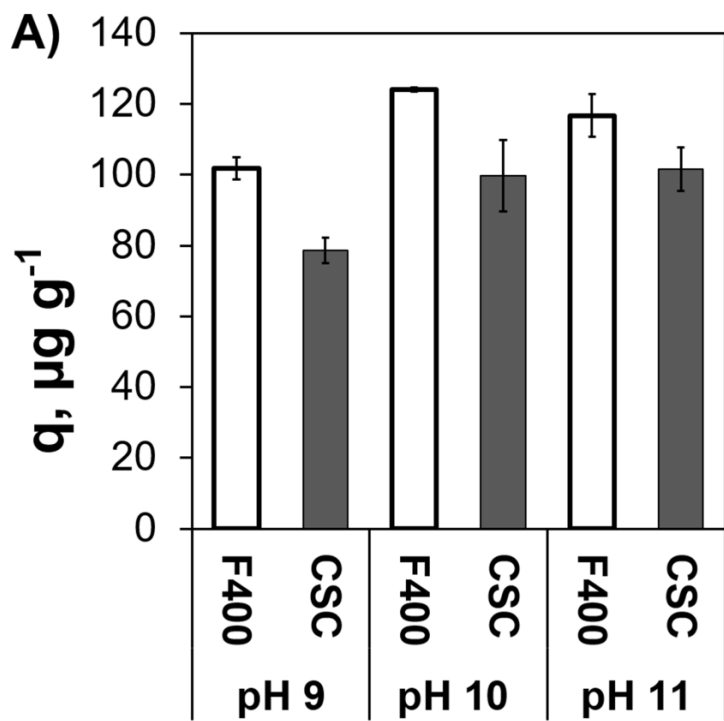


Fig. 6. Gold **A)** and silver **B)** adsorption-desorption from F400 and CSC at different temperatures using a mixture of 3 % NaOH and 1 % CN^- as eluent solution.

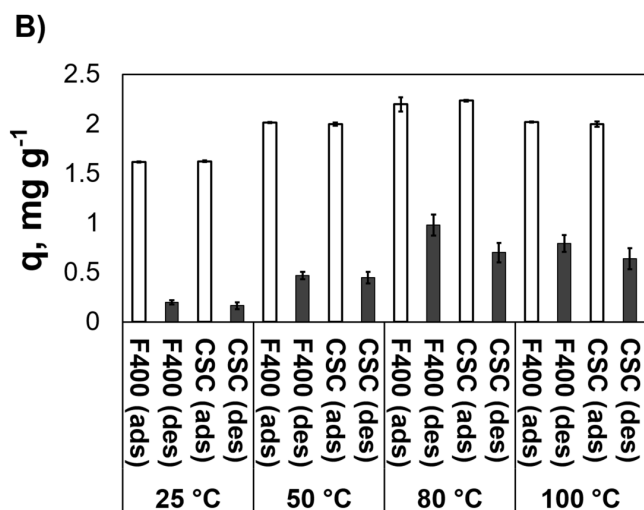
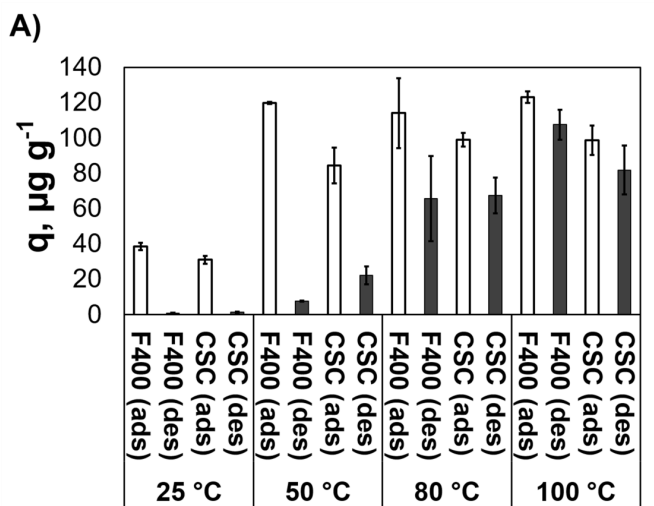


Fig. 7. Background curves for gold, silver and other ions in a packed bed column at initial pH of 11 ± 0.2 and ETBC of 15 min (The initial concentration of these ions is reported in Table 1S).

