

Article

# Coke-Based Carbon Sorbent: Results of Gold Extraction in Laboratory and Pilot Tests

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Received: 28 April 2020; Accepted: 29 May 2020; Published: 31 May 2020



**Abstract:** Coke-based carbon sorbent (CBCS) was produced using special coke fines with the following characteristics: ash, 4.5%; iodine adsorption capacity, 52%; specific surface area, 600 m<sup>2</sup> g<sup>-1</sup>; and total pore volume, 0.4 cm<sup>3</sup> g<sup>-1</sup>. Gold adsorption from real production cyanide solutions in batch and column laboratory experiments was studied. The optimum adsorbent/solution ratio was 0.2 g/20 cm<sup>3</sup>. Sorption equilibrium occurred after 60 min of phase-time contact. The CBCS maximum adsorption capacity for gold was found to be 1.2 mg g<sup>-1</sup>. Both the Langmuir and Freundlich isotherm models confirmed that gold adsorption by CBCS proceeds favorably, but the Freundlich isotherm best describes the adsorption equilibrium. The CBCS dynamic exchange capacity (100 g t<sup>-1</sup>) and full dynamic exchange capacity (4600 g t<sup>-1</sup>) for gold were determined in column tests. It was revealed using SEM that adsorbate was retained in sorbent pores. The possibility of completely eluting gold from CBCS was demonstrated. A CBCS pilot test to recover gold from 200 dm<sup>3</sup> of the cyanide solution containing (mg dm<sup>-3</sup>) 2.6 Au, 0.42 Ag, and 490 Cu was carried out. The total amount of noble metals (Au + Ag) adsorbed was 99.99% and gold ions was 94%. The CBCS maximum adsorption capacity for gold reached 2900 g t<sup>-1</sup>.

**Keywords:** carbon sorbent; special coke fines; gold; adsorption; removal

## 1. Introduction

Research into the processing of gold ores has been relevant for more than 100 years. There are many reviews and original articles discussing different methods of gold leaching, recovery from pregnant solutions, and waste rinse water [1–27]. Due to the fact that the Republic of Kazakhstan is one of the gold mining countries in the world this problem is interesting for local scientists and researchers [28]. The National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan RSE and its branches are Kazakhstani leaders in the creation of gold-containing raw-materials-processing technologies and the equipment to realize these processes. Dozens of gold mining and gold processing companies located in Kazakhstan, Russia, Uzbekistan, and China use these developments to produce noble metals [29,30].

Cyanidation is known to be a common commercial method of gold leaching, despite being criticized in recent years because of its environmental pollution. The traditional cyanide process is simple and cheap [2,4]. There are new scientific approaches to increase the efficiency of processing of refractory gold ores containing copper, “preg-robbing” carbon, arsenic compounds, and gold

concentrates (in particular, gravity concentrates). They typically use a combination of different methods and chemical reagents that can be used with cyanide-starved solutions as well [31–34]. Successful examples of industrial innovation are known in Australia and Kazakhstan [34].

Adsorption is the most appropriate method to recover dissolved gold from pregnant solutions because of its easy operation, low energy consumption, and large gold capacity of adsorbents used [7]. Activated carbon is considered one of the most popular and best adsorbents for gold recovery from solutions, especially cyanide solutions, due to the fact that it is cheaper than resins and has excellent texture characteristics and adsorption properties [1,3,11,13]. Activated carbon is known to demonstrate lower affinity for  $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$  in comparison with that of gold cyanide complexes [2,3]. However, the limited use of this adsorbent for gold recovery from thiosulfate solutions is currently being addressed. According to recent research, chemically-modified activated carbon is a prospective material for gold-thiosulfate complex ion adsorption [6,12].

The gold mining industry of the Republic of Kazakhstan is well developed. Gold processing enterprises using both vat and heap leaching processes operate in the country. However, heap leaching is a more popular technique because of low-grade ores. Therefore, sorbents for gold extraction from solutions are needed. Unfortunately, no sorbents are produced by local industries, although carbon and mineral sorbents are created for other spheres [35–37]. It was noted that coconut shells and coal are the most suitable raw materials to produce activated carbon with high quality [1]. Coal mining waste, crushed coke, and activated coke have been suggested for this purpose [38,39]. Since coconut shells are absent in Kazakhstan, it is preferable to use coal and coke in this country as raw resources for activated carbon preparation. We reported in previous papers the results of studies of coke-based carbon sorbent production possibilities [40,41]. The background was that special coke production using jetcoal was organized in one of the branches of the National Center on Complex Processing of Mineral Raw Materials. Special coke sized from 5 to 25 mm is a perfect reducing agent for metallurgical processes. However, special coke fines are not used, forming wastes. A method for the carbon sorbent production was developed to process these wastes. It was shown that the obtained sorbent is a good sorbent for gold recovery. However, like most newly created adsorbents, it was tested using synthetic solutions. Although positive results of gold recovery from complex model solutions were obtained, it would be interesting to estimate its activity in the process using a real production solution.

The current work deals with research of coke-based carbon sorbent in the gold extraction process from real production cyanide solutions in laboratory and pilot tests. Laboratory experiments under both batch and dynamic conditions were carried out to determine the best adsorption process parameters. Pilot tests were performed to research the behavior of the new sorbent in the sorption technology, similar to an industrial sorption technology, for processing of gold-bearing ores by the heap leaching method. The process of desorption was investigated to assess the possibility of sorbent reuse. The results obtained can be used to produce experimental batches of the coke-based carbon sorbent to be used in a trial at a gold processing plant.

## 2. Materials and Methods

### 2.1. Carbon Sorbent Preparation and Analysis

Fines with a fraction of +2–5 mm of special coke, produced at the thermal oxidation coking of coal unit in the Center of Metallurgy branch of the National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan RSE (East Kazakhstan Region) were used in this study as a raw material. The characteristics of the special coke fines are described in detail elsewhere [41].

The special coke fines were elutriated in water with slow stirring for 15 min according to the method presented in [42]. Due to the fact that mineral particles were heavier than carbon particles, they settled on the bottom, forming an ash fraction, and the carbon particles remained on the surface of the water, forming a carbon-containing fraction, in the quiescence state of the pulp. The carbon-containing material without prior drying was subjected to steam-gas activation with superheated water vapor at

850 °C for 30 min. The furnace heating was turned off at the end of the activation process, while water vapor continued to be supplied into the reactor for another 30 min to cool the activated product to 500 °C. After that, the vapor was cut off. The activated material was kept in the reactor until cooling to 60 °C. Water consumption for activation amounted to 19.3 kg per 1 kg of the sorbent.

The ash content of the sorbent ( $X$ ) was determined by the mass difference of 1 g of the initial sample ( $m_1$ ) and that of the sample calcined at 900 °C for 2 h ( $m_2$ ) according to the formula:

$$X = \frac{m_1 - m_2}{m_1} \cdot 100\% \quad (1)$$

Adsorption properties of the obtained sorbent were characterized by the iodine adsorption capacity ( $A_i$ ), which was determined according to [41].

