Disposal of highly toxic waste chromium solutions

Komil Mukhammadiev[1*], *Dilrabo* Mukhammadieva[1], *Akhan* Demeuov[1], and *Inoyatkhan* Tuichyeva [1]

[1]Tashkent State Transport University, 100069 Tashkent, Uzbekistan

Abstract. The aim of the study is to determine the effect of organic reductants (sawdust) on the degree of reduction of chromium (VI) ions in the complex processing of waste chromium-containing solution (electrolyte) of plating production, as at the same time to determine the optimum conditions of the process. Experimental results showed that organic reductants (sawdust, and lignin) in an acid environment work as a reagent-reductant of chromium (VI) ions. The process of reduction of chromium (VI) ions to chromium (III) proceeds intensively for the first 20-30 min and is completed within 50 minutes, while about 1.0-2.5% of chromium (VI) ions remain unreduced, and 97.0-99.0% of chromium (VI) ions of the total amount pass into trivalent form. Chromium (VI) ions are reduced at the first stage of the process, the bulk of them are converted into chromium (III) ions and emitted as chromium (III) hydroxide, and wastewater is further purified at the second stage. When using lignin, the reduction in the concentration of chromium (VI) ions is insignificant, since the number of active functional groups in its structure is limited. Model studies presented in this work and their approbation on production wastewater showed expediency and sufficiently high efficiency of using woodworking wastes (sawdust) to reduce chromium (VI) ions from the spent solutions. Sawdust consists mainly of cellulose; its structure contains functional groups that act as a reductant during oxidation. Further study of the process mechanism and characteristics is essential for the development of recommendations for their utilization.

1 Introduction

It is generally known that heavy metals are a major component of wastewater pollution from various industrial plants (Pellerin & Booker, 2000; Minas et al., 2017; Grace Pavithra et al., 2019). One of the hazardous pollutants is Cr (VI) ions, the disposal of which is a serious problem nowadays. Wastewater from chemical, electroplating, leather, textile, metallurgical, woodworking, pulp and paper, and paint industries that contain significant amounts of Cr (VI) ions causes serious damage to aquatic ecosystems (Zayed & Terry, 2003), and they also, in turn, affect humans through pollution of surface water, groundwater, and food chain poisoning. According to the US Environmental Protection Agency (USEPA) regulations and

* Corresponding author: komilmuhammadiev@yandex.ru

the maximum permitted concentrations (MPC) adopted in Uzbekistan, the concentrations of Cr (VI) ions in household and drinking water are 0.1 and 0.05 mg/l, respectively.

One of the major objectives of modern science is the creation of safe and efficient water management technologies. At present, in industry, there are a significant number of different methods of wastewater treatment from heavy metal ions and chromium compounds in particular. These include chemical precipitation, ion exchange, reverse osmosis, evaporation, solvent extraction, adsorption, electrocoagulation, electro-deionization, electrochemical reduction, membrane filtration, photocatalysis, biological treatment, etc. (Timofeev & Lykova, 1985; Shemyakina et al., 1995; Li JiaYu et al., 2003; Zakaria et al., 2009; Gunatilake, 2015; Erkabaev & Eshmetov, 2016; Un et al, 2017; Li et al., 2017; Erkabaev & Urozov, 2018; Rambabu, 2020; Ibrahim et al., 2022; Rajapaksha et al., 2022; Solovieva et al., 20224 Erkabaev & Mukhammadieva, 2022). Each method has both positive and negative sides, the main of them requires the use of expensive equipment, significant energy costs, and large areas, while the range of acceptable parameters of the effluent treatment is very narrow.

The purpose of this study is to determine the effect of the nature of organic reductants (sawdust of pine, birch, poplar, shredded cotton stalks, and cotton lignin) on the degree of reduction of chromium (VI) ions during complex processing of waste chromium solutions, and to determine the optimal conditions for the processing of waste highly toxic chromium solution.

2 Methodology

2.1 Research objects

The research was conducted in 2021-2022 in the production conditions of the plant "METFURSERVIS" LLC (Tashkent City, Uzbekistan). The main activity of "METFURSERVIS" LLC is the production of spare parts for vehicles produced by "UZAUTO MOTORS". The highly toxic waste solution from the chrome plating workshop and woodworking wastes such as sawdust of pine, birch, and poplar, as well as crushed cotton stalks and cotton lignin, was chosen as an experimental object.

