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REMOVAL OF CHROME AND ZINC FROM INDUSTRIAL WASTEWATER USING ELECTRICAL PRECIPITATION AND BENTONITE CLAYS

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Abstract: This study deals with removal of (Cr and Zn) from industrial wastewater resulted from production processes in the State Company of Electrical Industries (S.C.E.I.). The removal process of these metals includes two stages; the first stage is the electrical precipitation of Cr and Zn metals, where Cr concentrations before and after performing this stage are 262 ppm and 26.6 ppm, respectively, while it is 1865 ppm and 45ppm for Zn. The second stage includes treatment with bentonite clay to remove the remaining concentrations of heavy metals in industrial wastewater to be within Iraqi standard specification for discharging in to river. Concentrations are < 0.1 ppm and < 1.0 ppm after applying this stage. These processes are suggested to be an alternative method to that in the State Company of Electrical Industries which uses the chemical precipitation that produce wastes with high concentrations of chrome and zinc, which stored in containers until discarded.

Keywords: *industrial wastewater, electrical precipitation, chemical precipitation, bentonite.*

ازالة الكروم و الزنك من المياه الصناعية باستخدام الترسيب الكهربائي وأطيان البنتونايت

الخلاصة: في هذا البحث تمت دراسة ازالة (الكروم و الزنك) من مياه الصرف الصناعي المتكونة عن عمليات الإنتاج في الشركة العامة للصناعات الكهربائية. حيث تضمنت عملية الازالة مرحلتين، المرحلة الأولى هي الترسيب الكهربائي لعناصر الكروم و الزنك حيث كان تركيز عنصر الكروم 262 وبعد اجراء المرحلة الأولى اصبح 26.6 جزء في المليون، اما بالنسبة الى عنصر الزنك فقد كان 1865 واصبح 45 جزء في المليون. اما المرحلة الثانية فهي تتضمن المعاملة مع اطيان البنتونايت لإزالة ما تبقى من تراكيز العناصر الثقيلة في مياه الصرف الصناعي لجعلها مطابقة للمواصفات القياسية العراقية لتصريفها إلى النهر مرة أخرى. التراكيز هي (الكروم = < 0.1 جزء في المليون والزنك = < 1.0 جزء في المليون) بعد تطبيق هذه المرحلة. الطريقة اقترحت بديلا عن الطريقة التقليدية المتبعة في الشركة العامة للصناعات الكهربائية والتي تستخدم تقنية الترسيب الكيميائي عن طريق إضافة مواد كيميائية مختلفة ينتج عنها رواسب تحتوي على تراكيز عالية من الكروم والزنك التي تخزن في حاويات لحين التخلص منها.

1. Introduction

Iraqi rivers characterized by high rate of pollution as a result of throwing industrial wastewater and sewage directly without treatment in spite of the fact that dumped water contains high concentrations of heavy and toxic metals(mercury, lead, chromium, zinc and copper) which harms the human's health and the river's environment for long term.

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Pollution is a quantitative or qualitative change in living and non-living components of the environment and the environmental regulations are not estimated to absorb it without imbalance.

With reference to the change must be result of the work of human not of natural imbalance that may occur in the environment [1].

Heavy metals are dangerous because these tend to bioaccumulations. Bioaccumulation means an increase in the concentration of a chemical in an organism over time, compared to its concentration in the environment. Heavy metals may enter a water supply through industrial or consumer wastes releasing heavy metals into streams, lakes, rivers, and ground water [2,3].

The presence of heavy metals and their toxicity to the environment and to human beings poses a serious challenge to environmental engineers with respect to the treatment of wastewater effluents prior to discharge into the nearby water bodies. Several removal techniques have been developed and applied for the treatment of these wastes to remove the toxic metal ions. Technologies such as microbe-assisted phytoremediation, ion exchange, membrane filtration, photocatalytic oxidation and reduction and adsorption have their own advantages and disadvantages over metal ion sequestration from environmental matrices [4].

The waste water often comes from the dyes and pigment industries, film and photography, galvanometric, metal cleaning, electroplating, leather and mining industries. In this field, a lot of research has been conducted using some traditional techniques of waste water treatment such as precipitation and ion exchange. In general, these techniques used some expensive industrial materials such as activated carbon and some industrial ion exchange resins. Therefore, it was necessary to find a new strategy to remove these toxic heavy metals based on using cheap and abundant natural materials which is characterized by high efficiency [5, 6].