Specific surface area and total pore volume of the obtained sorbent were determined by the BET method for low-temperature nitrogen adsorption on an AccuSorb instrument (Micromeritics, Norcross, GA, USA).

The morphology and pore system were studied by scanning (SEM) and transmission (TEM) electron microscopy methods.

SEM and X-ray spectral micro-analysis were performed on the micro-analyzer Superprobe 733 (JEOL, Tokyo, Japan). The analysis of the element composition of the samples and the photographic survey in various types of radiation were performed using the energy-dispersive spectrometer INCA ENERGY (OXFORD INSTRUMENTS, London, UK), installed on the electron-probe micro-analyzer Superprobe 733, with an accelerating voltage of 25 kW and a survey current of 25 nA. The samples were preliminarily coated with the thin structureless film of gold in a facility for ionic sputtering, FINE COATE (Japan). Photos were made of the secondary electrons.

TEM was performed on a JEM 100CX transmission electron microscope (Japan) at the accelerating voltage of 100 kV within the range of 9–230 thousand times the electron microscopic magnification. For exposure of the samples, powder in the agate mortar was laid onto the object copper mesh, pre-coated with a substrate film of amorphous carbon, and fixed in the microscope object holder.

## 2.2. Gold Adsorption in the Batch Mode

In the laboratory batch experiments, gold adsorption was studied using an alkaline-cyanide solution obtained in gold-bearing ore processing (initial production solution). It contained the following elements,  $\text{mg dm}^{-3}$ : Au, 17.9; Cu, 112; Zn, 34; and Ag, 2. This solution was diluted to prepare solutions containing ~2, ~4, ~6, ~8, and ~10  $\text{mg dm}^{-3}$  of Au ions. The pH of the solutions was adjusted to be 11. The gold adsorption process was carried out at a room temperature. The contact time of the sorbent with the solution was 30, 60, and 90 min. The ratio of the sorbent mass to the solution volume ( $m$  (g): $V$  ( $\text{cm}^3$ )) was 0.2:20; 0.3:20; and 0.4:20.

The gold content in the solutions before and after sorption (as well as the content of other metals in all experiments in the framework of the current study) was analyzed in duplicate using the Agilent Technologies 240 FSAA atomic absorption spectrometer.

The amount of gold ions adsorbed at equilibrium ( $a$ ,  $\text{mg g}^{-1}$ ) and the degree of gold ions removal from the solutions were calculated using the expressions [43]:

$$a = \frac{(c_0 - c_e) \cdot V}{m} \quad (2)$$

$$\% \text{ removal} = \frac{(c_0 - c_e) \cdot 100}{c_0} \quad (3)$$

where  $c_0$  and  $c_e$  are the initial and equilibrium liquid phase concentrations ( $\text{mg dm}^{-3}$ ), respectively,  $V$  is the volume of the solution ( $\text{dm}^3$ ), and  $m$  is the weight of the sorbent used (g). The results presented are the average of three measurements.

For a quantitative description of the gold ions sorption equilibrium on the carbon sorbent surface during extraction from the solutions, the Langmuir and Freundlich isotherms models were used [44]:

$$a = \frac{a_m \cdot K_L \cdot c_e}{1 + K_L \cdot c_e} \quad (4)$$

$$a = K_F \cdot c^{1/n} \quad (5)$$

where  $a_m$  and  $K_L$  are the constants in the Langmuir equation and  $K_F$  and  $n$  are the constants in the Freundlich equation.

### 2.3. Gold Adsorption under Dynamic Conditions

During laboratory experiments under dynamic conditions, gold recovery was carried out in a glass column with a diameter of 17 mm and a length of 123 mm. The sorption column was filled with the carbon sorbent (6 g). The volume of the sorbent was 25.8 cm<sup>3</sup>. A production solution, prepared in gold ore processing, with content of Au, 5.85 mg dm<sup>-3</sup>; Ag, 0.34 mg dm<sup>-3</sup>; Cu, 38.07 mg dm<sup>-3</sup>; and Zn, 10.25 mg dm<sup>-3</sup>, pH 11 was continuously fed into the column from the bottom up at the rate of 100 cm<sup>3</sup> h<sup>-1</sup>. Concentrations of Au, Ag, Cu, and Zn were measured in filtrates every 30 min. The gold adsorption process was repeated three times.

The dynamic exchange capacity for gold ( $DEC$ , g m<sup>-3</sup>) and the full dynamic exchange capacity for gold ( $FDEC$ , g m<sup>-3</sup>) were calculated by the formulae:

$$DEC = \frac{V_f \cdot c \cdot 1000}{V_s} \quad (6)$$

$$FDEC = \frac{(V_{fe} \cdot c - \sum V_f \cdot c_f) \cdot 1000}{V_s} \quad (7)$$

where  $V_f$  is the total volume of the filtrate passed through the sorbent layer until gold ions appear in the filtrate (cm<sup>3</sup>),  $c$  is the gold concentration in the production solution (g dm<sup>-3</sup>),  $V_s$  is the sorbent volume (cm<sup>3</sup>),  $V_{fe}$  is the total volume of the filtrate passed through the sorbent layer until the gold concentrations in the filtrate and the production solution are equal (cm<sup>3</sup>), and  $c_f$  is the gold concentration in the filtrate after the appearance of gold ions in it (g dm<sup>-3</sup>).

The degree of gold ions and impurity metals removal in column experiments was determined according to the Expression (3).

### 2.4. Gold Desorption Procedure

The gold desorption procedure under laboratory conditions was carried out at 94 °C with constant stirring using a sodium hydroxide solution (6 g dm<sup>-3</sup>) as an eluant. The eluant/sorbent volume ratio was 4:1. The sorbent was separated from the alkaline solution and treated by a new portion of the eluant every half hour until the gold ions disappeared in the eluate.

### 2.5. Pilot Test

The pilot test of the carbon sorbent as an adsorbent for gold was carried out in the VNIItsvetmet branch of the National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan RSE using a pilot unit. Therefore, a pilot batch of a solution (200 dm<sup>3</sup>, pH 10–11) was prepared by one of the Kazakhstani deposits with gold-bearing ore cyanidation. The composition of the prepared solution (mg dm<sup>-3</sup>: Au, 2.6; Ag, 0.42; and Cu, 490; NaCN content, 0.06%) is similar to solutions commonly used in the industry, which is unfavorable for processing solutions because of a high copper amount. However, this is the solution used by many Kazakhstani gold processing enterprises.