2.2 Research methods and equipment

The research objectives included a sampling of the initial waste chromium-containing solution (electrolyte) of electroplating production and preparation of an identical model solution with a concentration of Cr (VI) ions - 50000.0 mg/l, laboratory analytical, and experimental work. All experiments were carried out on the model solutions of the waste electrolyte of the chromium plating site of the plant LLC "METFURSERVIS". In the solution samples the quantitative content of chromium ions was determined by spectrophotometry. All chemicals used were of analytical purity quality (Prolabo). Buffer solutions were prepared according to Leed (2003). A Helios Alpha model Unicam spectrophotometer with corresponding 1 cm quartz cuvettes was used to determine the content of Cr (VI) ions and iron (III) ions in the samples before and after the reduction process. All measurements were performed at 25◦C in triplicate, and the results were expressed as the average of these three measurements. The pH was measured using a Hanna pH meter.

The key objectives of this study were to evaluate the reducing ability of organic reductants different in nature (sawdust of pine, birch, poplar, as well as shredded cotton stalks, cotton lignin) in the reduction of Cr (VI) ions, to compare their reducing properties as well as to determine the optimal conditions of Cr (VI) ions reduction and integrated recycling of spent solutions.

The essence of the method consists of the preliminary release from iron (III) ions of a model sample of spent electroplating solution; chemical reduction of chromium (VI) ions to chromium (III) using organic reductants (sawdust, lignin); precipitation of chromium (III) hydroxide in the studied solution; its separation and obtaining chromium (III) oxide from it; determination of the influence of the nature of organic reductants on the degree of reduction.

2.3 Experiments

The following proportions of components were selected for the experiment: the volume of the model sample of the initial chromium-containing solution - 200 ml; the content of iron (III) ions - 10000.0 mg/l, the content of hexavalent chromium ions - 50000.0 mg/l; organic reductant added in the process - 20 g; concentrated sulfuric acid - 10 g; the process took place at 250°C without preheating; the duration of the process under stirring - 1.0 hour.

The experiment was performed in an enameled reactor with a stirrer and consisted of the following stages:

- filling a model sample of the initial chromium-containing solution of the calculated volume with the concentration of 50000.0 mg/l and neutralizing its pH from 7.3-8.1 with caustic soda;
- the process of precipitation of iron (III) ions;
- extraction of iron (III) hydroxide precipitate on Nutsche filter;
- addition of an organic reductant (sawdust, lignin) in a 1:1 ratio with calculated chromium (VI) ions;
- oxidation of the medium in the reactor with sulfuric acid to pH 3-4;
- reduction process of chromium (VI) ions for 1 hour, with slow stirring;
- the neutralization of the environment with caustic soda to pH 4.9-6.8;
- the process of precipitation of chromium (III) ions as Cr(OH)3↓ and its separation by filtration on the Nutsche filter;
- Precipitation of excess SO42- ions in the filtrate, with the addition of hydrated lime (Ca(OH)2), with subsequent separation as gypsum (CaSO4 x 2H2O);
- drying of chromium (III) hydroxide and roasting (obtaining chromium (III) oxide);
- chromium pigment grinding and packaging.

To establish the optimal conditions for the reduction process of Cr(VI) ions using wood sawdust, the influence of the following parameters on the degree of their reduction was studied:

- the influence of the variety of organic reductant;
- the influence of the relative amount of reductant used in the reduction process;
- the influence of the contact time of the reagent and the reductant;
- the influence of concentrations of hexavalent chromium ions in the initial chromate-containing solutions.

3 Results and discussion

In order to evaluate the capacity of organic reductants different in nature (sawdust of pine, birch, poplar, shredded cotton stalks, cotton lignin) to reduce Cr (VI) ions, to compare their reducing properties, to determine the optimal conditions of Cr (VI) ions reduction, a series of experiments were conducted on the model waste solution of the galvanic workshop.

In the course of the study, the experimental model solution, released from iron (III) ions, was mixed with a certain amount of organic reductants and incoming concentrated sulfuric acid in small doses. Due to the exothermic reaction, the temperature of the solution rose to 600-700C and the color of the solution gradually turned green, which directly indicates the reduction of Cr (VI) ions to Cr (III) ions. Studies have shown that in the process, the wood species does not significantly affect the degree of reduction (see Table 1).

