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Studies Concerning the Heavy Metals Removal from Residual Waters Resulted from Thermal Zinc Coating

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Abstract: In this paper we made studies regarding the heavymetals removal from residual waters resulted from thermal zinc coating. In the view of the optimum conditions establishment of heavymetals removal from the residual waters we used different neutralisation agents (sodium hydroxide solution 30%, sodium carbonates 10%, calcium oxide, mixture of sodium hydroxide and sodium carbonates, and sodium hydroxide with aeration).

Keywords: waste waters, heavymetal removal, neutralisation

1. Introduction

Thermal zinc coating is a galvanic coating process of the metal surfaces in the view of the proprieties improvements of the metals pieces.

Before the thermal zinc coating the pieces are submit of a preparing process which consist in degreasing, chemical cleaning, washing, fluidizer treatment and pre warming [1]. After these operations result residual waters with a higher content of heavymetals.

The heavymetals can have a pollutant effect on the environment. A part from these metals are considered microelement, they having a special importance in plant growing and animal nutrition if they don't over a maxim concentration over which they can become very toxically for the plant and animals and human health [2, 3].

For the removal and recovering of heavymetals from the residual waters are used different methods: precipitation, ionic exchange, membrane separation, cementation, by electrochemical methods [4-7].

In this paper was study the optimum conditions establishment of the metals ions removal process by residual waters treatment resulted from thermal zinc coating with different neutralisation agents.

2. Experimental

The residual waters resulted from the chemical cleaning and degreasing were analysed in the view of these acidity, respective alkalinity establishment.

These waters with the washing waters were mixed in a ratio 1:1:1 and the resulted solution was also analysed.

For the removal and recovering of heavy metals from this solution we used different neutralisation agents: sodium hydroxide solution 30%, sodium carbonates 10%, calcium oxide, mixture of sodium hydroxide and sodium carbonates, and sodium hydroxide with aeration.

In the view of metals ions removal with sodium hydroxide and sodium carbonates was determinate the stoechiometry content of the neutralisation agent for 100 ml residual solution.

In the case of calcium oxide use for neutralisation we used two different type of oxide in solid and suspensions forms.

When we used for the residual waters neutralisation the sodium hydroxide and aeration we used an air debit of 80 dm^3/min.

After neutralisation the formed precipitate were filtrated and in the solution were determined the residual concentration of heavymetals and the degree of separation.

We determined the dependence of the heavymetals residual concentration and of the degree of separation function of the time of agitation, pH and the ratio solution : neutralisation agent.

The alkalinity, acidity and the iron ions concentration were determined by titration and the zinc and lead concentration were determined by atomic absorption spectrophotometer method using an spectrophotometer VARIAN SpectrAA 110.

The pH solutions were determined with a pH-meter DENVER 50.

3. Results and discussion

3.1. The residual waters analyse

The experimental data regarding the analyses of the solution resulted from the chemical cleaning and degreasing are presented in table 1.

TABLE 1. The solution resulted from chemical cleaning and degreasing analyses.

No. crt	Parameter / Sample	Acidity	Alkalinity	Conc. of iron ions
1.	Sol. resulted from chemical cleaning	227.049 g/L HCl	-	78.4g/L
2.	Sol. resulted from degreasing	-	42.4g/L Na_2CO_3 48g/L NaOH	1.12g/L

These waters with the washing waters were mixed in a ratio 1:1:1 and the resulted solution was also analysed. The experimental data regarding the analyses of the resulted solution are presented in table 2.

TABLE 2. The analyses of the resulted solution by the mixing in ratio 1:1:1 of the solution resulted from chemical cleaning, degreasing and washing.

No.	Parameter	Value
1.	Acidity	52.71 g/L HCl
2.	Fe Conc.	28.56 g/L
3.	Zn Conc.	2.838 g/L
4.	Pb Conc.	4.95mg/L

We can observe that by the mixing of those3 solution in ratio 1:1:1 take place a decreasing of the acidity and of the iron ions concentration so it is produce a partial neutralisation of the waters resulted from chemical cleaning.

3.2. Studies regarding the removal of heavy metals from solution with NaOH 30%

The experimental data regarding the dependence of the residual concentration of heavy metals and the degree of removal function of the agitation time are presented in table 3.

From the experimental data we can observe that the residual concentration of heavy metals and the separation degree don't depend in a big measure by the time of agitation. We consider the optimum time of agitation the time of 30 minutes.

TABLE 3. The dependence of the heavy metals residual concentration and the degree of separation function of the agitation time.