Sorption was carried out using a cascade of five series-connected sorption columns in a continuous mode for 10 days. Each column was filled with the synthesized sorbent in an amount of 20 g. The

production solution was fed into the first column initially at the maximum allowable specific load in an industrial plant (specific load is the ratio of the volume of the solution passed through the column per unit time to the sorbent volume). The specific load was  $16 \text{ h}^{-1}$ , which corresponded to a solution feed rate of  $1.25 \text{ dm}^3 \text{ h}^{-1}$ . Then, the solution passed by itself from one column to another. An effluent at the outlet of the last column of the cascade was analyzed every 24 h (1x/day) to determine gold, silver, and impurity metals content in order to monitor and control the process. The specific load was changed during the experiment depending on the gold concentration in the effluents. Samples of gold cyanide-containing filtrates at the outlet from each cascade column were taken every 2 h during the day shift as well. These portions were mixed to form a combined daily sample after each column, in which the content of only gold ions was determined.

At the end of the pilot test, the carbon sorbent was analyzed for all metals present. For this, 1 g of the carbon sorbent was burned in a muffle furnace at  $750 \text{ }^\circ\text{C}$  for 3 h. The mineral residue was decomposed with  $30 \text{ cm}^3$  of aqua regia during boiling for 1.5 h. The solution was accurately transferred to a  $250 \text{ cm}^3$  volumetric flask using a 1 M hydrochloric acid solution and then analyzed for the metals content. Similarly, the residual content of metals on the sorbent surface after gold desorption was determined.

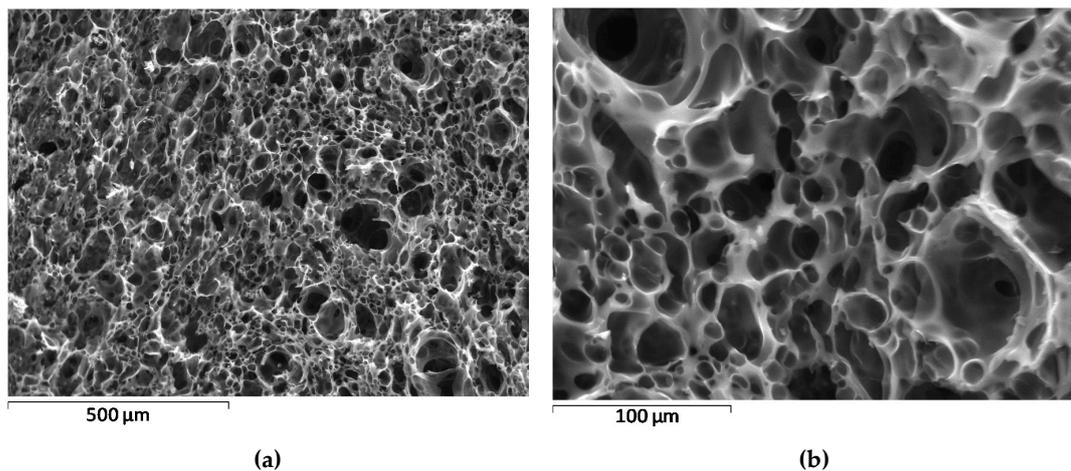
Gold was desorbed from the sorbents from different columns in different ways. From the first, second, and third columns, it was eluted by a  $20 \text{ g dm}^{-3}$  sodium hydroxide solution at  $180 \text{ }^\circ\text{C}$  in an autoclave with stirring for 3 h at the eluant/sorbent volume ratios of 10.5, 6.6, and 10.5, respectively. A mix of 20% ethanol with a  $6 \text{ g dm}^{-3}$  sodium hydroxide solution was used as an eluent to elute gold from the fourth and fifth columns. For this, the eluent was passed through a sorbent layer at  $70 \text{ }^\circ\text{C}$  until the gold ions disappeared in the eluate. From the first, second, and third columns, after their reuse, gold was eluted by a  $6 \text{ g dm}^{-3}$  sodium hydroxide solution at  $94 \text{ }^\circ\text{C}$  with stirring for 3 h at the eluant/sorbent volume ratio of 4:1. This procedure was repeated three times.

### 3. Results and Discussion

#### 3.1. Coke-Based Carbon Sorbent Characterization

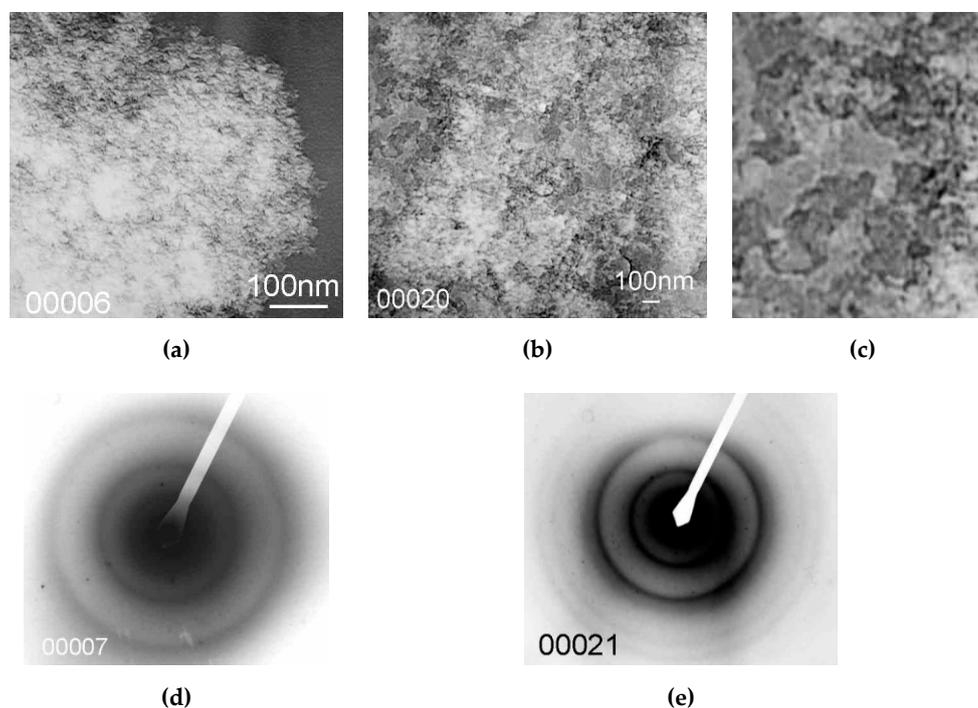
Coal coke is known to be a hard-to-activate material because of its specific carbon structure. The activation process generally involves several stages, such as heating and calcination, which are performed in an inert atmosphere using chemical reagents (predominantly alkali). This process usually takes a few hours. Activation under oxidative conditions reduces the yield of the active carbon and increases its ash content. To avoid this, the special coke fines were elutriated in water. The yield of the carbon-containing fraction was 70 wt % and the yield of the ash fraction was 30 wt %. The carbon-containing fraction with humidity value of 50% was activated and cooled by superheated water vapor according to the developed method. As a result, the yield of the activated product was almost 60 wt % in terms of dry matter of carbon-containing fraction charge. The finished coke-based carbon sorbent (CBCS) was characterized by the following parameters: ash content, 4.5%; sorption capacity for iodine, 52%; specific surface area,  $600 \text{ m}^2 \text{ g}^{-1}$ ; total pore volume,  $0.4 \text{ cm}^3 \text{ g}^{-1}$ .