Table 1. Influence of the variety of organic reductant (OR) on the degree of reduction of chromium (VI) ions

($V_{solution}$ = 200 ml, OR = 20 g, H_2SQ_4 = 10 g, τ = 1,0 h)

Organic reductant	Initial concentration of chromium ions in solution, mg/l			Final concentration of chromium ions in solution, mg/l		
	Cr^{6+}	Cr total	Cr^{3+}	Cr^{6+}	Cr total	Cr^{3+}
Pine tree sawdust	44500,0	50000,0	5500,0	65,0	49853,0	49760,0
Birch sawdust	44500,0	50000,0	5500,0	87,5	49792,0	49670,0
Poplar sawdust	44500,0	50000,0	5500,0	81,0	49711,0	49580,0
Cotton stalk	44500,0	50000,0	5500,0	99,4	40570,0	49540,0
Cotton lignin	44500,0	50000,0	5500,0	29540,0	49692,0	19320,0
Note: Due to the loss of chromium (about 0.1-0.3%) during reduction, a slight deviation in the concentration of $C_{Cr\ total}$ before and after reduction.						

All samples of organic reductants showed positive results and the content of chromium (VI) ions decreased from 50,000.0 mg/l to 65.0 mg/l, i.e. the residual concentration of chromium (VI) ions below 100 mg/l, which can be explained by the relatively large number of functional groups in the structure of cellulose in the wood and cotton stems. When lignin was used, the content of chromium (VI) ions decreased from the initial 50,000.0 mg/l only to 29340.0 mg/l, which indicates a lack of active functional groups in its structure.

The experiments used 5 to 25 g of sawdust, shredded cotton stalks, and cotton lignin. The results of the experiments showed that for the reduction of chromium (VI) ions, 10 g of sawdust is enough, which corresponds to the ratio - "organic reductant: chromium (VI)" in the initial solution of about 1:1 ratio (see Table 2).

Table 2. Degree of reduction of chromium (VI) ions to chromium (III) from the amount of organic reductants

($CCr_{origin.}$ = 50000 mg/l; $V_{solution}$= 200ml; H_2S0_4 = 10 g; τ = 1,0 h)

Amount of organic reductants, g	Initial concentration chromium ions in the solution, mg/l			Final concentration chromium ions in the solution, mg/l			Solution color
	Cr^{6+}	Cr_{total}	Cr^{3+}	Cr^{6+}	Cr_{total}	Cr^{3+}	
1	47750	50000	1250	47235	49833	2720	pale yellow
3	47750	50000	1250	42923	49871	6932	pale yellow
5	47750	50000	1250	32562	49876	17939	pale yellow
7	47750	50000	1250	11325	49912	38698	pale green
8	47750	50000	1250	6562	49880	43320	pale green
10	**47750**	**50000**	**1250**	**99,6**	**49903**	**49855**	green
15	47750	50000	1250	86,1	49856	49877	green
20	47750	50000	1250	55,7	49810	49902	yellow-green
25	47750	50000	1250	53,2	49801	49878	yellow-green

Determining the dependence of the degree of reduction of chromium (VI) ions to chromium (III) ions on the contact time of the components of the experiment showed that the recovery is most intense in the first 25-25 minutes of the process when the bulk of chromium (VI) ions is reduced - up to 80-90% (see Table 3).

Table 3. Influence of the variety of organic reductants (OR) on the degree of reduction of chromium (VI) ions

($V_{solution}$= 200 ml, OR = 20 g, H_2SO_4 = 10 g, τ = 1,0 h)

Time, min	**Initial concentration of chromium in the solution, mg/l**			**Final concentration of chromium in solution, mg/l**					
	Cr^{6+}	Cr_{total}	Cr^{3+}	Cr^{6+}	%	$Cr_{общ}$	%	Cr^{3+}	%
5	47500.0	50000.0	2500.0	580.5	52.65	49420.0	98.01	37620.0	47.35
10	47500.0	50000.0	2500.0	375.8	37.8	49420.0	98.04	42620.0	62.20
15	47500.0	50000.0	2500.0	375.8	18.7	49420.0	98.04	42620.0	81.30
20	47500.0	50000.0	2500.0	375.8	7.80	49420.0	98.04	42620.0	92.20
25	47500.0	50000.0	2500.0	286.5	4.59	49560.0	98.75	49720.0	95.41
30	47500.0	50000.0	2500.0	136.5	2.48	49600.0	98.67	48260.0	97.52
40	47500.0	50000.0	2500.0	98.0	1.63	49720.0	98.61	48240.0	98.37
50	**47500.0**	**50000.0**	**2500.0**	**62.0**	**0.52**	**49720.0**	**98.61**	**49240.0**	**99.44**
60	47500.0	50000.0	2500.0	61.0	0.52	49720.0	98.61	49240.0	99.48