No.	Time of agitation, min	pH	Fe		Zn		Pb	
			Res. conc., g/L	η %	Res. conc., g/L	η %	Res. conc., mg/L	η %
1.	15	7.60	1.12	96.08	0	100	0	100
2.	30	7.69	0.56	98.04	0	100	0	100
3.	45	7.70	0.56	98.04	0	100	0	100
4.	60	7.78	0.56	98.04	0	100	0	100

TABLE 4. The dependence of heavy metals residual concentration and the degree of separation function of pH and the ratio solution:NaOH at the agitation time of 30 min.

No.	Ratio solution:NaOH	pH	Fe		Zn		Pb	
			Res. conc., g/L	η %	Res. conc., g/L	η %	Res. conc., mg/L	η %
1.	1: 0.9	6.55	9.52	66.66	0.874	99.97	0	100
2.	1: 1	7.69	0.56	98.04	0	100	0	100
3.	1:1.5	11.63	0	100	2.27	99.92	0	100

The experimental data regarding the dependence of the heavy metals residual concentration and the degree of separation function of the pH and the ratio solution:NaOH at the agitation time of 30 minutes are presented in table 4.

From the experimental data we can observe that the optimum pH of the metal ions removal is 7.69 obtained at the ratio solution:NaOH 1:1. With the increasing of the ratio, respective of the pH the degree of removal of the Fe and Pb ions increase respective the residual concentration decrease, but in the case of Zn ions take place the re dissolving of these.

3.3. Studies regarding the removal of heavy metals from solution with Na_2CO_3 10%

The experimental data regarding the dependence of the residual concentration of heavy metals and the degree of removal function of the agitation time are presented in table 5.

From the experimental data we can observe that the residual concentration of heavy metals and the separation degree don't depend in a big measure by the time of agitation. We consider the optimum time of agitation the time of 30 minutes.

TABLE 5. The dependence of the heavy metals residual concentration and the degree of separation function of the agitation time.

No.	Time of agitation, min	pH	Fe		Zn		Pb	
			Res. conc., g/L	η %	Res. conc., g/L	η %	Res. conc., mg/L	η %
1.	15	6.62	6.16	78.43	3.528	99.87	0	100
2.	30	6.71	5.60	80.39	3.290	99.88	0	100
3.	45	6.79	5.04	82.35	2.940	99.89	0	100
4.	60	6.80	4.48	84.31	1.498	99.94	0	100

TABLE 6. The dependence of heavy metals residual concentration and the degree of separation function of pH and the ratio solution:Na_2CO_3 at the agitation time of 30 min.

No.	Ratio solution:Na_2CO_3	pH	Fe		Zn		Pb	
			Res. conc., g/L	η %	Res. conc., g/L	η %	Res. conc., mg/L	η %
1.	1: 0.9	5.98	10.08	64.71	7.32	99.74	0	100
2.	1: 1	6.71	5.60	80.39	3.29	99.88	0	100
3.	1:1.5	8.94	0.56	98.04	0	100	0	100

The experimental data regarding the dependence of the heavy metals residual concentration and the degree of separation function of the pH and the ratio solution:Na_2CO_3 at the agitation time of 30 minutes are presented in table 6.

From the experimental data we can observe that with the increasing of the ratio solution:Na_2CO_3, respective with the increasing of pH decrease the heavy metal residual concentration and increase the degree of removal.

3.4. Studies regarding the removal of heavy metals from solution with CaO

The experimental data regarding the solution pH dependence function of the agitation time are presented in table 7.

We can observe that even after 48 hours of agitation wasn't achieved the optimum pH of neutralisation between 7 and 8. The residual concentration of the heavy metals and those degrees of removal in the case of use for neutralisation of the calcium oxide are presented in table 8.

TABLE 7. The dependence of the solution pH function of the time of agitation

	Time / Sample	15 min	1h	2h	24h	27h	48h
		pH					
Type 1	Suspension	5.65	5.75	5.82	5.76	5.92	5.95
	Solid	5.49	5.65	5.83	5.65	5.74	5.62
Type 2	Suspension	1.02	1.23	1.37	1.41	1.52	1.71
	Solid	1.17	1.24	1.37	1.37	1.54	1.63

TABLE 8. The residual concentration and the degree of separation of the heavymetals in the case of solution neutralisation with calcium oxide

Sample		Fe		Zn		Pb	
		Res. con.c. (g/L)	η (%)	Res. conc. (g/L)	η (%)	Res. conc. (mg/L)	η (%)
Lime type 1	Suspension	8.4	70.58	2.685	5.3	1.71	65.45
	Solid	16.24	43.13	2.685	5.3	1.96	60.40
Lime type 2	Suspension	20.56	28	2.7	4.86	3.95	20.2
	Solid	24.58	13.9	2.75	3.1	4	19.19

TABLE 9. The analyse of the obtained sludge by the neutralisation of the solution with the calcium oxide