According to SEM the synthesized sorbent has a developed porous structure (Figure 1a). Pores of a round or oval shape with a cross-sectional size of up to  $20 \text{ }\mu\text{m}$  are mainly present; large cavities penetrated by deep pores with a size of  $10\text{--}20 \text{ }\mu\text{m}$  across were observed (Figure 1b). X-ray spectral micro-analysis showed that carbon sorbent consists of the following elements, %: C, 92.1; O, 6.18; Na, 0.13; Mg, 0.14; Al, 0.3; Si, 0.25; S, 0.45; Ca, 0.28; and Fe, 0.18.



**Figure 1.** SEM micrographs of the coke-based carbon sorbent (CBCS) sample at smaller (a) and larger (b) magnifications.

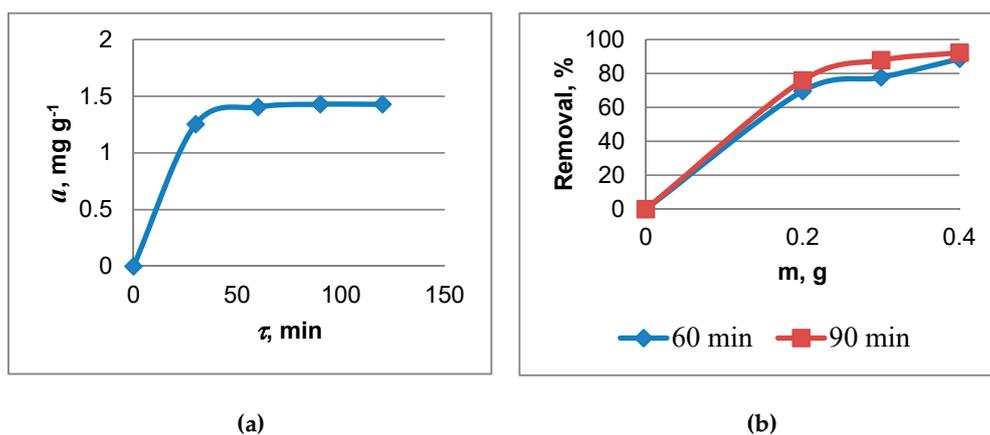
It was determined by the TEM method that the carbonaceous substance of the CBCS sample is formed by small translucent formations with a size of 6–10 nm (Figure 2a,b). There are large (200 nm and larger) flattened particles with low density shown in Figure 2b,c (Figure 2c is a fragment of Figure 2b). According to the micro-diffraction pattern (Figure 2d), the small carbon formations are characterized as fine crystalline particles. The micro-diffraction pattern from the large particles is represented by rings with interplanar distance  $d_{002} \sim 0.36\text{--}0.38$  nm (Figure 2e). Both micro-diffraction patterns have reflections indicating the presence of mineral inclusions in the CBCS sample. Pore nanoscales were not observed.



**Figure 2.** TEM microphotographs and micro-diffraction patterns of the CBCS sample: (a) Translucent formations; (b) Translucent formations and flattened particles; (c) Flattened particles; (d) The micro-diffraction pattern from the translucent formations; and (e) The micro-diffraction pattern from the flattened particles.

### 3.2. Gold Adsorption Kinetics and Isotherms

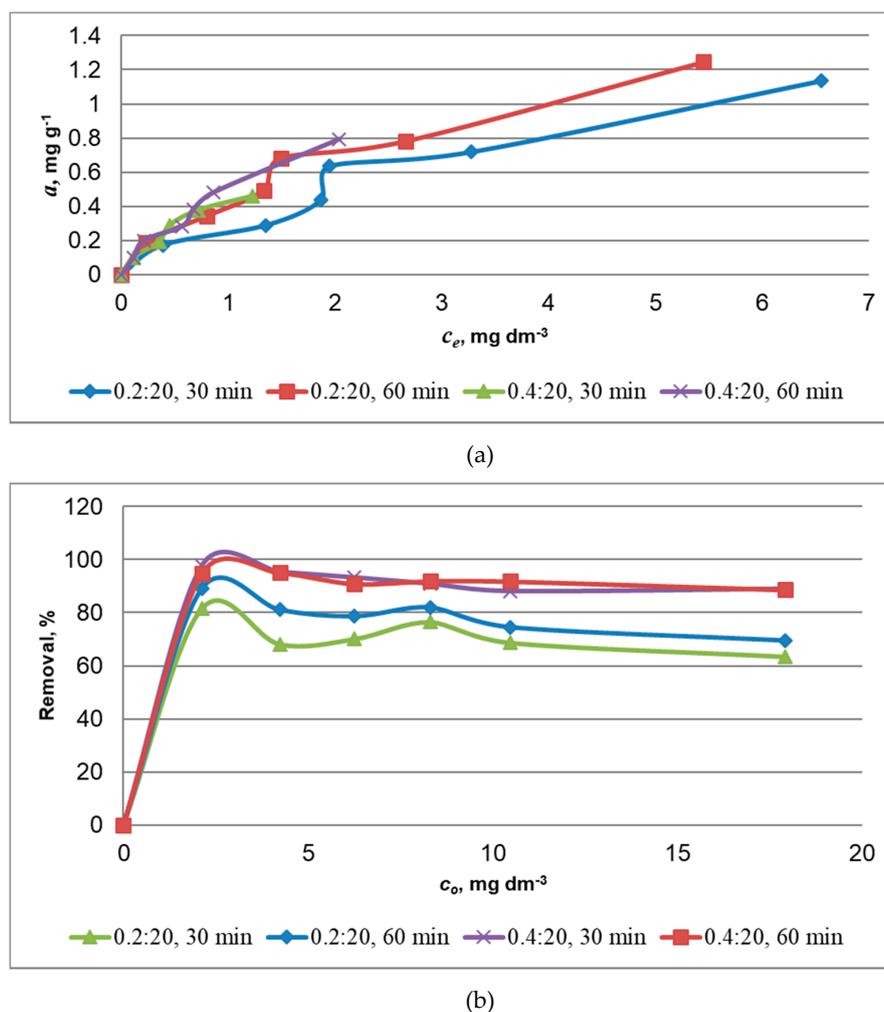
The kinetic curve of gold ions adsorption from the production solution with the gold concentration of  $18 \text{ mg dm}^{-3}$  by the CBCS at the ratio of  $m/V = 0.2:20$  in the batch mode is shown in Figure 3a. It can be seen from this figure that the amount of gold ions adsorbed increases slightly while the sorbent/solution contact time rises from 30 to 120 min. Sorption equilibrium occurs after 60 min. Figure 3b shows a gradual growth of the degree of gold ions removal from the solution from 70% up to 90% with an increase in the sorbent mass from 0.2 up to 0.4 g per the same unit volume ( $20 \text{ cm}^3$ ) of the solution.