The most heavy metals present in the industrial wastewater are chrome and zinc Chrome is most commonly present in the environment in three forms: trivalent (Cr^{+3}), hexavalent (Cr^{+6}) and Cr, the metal form. (Cr^{+3}) is an essential micro-nutrient in the human diet and generally not considered toxic. (Cr^{+6}) is known to pose human health risks from inhalation [4].

Zinc is also an essential element in our diet, too much zinc, however, can also be damaging to health, zinc toxicity in large amounts causes nausea and vomiting in children, a higher concentration of zinc may cause anemia and cholesterol problems in human beings [7].

In this research used electrical cell to reduce concentrations of chrome and zinc as well as used bentonite clay for the same purpose, after ending of two stages we can discharge industrial wastewater without any toxics on fluvial environment and become within the permissible concentrations of the Iraqi Standard Specification [8]. as showed in methods of work..

Many researchers and Techniques have investigated the removal of industrial wastewater from (Cr and Zn) are some assorted studies; Petruzzelli [7] showed the possibility of ion exchange removal of chromium process is based on a weak electrolyte carboxyl resin, able to remove the metals from the liquid effluent followed by selective separation and recovery during a regeneration step, the resin is regenerated with alkaline hydrogen peroxide brines (0.15 M) H_2O_2, (1M) NaCl, (O.1M) NaOH, pH =11 through an internal oxidation of chromic species to chromate, another studying of Fenglian [4] who studied various methods for heavy metal removal from wastewater that have been extensively studied with using technologies include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation–flocculation, flotation and electrochemical methods, two research for Abdel munaem [6] and Lutfi [1] the first studied soil pollution with heavy metals and its impact on the plants and the potential for their groundwater sources and explained several preventive methods designed to protect the soil from heavy elements and the second invented innovative way to remove heavy metals from water (Ba^{2+},Cr^{6+},Pb^{2+},Hg^{2+},As^{3+}) by using nanomaterial's.

The study included a wide range of tests in different degrees of acidity and basal (ph) materials. They were able to remove 80% of arsenic (III), and 99% of lead (II), and 98% of chromium (VI), and 95% of barium (II).

2. Materials and Methods

2.1. *Materials*

2.1.1. Bentonite

Bentonite clay was brought from Bashera Valley region, in the Iraqi Western Desert. It is high quality calcium and milled for up to (75 micron), the chemical composition of clay which analyzed by Iraq geosurve laboratories and shown in Table [1]**.**

Table 1. Chemical analysis of the bentonite clay.

SiO_2%	Al_2O_3%	Fe_2O_3%	CaO%	MgO%	Na_2O%	K_2O %	L.O.I %
56.83	19.51	3.81	4.25	4.71	1.65	1.2	8.03

2.1.2. Industrial hydrochloric acid

Hydrochloric acid is an industrial type with 16% concentration which take from rests industrial processes add to samples before put it in electrical cell.

2.1.3. Industrial wastewater

Industrial wastewater samples which brought from the State Company for Electrical Industries, analyzed using the Atomic Absorption Spectroscopy Device type AA240FS to knowledge the chemical compositions and acidic functions are shown in Table [2]**.**

Table 2. The types of industrial wastewater and chemical analyses, acidic functions

No.	Sample	pH	Chemical analysis (ppm)		Details
			Cr^{+6}	Zn	
1	A_1	7	262	81	It has been brought directly from tank containing chrome
2	A_2	6.5	156	39	It has been brought directly from treatment basin containing chrome
3	B_1	6.5	21	1865	It has been brought directly from tank containing zinc
4	B_2	6	78	690	It has been brought directly from treatment basin containing zinc

2.1.4. Electrical Precipitation Cell

The electrical precipitation cell used in this work is shown in Fig. [1]. and it composed of the following parts:

- Power supply D.C.
- cathode and anode poles (30 cm × 20 cm × 30 cm).
- Ammeter for measuring the intensity of electrical current.
- Voltmeter for measuring the voltage differences between the poles.
- Basin made of Pyrex glass resistant of chemical materials to put the electrolyte solution and electrodes.
- Electrolyte solution containing ions element which will be precipitated.
- copper wire for electrical connecting to the solution.