Sample		Fe		Zn		Pb		Ca		Insolubles	
		Conc (g/L)	η (%)	Conc mg/L	η (%)	Conc (mg/L)	η (%)	Conc. (g/L)	η (%)	Content (g)	η (%)
Lime type 1	Suspension	0.56	5.6	6.14	0.06	0.3	0.003	2	20	0.22	22
	Solid	0.56	5.6	6.06	0.06	0.21	0.002	1.2	12	0.358	35.8
Lime type 2	Suspension	0.56	5.6	2.63	0.02	0.3	0.003	2.2	22	0.415	41.5
	Solid	0.56	5.6	2.65	0.02	0.29	0.002	1.4	14	0.721	72.1

From those two types of lime used we can observe that the first type is more efficient, we obtained smaller residual concentration of the heavy metals, respective bigger degrees of separation when this is used under suspension form.

The higher efficiency of the first type of calcium oxide can be observed also from the experimental data regarding the sludge analyse obtained in these conditions, presented in table 9. The sludge analysis was made by dissolving 1 gram of sludge in 20 ml HCl 20%. Than the solution was filtrated, and in this we determined the metals ions concentration extracted from sludge. The precipitates from the filtrate paper represent the insolubles.

From the experimental data we can observe the higher content of insoluble, with consist in the fact that the second type of lime is more impure, also we can observe the lower quantity of metals ions from sludge, which shows the fact that this procedure of metals ions removal from residual waters resulted from thermal zinc coating doesn't present very good results.

3.5. Studies regarding the removal of heavymetals from solution with mixture of NaOH and Na_2CO_3

NaOH give very good efficaciousness, but has the disadvantage that is very expensive. Using Na_2CO_3 we obtain also good efficaciousness, but this present the disadvantage of the abundant frothing.

To eliminate these disadvantages we use NaOH until the pH=6.4, in this way is neutralised a portion of the free acid, than we introduce Na_2CO_3 until the pH=7.9. In this way we use a lower quantity of NaOH and we avoid the frothing of the mass reaction.

The experimental data regarding the residual concentration of the metals ions, respective the degrees of separation in the case of use for neutralisation of the mixture NaOH with Na_2CO_3 are presented in table 10.

TABLE 10. Residual concentrations of the metals ions, respective the degrees of separation in the case of use for neutralisation of the mixture NaOH with Na_2CO_3

No.	Element	Concentration (g/L)	η (%)
1.	Fe	0.56	98.04
2.	Zn	0	100
3.	Pb	0	100

3.6. Studies regarding the removal of heavy metals from solution with NaOH and aeration

The experimental data regarding the dependence of the metals ions residual concentration, of the degrees of removal and of pH function of the aeration time are presented in table 11.

From the experimental data we can observe an accentuated decrease of the residual concentration and an increasing of the degree of separation only after 24 hours of aeration.

TABLE 11. Dependence of the metals ions residual concentration, of the degrees of removal and of pH function of the aeration time

No.	Aeration time	pH	Fe		Zn		Pb	
			Res. con.c. (g/l)	η (%)	Res. conc. (g/l)	η (%)	Res. conc. (mg/l)	η (%)
1.	15 min	6.79	5.6	80.39	2.63	7.33	0.81	83.63
2.	30 min	6.80	5.6	80.39	2.63	7.33	0.81	83.63
3.	1 hour	6.78	5.04	82.35	2.48	12.61	0.65	86.86
4.	24 hours	6.75	2.91	89.81	0.18	93.65	0	100

4. Conclusions

In this paper we followed the optimum conditions establishment of the metals ions (Fe, Zn and Pb) removal from residual waters resulted from thermal zinc coating.

The waters resulted from the phases of chemical cleaning, degreasing and washing of the thermal zinc coating process were mixed in the ratio 1:1:1 in this way was realised a partial neutralisation of waters resulted from chemical cleaning and a reduction of the iron ions concentration.

In the view of removal and recovering of heavymetals from this solution we used different neutralisation agents: sodium hydroxide solution 30%, sodium carbonates 10%, calcium oxide, mixture of sodium hydroxide and sodium carbonates, and sodium hydroxide with aeration.

From the experimental data we can observe that from all the used neutralisation agents the most efficient is NaOH, but this is the most expensive too. Using Na_2CO_3 we obtain also good efficaciousness, but this present the disadvantage of an abundant frothing of the mass reaction. To eliminate these two disadvantages we use a mixed of NaOH and Na_2CO_3. In the case of solutions neutralisation with NaOH and aeration we obtain satisfactory results but only after 24 hours of aeration. The use of calcium oxide doesn't present higher efficiency and also we need a minimum 24 hours of agitation.

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