**Figure 3.** Gold ions adsorption by the CBCS sample from the production solution (composition,  $\text{mg dm}^{-3}$ : Au, 17.9; Cu, 112; Zn, 34; Ag, 2): (a) Kinetic curve of adsorption (the sorbent mass (g) to the solution volume ( $\text{cm}^3$ ) ratio of 0.2:20); (b) Influence of the sorbent mass on gold ions removal for different contact times.

Figure 4a demonstrates adsorption isotherms of gold ions from the solutions with Au contents of  $\sim 2$ ,  $\sim 4$ ,  $\sim 6$ ,  $\sim 8$ ,  $\sim 10$ , and  $\sim 18 \text{ mg dm}^{-3}$ . The isotherms have a characteristic form. Adsorbed gold tends to increase as the equilibrium gold concentration increases. Figure 4b shows the effect of the initial gold concentration on the degree of extraction under different conditions. It can be seen that the percentage of gold extraction declines gradually in the concentration range from 2 to  $18 \text{ mg dm}^{-3}$ . According to results shown in Figure 4, the ratio of  $m/V = 0.2:20$  and contact time of 60 min are optimal adsorption process parameters.

Therefore, data of the experiment carried out at these adsorbent/solution ratios and contact time values were used to describe the behavior of gold ions during the sorption process by the CBCS. For this, models of the Langmuir and Freundlich isotherms were used. Constants of the Langmuir and Freundlich equations were calculated using the corresponding isotherms (Table 1). According to the values of these parameters ( $a_m = 3.27$ ,  $K_L = 0.19$ ,  $K_F = 2.23$ , and  $1/n = 0.49$ ) and discussions published elsewhere [44,45], gold ions sorption from the production solutions by the CBCS proceeded favorably. Taking into account the correlation coefficient  $R^2$ , the Freundlich model has the best fit for gold adsorption by the CBCS.



**Figure 4.** Gold ions adsorption by the CBCS sample from solutions with Au concentrations, mg dm<sup>-3</sup>: ~2; ~4; ~6; ~8; ~10; ~18: (a) Isotherms of adsorption; (b) Influence of the initial gold concentration on the degree of gold ions removal at different sorbent mass (g) to solution volume (cm<sup>3</sup>) ratios and contact times.

**Table 1.** Values of isotherm constants for gold ions adsorption by the CBCS.

Parameter	Langmuir Model	Parameter	Freundlich Model
$a_m, \text{mg g}^{-1}$	3.2712	$n$	2.0505
$K_L, \text{dm}^3 \text{mg}^{-1}$	0.1911	$K_F, (\text{mg g}^{-1}) (\text{dm}^3 \text{mg}^{-1})^{1/n}$	2.2255
$R^2$	0.8812	$R^2$	0.9742

### 3.3. The Distribution of Adsorbed Metals on the Surface of the CBCS

To study the distribution of noble and impurity metals on the surface of the CBCS, it was necessary to load of the sorbent as much as possible. In this connection, the sorption process was performed under dynamic conditions in a laboratory using the production solution with the metals concentrations as follows, mg dm<sup>-3</sup>: Au, 5.85; Ag, 0.34; Cu, 38.07; Zn, 10.25. The appearance of the first gold ions in the filtrate was observed after four specific volumes (specific volume means the ratio of the volume of the solution passed to the volume of the sorbent) were passed through the sorbent layer (Table 2). The dynamic exchange capacity for gold was 22.7 g per 1 m<sup>3</sup> of carbon sorbent or 100 g t<sup>-1</sup>. The full dynamic exchange capacity for gold was achieved after passing 279 specific volumes (i.e., 7.2 dm<sup>3</sup>). It was 1632 g per 1 m<sup>3</sup> of carbon sorbent or 4600 g t<sup>-1</sup>. Metals removal degrees were 67%, 41.6%, 2.4%,

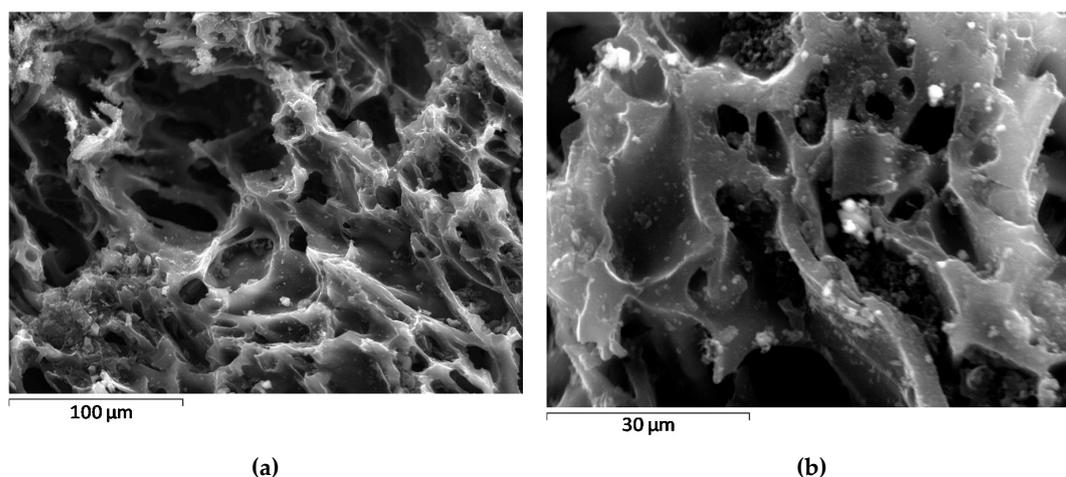
and 14.4% for gold, silver, copper, and zinc, respectively (Table 2). The proportion of noble metals (Au + Ag) after complete saturation of the sorbent with gold was at the level of 60.8%.

**Table 2.** The metals removal degree from the production solution by the CBCS at different specific volume values.

Metal Ion	Metal Removal Degree, %			
	4	209	221	279
Au	95.6	75.2	74.1	67.1
Ag	85.3	45.3	44.9	41.6
Cu	41.7	1.8	1.9	2.4
Zn	78.0	-0.4	0.8	14.4

The results demonstrate a high sorption ability of the CBCS synthesized on the basis of special coke fines in relation to noble metal ions. At the same time, Table 2 indicates that the active loading of the carbon sorbent with noble metals occurs at up to 209 specific volumes of the passed solution. In this case, the proportion of noble metals on the sorbent reached 87.7% due to the displacement of impurity metal ions and their washing out into the solution. The adsorption of precious metals decreased while the amount of impurity metals increased on the CBCS with further passing of the solution through the sorbent.