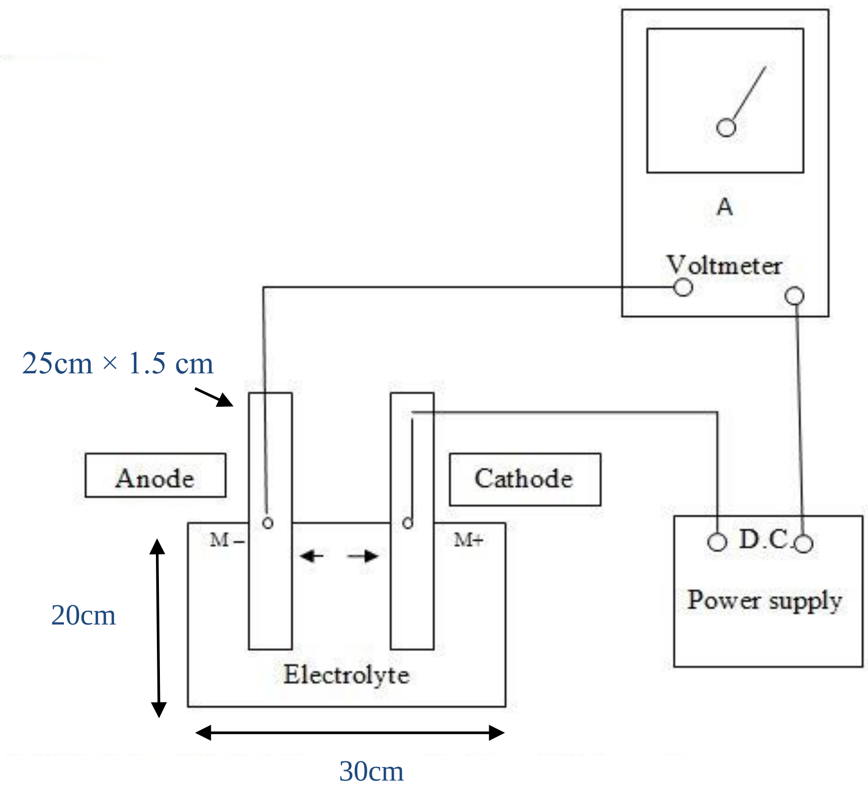

Figure 1. simplified plot of the electrical precipitation cell

2.2. *Methods*

Removal process include two stages are explained in details as follows:

2.2.1. Electrical Precipitation of Cr and Zn Metals

In this stage must modified the acidity of samples to pH=1 to make the solution appropriate for electrical precipitation by adding HCL(16%) for each sample 1liter, with using electric cell which contain cathode electrodes (made of copper) and anode electrodes (made of graphite) with different intensity for every sample.

After many periods of time notes formed light green sediments from samples containing chrome, gray sediments from solutions containing zinc (both Deposits on cathode pole). Observed when using low intensity current (1-2) amp. consist sediments with little quantity therefore, installed the power supply on the intensity current (5) amp. and change the time (1, 2 and 3) hours to note the weight of the deposit formed, Table [3] shows the amount of deposit formed according to these variables.

Table 3.The amount of precipitate formed after 1, 2 and 3 hours

No.	The sample	Size of the solution (L)	Intensity of the current	(Time hours)	Precipitate weight (g.)
				1	2.1
1	A_1	1	5	2	3.2
				3	1.2
				1	2.4
2	A_2	1	5	2	2.9
				3	2.6
				1	0.3
3	B_1	1	5	2	1
				3	0.6
				1	0.5
4	B_2	1	5	2	0.6
				3	0.9

Sediments which formed is scraped from the cathode electrode and collected in a filter paper, washed several times with distilled water and dry several times in an electric oven at a temperature of 100C˚. The sediments are weighed by a sensitive balance. Finally, the sediments and remaining solutions after finishing the electrical precipitation are sent to the chemical analysis in Iraq geosurve laboratories to determine the optimal conditions for precipitation and chemical analysis of deposit and remaining solutions, as it can be seen from the chemical analysis in Table [4],Table [5].

Table 4. Optimal conditions and Chemical analysis of the precipitate

No.	The sample	Size of the solution (L)	Intensity of the current	Time (hour)	Precipitate weight (g.)	Chemical analysis of precipitate	
						Cr%	Zn%
1	A_1	1	5	2	3.2	<0.1	0.0016
2	A_2	1	5	2	2.9	0.01	0.26
3	B_1	1	5	2	1	0.1	0.44
4	B_2	1	5	3	0.9	0.004	0.12

Table 5.Chemical analyses of industrial wastewater after the end of the first stage

No.	The sample	Chemical analysis (ppm)	
		Cr	Zn
1	A_1	26.6	7.5
2	A_2	15.2	< 0.5
3	B_1	< 0.1	45
4	B_2	2	< 0.5

2.2.2. Treatment with Bentonite Clay

This stage includes adsorption with bentonite clay by taking four samples of 500 ml of industrial wastewater solution and adjustment pH industrial wastewater solution to pH=8 by using NaOH to all samples to prepare them for bentonite treatment (adding 0.5 gm of bentonite to these solutions).It is worth mentioning that the bentonite powder is milled and sifted smoothly by using an electric mixer process by electrical shaker device for 15 minutes and speed (200 rpm).Then the mixed solution is left to settle down. This is followed by a filtration process by using filtration pressure device to isolate the filtrate and sending it to the chemical analysis. The results of this process are shown in Table [6].