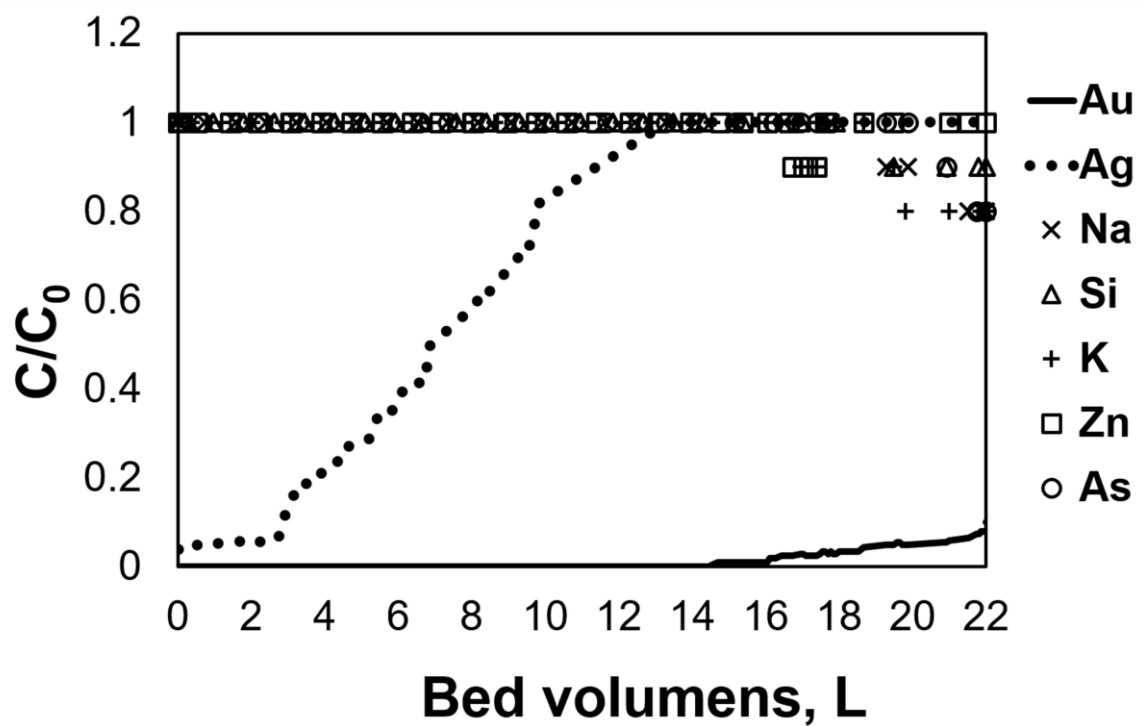
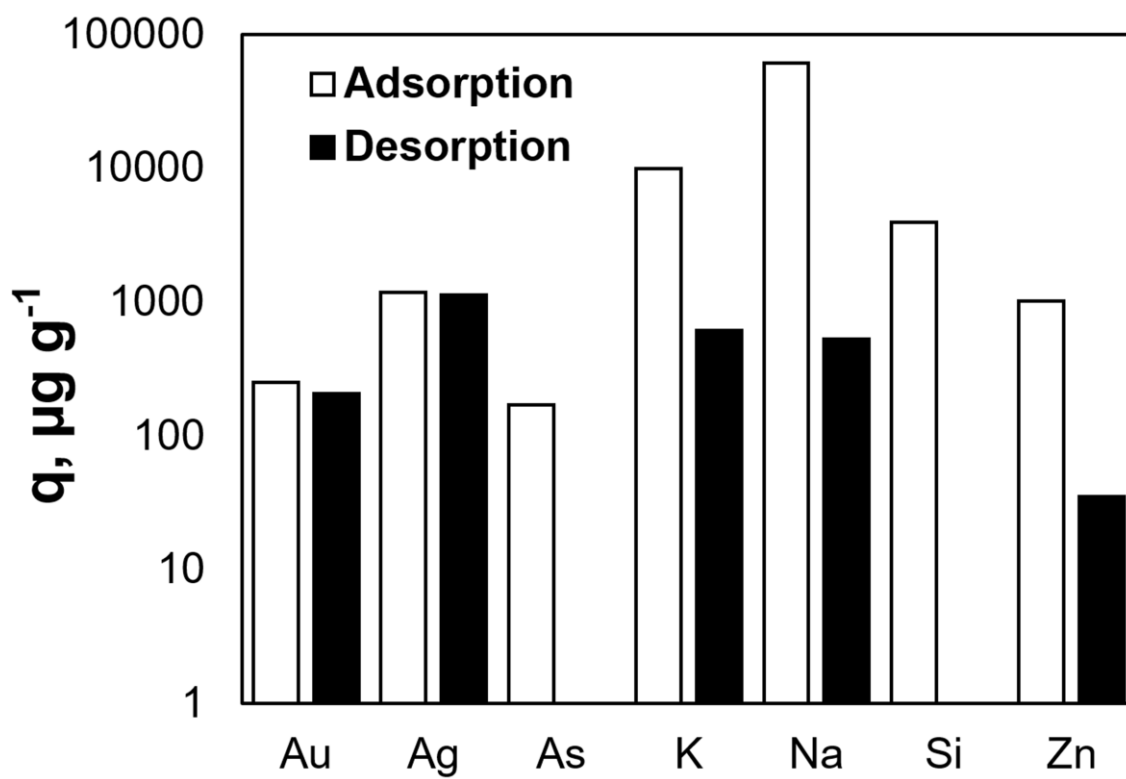
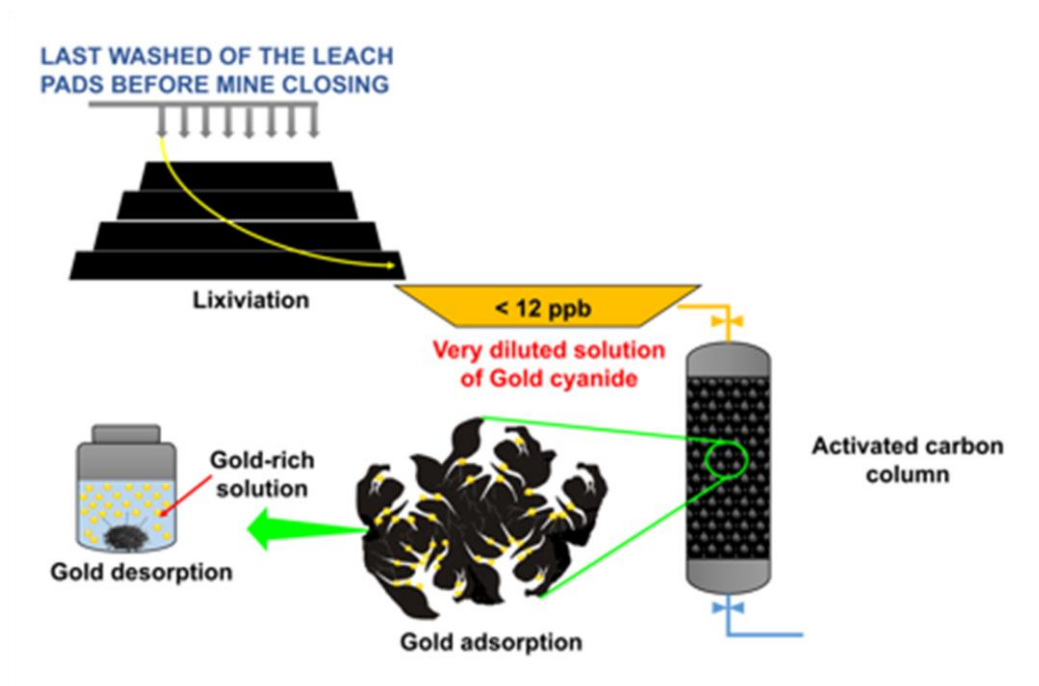


Fig. 8. Adsorption and desorption of gold and silver cyanide and other elements from activated carbon F400 used in the packed bed column (using 1 % CN.and 3 % NaOH at 100 °C).





Graphical abstract

Highlights

- Activated carbon can be used to recover Au and Ag from extremely diluted solutions.
- Activated carbon F400 and CSC removed 86 and 81 $\mu\text{g g}^{-1}$, respectively, at pH 11 and C_e of 10 $\mu\text{g L}^{-1}$ in about 4 h.
- Desorption test by NaOH and CN^- showed a gold recovery of up to 86%.
- 100% of gold is recovered in the first 14.5 bed volumes in continuous experiment.

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