It is believed that adsorption of cyanide complexes from alkaline and acidic solutions proceeds at the most preferred sites on the carbon surface [1]. Based on the comparison of the SEM micrographs of the CBCS samples before and after the adsorption process (Figures 1 and 5), it can be assumed that the preferred sites for sorption of gold from alkaline cyanide solutions are mainly in the deep slit-like and open pores of the CBCS. This thesis fits well with McDougall and Hancock's conclusion about the most probable mechanisms of sorption of the gold cyanide complexes [1]. According to one of these mechanisms, sorption of  $M^{n+}[Au(CN)_2^-]_n$  complexes takes place when  $M^{n+}$  ions are the metals present in the carbon ash. It is logical that  $M^{n+}$  ions, as the most accessible components of ash, are located in the pores, i.e., in the locations formed as a result of carbon or hydrocarbons removal during the activation process of the special coke fines. Therefore, in the case of the gold adsorption by the CBCS from alkaline solutions the  $Au(CN)_2^-$  anion remains in the sorbent pores as an  $M^{n+}[Au(CN)_2^-]_n$  complex.



**Figure 5.** SEM micrographs of the CBCS sample after the adsorption process at smaller (a) and larger (b) magnifications.

### 3.4. Gold Desorption Study under Laboratory Conditions

It is known that the treatment of sorbent with an alkali solution, especially in an autoclave, is the most popular gold desorption method. In this experiment, gold desorption was carried out under milder conditions. The gold-loaded CBCS was treated with a  $6 \text{ g dm}^{-3}$  sodium hydroxide solution during boiling. The process of complete desorption of gold took 10 h. The maximum gold concentration reached  $100 \text{ mg dm}^{-3}$  in the first portion of an eluate (see Supplementary Materials Table S1). In general, a potential for deep extraction of noble metal into solution was found.

### 3.5. The CBCS Testing at the Pilot Unit

The results of the gold sorption from the production solution with Au concentration of  $2.6 \text{ mg dm}^{-3}$  by the CBCS at the pilot unit showed that almost complete recovery of gold (92–99%) was achieved during the first three days of the experiment, when  $90 \text{ dm}^3$  of the solution was processed (see Supplementary Materials Table S2). The residual content of Au ions in the solution after sorption was  $0.03 \text{ mg dm}^{-3}$ ,  $0.07 \text{ mg dm}^{-3}$ , and  $0.21 \text{ mg dm}^{-3}$  after the first, second, and third days, respectively. Then, the concentration of gold in the solution started to increase and reached  $0.73 \text{ mg dm}^{-3}$ . Therefore, the specific load value was reduced gradually from 16 to  $4 \text{ h}^{-1}$ . Moreover, the first three columns were treated by the sodium hydroxide solution in an autoclave to elute gold (see Supplementary Materials Table S3). This provided a decrease in the gold concentration in the solution after sorption to  $0.07 \text{ mg dm}^{-3}$  (see Supplementary Materials Table S2). The specific load was increased up to  $7\text{--}8 \text{ h}^{-1}$ . The concentrations of gold ions in the filtrates were  $0.13 \text{ mg dm}^{-3}$ ,  $0.14 \text{ mg dm}^{-3}$ ,  $0.29 \text{ mg dm}^{-3}$ , and  $0.41 \text{ mg dm}^{-3}$  after the seventh, eighth, ninth, and tenth days of the unit operation, respectively. An average value of gold removal was 90%. Results of analysis of loaded sorbent showed that the CBCS extracted only noble metals from the solution (see Supplementary Materials Table S4). The proportion of noble metals (Au + Ag) on the sorbent amounted to 99.99% and gold ions content was 94.19%. The maximum amount of gold adsorbed on the CBCS was  $2900 \text{ g t}^{-1}$ .

Following a comparison of the test results of the CBCS in a laboratory and pilot unit, a difference between the full dynamic exchange capacity for gold ( $4600 \text{ g t}^{-1}$ ) and the maximum amount of gold adsorbed on one column of the pilot unit ( $2900 \text{ g t}^{-1}$ ) was noted. This difference demonstrates that the potential of the CBCS was not used completely during the pilot test. On the other hand, the capacitive characteristics of the CBCS, identified during the pilot test, confirmed its conformity with the performance of Kazakhstani gold processing enterprises, which use known sorbents for gold extraction from solutions with similar compositions. Equally important is the fact that the cost of the new sorbent is 5 times lower than the cost of the applied sorbents.

The eluting of gold cyanide adsorbate from the surface of the loaded CBCS was performed in different ways, as mentioned above, for comparison. The highest gold extracting degree (90% and higher) was, as expected, in the case of the sorbent treatment by the sodium hydroxide solution in an autoclave for 3 h. The treatment by the sodium hydroxide solution during boiling provided 45% elution of the adsorbed gold for the same period of time. The gold eluting by a mixture of ethyl alcohol and sodium hydroxide solution resulted in 80% gold extraction, which was reached after 8 h. However, in this way, highly concentrated eluates ( $140\text{--}160 \text{ mg dm}^{-3}$ ) were produced with minimal sorbent losses (5%).

## 4. Conclusions

A carbon sorbent based on special coke fines, having a low ash content and developed pore system, was produced. Its activity to recover gold ions from real production cyanide solutions was investigated. A distinctive feature of the synthesized CBCS is the ability to rapidly achieve sorption equilibrium (60 min). The process of gold adsorption by the CBCS was described by the Freundlich model. The CBCS is characterized by a high affinity for gold ions in comparison with other metals. It removes

more than 90% of gold from cyanide solutions with different metal concentrations. Gold-cyanide adsorbate is placed mainly in sorbent pores and can be desorbed completely by different methods.

The results of the pilot test confirm the data of the laboratory experiments. The CBCS works in the same way as sorbents are used to extract gold from solutions with high copper concentrations in heap leaching technology. It is possible to reuse the CBCS after gold eluting without additional regeneration. Taking into account the low cost of the sorbent, it is a promising product for the Kazakhstani gold processing industry.

## 5. Patents

Authors have the KZ Patent 34132 called “Method of obtaining carbon sorbent on the basis of special coke” resulting from the current study. Full data are presented in [41].

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2075-163X/10/6/508/s1>, Table S1: Laboratory desorption results of gold from the CBCS, Table S2: The results of metal removal from the production solution by the CBCS in the pilot test, Table S3: The dynamics of changes in the concentration of gold in the solutions after sorption for the day shift on each column during testing at the pilot unit, Table S4: The metals content on the surface of the CBCS after sorption and desorption during testing at the pilot unit.

**Author Contributions:** Conceptualization, S.Y. (Svetlana Yefremova) and A.T.; methodology, S.Y. (Svetlana Yefremova), L.B., and L.K.; investigation, S.Y. (Svetlana Yefremova), A.T., A.K., L.B., L.K., Y.S., S.Y. (Sergey Yermishin), and V.S.; data curation, S.Y. (Svetlana Yefremova), A.T., and A.Z.; writing-original draft preparation, S.Y. (Svetlana Yefremova); writing-review and editing, A.Z. and V.S.; supervision, A.Z.; project administration, A.T. and S.Y. (Svetlana Yefremova); funding acquisition A.Z. and A.T. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Ministry of Industry and Infrastructural Development of the Republic of Kazakhstan, program number 0066/PTsF-OT-18.