Not reduced remain about 1.0-2.5% of chromium (VI) ions, and in the trivalent form go 98-99% of the total amount of chromium. Some amount of chromium (III) ions is sorbed in sawdust, which can be easily desorbed by washing with 1% nitric acid solution, 1% hydrogen peroxide solution or warm water. The separated residue of the organic reducing agents (the volume will decrease by a factor of about 3-4) can be used to recover a new portion of the spent chromium solution. Increasing the contact time of the components in the reaction medium for more than 1.0 hour does not affect the degree of reduction of chromium (VI) ions and it was found that the optimal time of the process is 50-60 min.

Studies have shown that sawdust, under certain conditions, can reduce chromium (VI) ions at their high concentrations, the degree of reduction also affects the content of hexavalent chromium ions in the initial solution.

To determine the effect of the initial concentration of Cr (VI) ions on the process of its reduction, the dependence of the reduction of Cr (VI) ions on different initial concentrations of chromium in the solution was determined. Model solutions with initial concentration of Cr (VI) ions - 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 120, 150 g/l were prepared.

Experimental results showed that with decreasing concentration of Cr (VI) ions in the initial solution, respectively, the residual concentration of Cr (VI) ions in the final solution after the reduction process decreases (see Fig. 1). At initial concentrations of chromium in solutions not exceeding 100 g/l, the reduction process of Cr (VI) ions proceeded without difficulty and the residual concentration of Cr (VI) ions decreased to acceptable values. Such solutions can be directly sent for final chemical or electrocoagulation purification to the required maximum permissible concentrations.

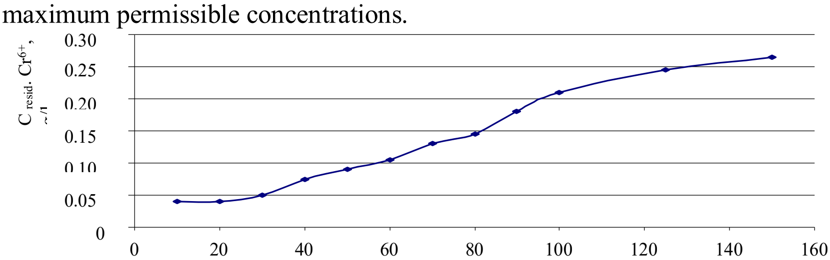

Fig. 1. Changes in the residual concentration of Cr (VI) ions after reduction, depending on the initial concentration of the chromium-containing solution. OR – 10 g; $H_2SO_{4concent.}$ = 10 г; $V_{solution}$= 200 ml; τ = 50 min

At initial chromium concentrations in solutions exceeding 100 g/l, foaming of the solution and formation of a thick mass of sediment were noted. If the concentration of Cr(VI) initial solution exceeds this limit, dilution to a concentration of 50-100 g/l is recommended.

Experiments to study the capacity to reduce chromium (VI) ions of various organic reducing agents by nature carried out on the model spent solution of the galvanic shop showed that sawdust effectively reduces chromium (VI) ions. In this case, the species of wood from which sawdust is obtained does not significantly affect the degree of reduction, and cotton lignin because of the limited functional groups in its structure showed relatively low results. The technical result of the experiments on the model spent solution of the plating shop is a completely effective utilization of highly toxic liquid waste containing chromium (VI) ions using wood sawdust and obtaining chromium pigment powder, a valuable commercial material.

4 Conclusion

The method of purification of spent solutions from chromium (VI) ions was developed and tested on a model spent solution of the galvanic shop using organic reductants (sawdust of pine, birch, poplar, and shredded cotton stalks). The results showed that during the reduction of chromium (VI) ions to chromium (III) ions, the different nature of the studied organic reductants does not affect the degree of the reduction process. The reduction properties of sawdust are relatively higher than those of cotton stalks, which is due to the large number of functional groups in the structure of cellulose in wood, while the number of functional groups in cotton lignin is limited. The process of reduction of chromium (VI) ions proceeds for 50 min, but most actively in the first half of the process, when the bulk of chromium (VI) ions is reduced (up to 70-80%).

The method is environmentally acceptable and energy-saving since the process occurs by the exothermic effect of the interaction reaction, which determines the high rate of flow. It can be recommended to enterprises where highly concentrated spent chromium-containing solutions are formed, as well as in combination with other methods of purification (post-treatment) depending on the objectives.

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