**Acknowledgments:** The authors would like to thank V. Levin, Head of the Mineralogy Laboratory of the K.I. Satpayev Institute of Geological Sciences, Candidate of Geological and Mineralogical Sciences, for performing the scanning electron microscopy; T. Shabanova, Head of the Group on Micro- and Nanomineralogy of the K.I. Satpayev Institute of Geological Sciences, Doctor of Chemical Sciences, for performing the transmission electron microscopy; N. Linnikova, Head of the V.I. Karpenko Physical and Analytical Laboratory of the National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan RSE and G. Alikbayeva, Leading Researcher of the V.I. Karpenko Physical and Analytical Laboratory of the National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan RSE, for performing the analytical analysis.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. McDougall, G.J.; Hancock, R.D. Gold complexes and activated carbon. *Gold Bull.* **1981**, *14*, 138–153. [CrossRef]
2. Xu, B.; Kong, W.; Li, Q.; Yang, Y.; Jiang, T.; Liu, X. A Review of Thiosulfate Leaching of Gold: Focus on Thiosulfate Consumption and Gold Recovery from Pregnant Solution. *Metals* **2017**, *7*, 222. [CrossRef]
3. Dong, Z.; Jiang, T.; Xu, B.; Yang, Y.; Li, Q. Recovery of Gold from Pregnant Thiosulfate Solutions by the Resin Adsorption Technique. *Metals* **2017**, *7*, 555. [CrossRef]
4. Syed, S. Recovery of gold from secondary sources—A review. *Hydrometallurgy* **2012**, *115*, 30–51. [CrossRef]
5. Vargas, C.; Navarro, P.; Araya, E.; Pavez, F.; Alguacil, F.J. Recovery of gold from solutions with ammonia and thiosulfate using activated carbon. *Rev. Met.* **2006**, *42*, 222–233. [CrossRef]
6. Yu, H.; Zi, F.; Hu, X.; Nie, Y.; Xiang, P.; Xu, J.; Chi, H. Adsorption of the gold–thiosulfate complex ion onto cupric ferrocyanide (CuFC)-impregnated activated carbon in aqueous solutions. *Hydrometallurgy* **2015**, *154*, 111–117. [CrossRef]
7. Lam, K.F.; Fong, C.M.; Yeung, K.L. Separation of precious metals using selective mesoporous adsorbents. *Gold Bull.* **2007**, *40*, 192–198. [CrossRef]
8. Riveros, P. Selectivity aspects of the extraction of gold from cyanide solutions with ion exchange resins. *Hydrometallurgy* **1993**, *33*, 43–58. [CrossRef]
9. Aveston, J.; Everest, D.A.; Wells, R.A. 48. Adsorption of gold from cyanide solutions by anionic resins. *J. Chem. Soc.* **1958**, 231. [CrossRef]

10. Chaparro, M.; Munive, G.; Guerrero, P.; Parga, J.R.; Vazquez, V.; Valenzuela, J.L. Gold adsorption in thiosulfate solution using anionic exchange resin. *J. Multidiscip. Eng. Sci. Technol.* **2015**, *2*, 2159–2163.
11. Nguyen, N.V.; Jeong, J.; Shin, D.; Kim, B.-S.; Lee, J.-C.; Pandey, B.D. Simultaneous Recovery of Gold and Iodine from the Waste Rinse Water of the Semiconductor Industry Using Activated Carbon. *Mater. Trans.* **2012**, *53*, 760–765. [[CrossRef](#)]
12. Yu, H.; Zi, F.; Hu, X.; Nie, Y.; Chen, Y.; Cheng, H. Adsorption of gold from thiosulfate solutions with chemically modified activated carbon. *Adsorpt. Sci. Technol.* **2017**, *36*, 408–428. [[CrossRef](#)]
13. Navarro, P.; Vargas, C.; Alonso, M.; Alguacil, F.J. The adsorption of gold on activated carbon from thiosulfate-ammoniacal solutions. *Gold Bull.* **2006**, *39*, 93–97. [[CrossRef](#)]
14. Tauetsile, P.; Oraby, E.; Eksteen, J. Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 2: Kinetics. *Sep. Purif. Technol.* **2019**, *211*, 290–297. [[CrossRef](#)]
15. Fomkin, A.A.; Tsivadze, A.Y.; Shkolin, A.V.; Mukhin, V.M.; Dudarev, V.I. Carbon sorbents in cyanide gold recovery technology. *Physical Chem. Surf. Prot. Mater.* **2014**, *50*, 563–567. [Fizikokhimiya Poverkhnosti i Zashita Materialov. (In Russia)] [[CrossRef](#)]
16. Gallagher, N.P.; Hendrix, J.L.; Milosavljević, E.B.; Nelson, J.H.; Solujić, L. Affinity of activated carbon towards some gold(I) complexes. *Hydrometallurgy* **1990**, *25*, 305–316. [[CrossRef](#)]
17. Chang, Y.-C.; Chen, D.-H. Recovery of gold(III) ions by a chitosan-coated magnetic nano-adsorbent. *Gold Bull.* **2006**, *39*, 98–102. [[CrossRef](#)]
18. Kononova, O.; Kholmogorov, A.; Kononov, Y.; Pashkov, G.; Kachin, S.; Zotova, S. Sorption recovery of gold from thiosulfate solutions after leaching of products of chemical preparation of hard concentrates. *Hydrometallurgy* **2001**, *59*, 115–123. [[CrossRef](#)]
19. Alguacil, F.J.; Adeva, P.; Alonso, M. Processing of residual gold (III) solutions via ion exchange. *Gold Bull.* **2005**, *38*, 9–13. [[CrossRef](#)]
20. Zhang, H.; Dreisinger, D. The adsorption of gold and copper onto ion-exchange resins from ammoniacal thiosulfate solutions. *Hydrometallurgy* **2002**, *66*, 67–76. [[CrossRef](#)]
21. Al-Merey, R.; Hariri, Z.; Abu Hilal, J. Selective separation of gold from iron ore samples using ion exchange resin. *Microchem. J.* **2003**, *75*, 169–177. [[CrossRef](#)]
22. Mohebbi, A.; Mahani, A.A.; Izadi, A. Ion Exchange Resin Technology in Recovery of Precious and Noble Metals. In *Applications of Ion Exchange Materials in Chemical and Food Industries*; Springer Science and Business Media LLC: Berlin/Heidelberg, Germany, 2019; pp. 193–258.
23. Jeffrey, M.; Hewitt, D.; Dai, X.; Brunt, S. Ion exchange adsorption and elution for recovering gold thiosulfate from leach solutions. *Hydrometallurgy* **2010**, *100*, 136–143. [[CrossRef](#)]
24. Fleming, C.A.; McMullen, J.; Thomas, K.G.; Wells, J.A. Recent advances in the development of an alternative to the cyanidation process: Thiosulfate leaching and resin in pulp. *Min. Met. Explor.* **2003**, *20*, 1–9. [[CrossRef](#)]
25. Alguacil, F.J. Mechanistic investigation of facilitated transport of gold(III) from HCl media using ionic liquid Cyphos IL102 as carrier across a supported liquid membrane. *Gold Bull.* **2019**, *52*, 145–151. [[CrossRef](#)]
26. Panda, R.; Dinkar, O.S.; Jha, M.K.; Pathak, D.D. Novel approach for selective recovery of gold, copper, and iron as marketable product from industrial effluent. *Gold Bull.* **2020**, *53*, 11–18. [[CrossRef](#)]
27. Nguyen, N.V.; Lee, J.-C.; Kim, S.-K.; Jha, M.K.; Chung, K.-S.; Jeong, J. Adsorption of gold(III) from waste rinse water of semiconductor manufacturing industries using Amberlite XAD-7HP resin. *Gold Bull.* **2010**, *43*, 200–208. [[CrossRef](#)]
28. Surimbayev, B.N.; Baikonurova, A.O.; Bolotova, L.S. Prospects for the development of the process of intensive cyanidation of gold-containing products in the Republic of Kazakhstan. *News Natl. Acad. Sci. Repub. Kazakhstan Ser. Geol. Tech. Sci.* **2017**, *4*, 133–141.
29. Bolotova, L.S.; Romanenko, A.G. RIP/RIL/RIS technologies in hydrometallurgy of gold. *Miner. Process. J.* **2006**, *5*, 12–15. [Obogashcheniye Rud. (In Russia)]
30. Zharmenov, A.A.; Shalgymbayev, S.T.; Bolotova, L.S.; Petrov, A.I.; Romanenko, A.G. Gold technologies and projects of Kazmekhanobr. In Proceedings of the Abishev readings-2016 International Scientific and Practical Conference «Innovations in the Complex Processing of Mineral Raw Materials»; Almaty, Kazakhstan, 21–22 January 2016; Terlikbayeva, A.Z., Yefremova, S.V., Eds.; Poligrafservis: Almaty, Kazakhstan, 2016; pp. 258–263. [Mezhdunarodnaya nauchno-prakticheskaya konferenciya Abishevskie chteniya-2016 “Innovatsii v kompleksnoj pererabotke mineralnogo cyriya”. (In Russia)].

31. Surimbayev, B.; Bolotova, L.; Mishra, B.; Baikonurova, A. Intensive Cyanidation of Gold from Gravity Concentrates Ina Drum-Type Apparatus. *NEWS Natl. Acad. Sci. Repub. Kazakhstan* **2018**, *431*, 32–37. [[CrossRef](#)]
32. Surimbayev, B.; Bolotova, L.; Baikonurova, A.; Shalgymbayev, S. Application of Acetic ACID as a Reagent-Activator in Intensive Cyanidation of Gravity Concentrates. *Kompleks. Ispol'zovanie Mineral'nogo syr'a/Complex Use Miner. Resources/Miner. Shikisattardy Keshendi Paid* **2019**, *1*, 83–88. [[CrossRef](#)]
33. Surimbayev, B.; Bolotova, L.; Baikonurova, A.; Mishra, B. Intensive cyanidation of gold using an organic reagent-activator. *J. Chem. Technol. Metall.* **2019**, *54*, 387–390.
34. Shalgymbayev, S.T.; Bolotova, L.S.; Dzhhalolov, B.B.; Yakovenko, G.V. Prospects for the processing of carbonaceous arsenic gold-bearing sulfide ores. In Proceedings of the Ninth International Congress “Non-Ferrous Metals & Minerals”, Krasnoyarsk, Russia, 11–15 September 2017; pp. 1315–1316.
35. Efremova, S. Scientific and technical solutions to the problem of utilization of waste from plant- and mineral-based industries. *Russ. J. Gen. Chem.* **2012**, *82*, 963–968. [[CrossRef](#)]
36. Efremova, S. Water treatment with a shungite sorbent and biosorbents on its base. *Russ. J. Appl. Chem.* **2006**, *79*, 397–402. [[CrossRef](#)]
37. Zharmenov, A.; Yefremova, S.; Sukharnikov, Y.; Bunchuk, L.; Kablanbekov, A.; Anarbekov, K.; Murtazayeva, D.; Yessengarayev, Y. Carbonaceous materials from rice husk: Production and application in industry and agriculture. *Inzynieria Miner. J. Polish Miner. Eng. Soc.* **2018**, *1*, 263–274. [[CrossRef](#)]
38. Ahmadvpour, A.; Do, D. The preparation of active carbons from coal by chemical and physical activation. *Carbon* **1996**, *34*, 471–479. [[CrossRef](#)]
39. Zhang, C.; Chen, Z.; Li, J.; Guo, Y.; Cheng, F. Removal of recalcitrant organic pollutants from bio-treated coking wastewater using coal-based carbonaceous materials. *Desalin. Water Treat.* **2017**, *88*, 75–84. [[CrossRef](#)]
40. Yefremova, S.; Kablanbekov, A.A.; Anarbekov, K.K.; Bunchuk, L.V.; Sukharnikov, Y.I.; Bogdanovich, N.I.; Terlikbaeva, A.Z.; Zharmenov, A.A. Carbon Sorbent Based on Special Fine Coke for the Extraction of Gold. *Solid Fuel Chem.* **2019**, *53*, 208–213. [[CrossRef](#)]
41. Yefremova, S.; Kablanbekov, A.; Anarbekov, K.; Bunchuk, L.; Terlikbayeva, A.; Zharmenov, A. Coke-Based Carbon Adsorbent. In *Proceedings of the 18th Symposium on Environmental Issues and Waste Management in Energy and Mineral Production*; Springer Science and Business Media LLC: Berlin/Heidelberg, Germany, 2018; pp. 217–224.
42. Zharmenov, A.A.; Terlikbayeva, A.Z.; Yefremova, S.V.; Bunchuk, L.V.; Kablanbekov, A.A.; Anarbekov, K.K. Method of obtaining carbon sorbent on the basis of special coke. KZ Patent 34132, 17 April 2020.
43. Pernyeszi, T.; Farkas, R.; Kovács, J. Methylene Blue Adsorption Study on Microcline Particles in the Function of Particle Size Range and Temperature. *Minerals* **2019**, *9*, 555. [[CrossRef](#)]
44. Kołodziejka, D.; Fila, D.; Hubicki, Z. Evaluation of possible use of the macroporous ion exchanger in the adsorption process of rare earth elements and heavy metal ions from spent batteries solutions. *Chem. Eng. Process. Process. Intensif.* **2020**, *147*, 107767. [[CrossRef](#)]
45. Olalekan, A.P.; Dada, A.O.; Okewale, A.O. Comparative adsorption isotherm study of removal of Pb<sup>2+</sup> and Zn<sup>2+</sup> onto agricultural waste. *Res. J. Chem. Environ. Sci.* **2013**, *1*, 22–27.