Table 6. Chemical analyses of industrial wastewater samples after second stage

No.	The sample	Chemical analysis (ppm)	
		Cr	Zn
1	A_1	< 0.1	< 1
2	A_2	< 0.1	< 1
3	B_1	< 0.1	< 1
4	B_2	< 0.1	< 1

3. **Results and Discussion**

3.1. Removal of The Cr and Zn Metals by Electrical Precipitation

When observed the results of Table [2] and Table [5] note a little decrease of chrome concentration compared with zinc concentration which is significantly decreased because the high concentration of zinc in industrial wastewater in spite of chrome metal is precipitated before zinc metal in electrical precipitation, this is related to the standard electrode potential for chrome is higher than zinc, from the periodic table notes that the value of the standard electrode potential of the elements Zn = - 0.76, Cr = 1.34 [9]. as shown:

Electronegativity Increase ⟶ Ionization Energy Increase ⟶ Atomic Radius Decrease

The remaining concentrations are higher than the environmentally allowable ratio so that bentonite clays should use to complete the work in the second stage.

3.2. Removal the Remaining of Metals Cr and Zn by Bentonite Clay

The second stage begin where finishing the first stage, started with treated samples by bentonite clay to reduce the concentration of zinc and chrome to make it accepted locally and globally. Table [7] shows the different between the concentrations of metals after treatment and the ratio environmentally permitted.

Table 7. Comparison between the metals concentrations in the wastewater treatment and the ratio permitted environmentally.

Details	Metal concentration in processing wastewater (ppm)	
	Cr	Zn
Processing wastewater typeA_1	< 0.1	< 1
Processing wastewater type A_2	< 0.1	< 1
Processing wastewater type B_1	< 0.1	< 1
Processing wastewater type B_2	< 0.1	< 1
Allowable concentrations for wastewater and discharge of river according to system (Maintenance of rivers from pollution)Iraqi No.417 , 2001	0.05	3
Allowable concentrations of industrial wastewater according to the global system.	0.2	2

3.3. The Optimal Conditions for a Larger Precipitate

It is obvious from Table [3] that optimal conditions for larger precipitate weight for all types of industrial wastewater solutions in the first stage is 3.2 gm. for solution A_1 during two hours and 2.9 gm. for solution A_2 during two hours and for solution B_2 the precipitation is 0.9 gm. during three hours.

3.4. Comparison Between The Present Method and Classical Method

The classical method used in the State Company for Electrical Industries is the chemical precipitation, when comparison between the results of present research and of the classical method, we can notice that it is possible to use the present method as an alternative to the chemical precipitation method because a little of chemical materials used which is industrial hydrochloric acid concentration of 16% and the amount of up to 15 ml/L for the first stage as well as NaOH solution concentration of 10% and the amount of 10 ml in the second stage as explained in Table [8] which shows the types and quantities of chemical materials used to treat 10 m^3 of industrial wastewater per week in S.C.E.I. Table [9] shows the comparison between concentration of metals in all industrial wastewater solution samples before and after conducting the experiences.

Table 8. Types and quantities of chemicals used to treat 10 m^3 of industrial wastewater per week in State Company for Electrical Industries

Precipitate weight	Adding chemical materials				
	Iron Flak	CaCl 10%	Na_2SO_4 10%	NaOH 10%	H_2SO_4 10%
5 Kg	0.5 Kg	0.5 Kg	5 Kg	20L	10 L

Table 9. Comparison between metal concentrations in all industrial wastewater samples before and after treatment

No.	The sample	Concentration in ppm		Concentration after first stage ppm		Final concentration (second stage) ppm	
		Cr	Zn	Cr	Zn	Cr	Zn
1	A_1	262	81	26.6	7.5	< 0.1	< 1
2	A_2	156	39	15.2	< 0.5	< 0.1	< 1
3	B_1	21	1865	< 0.1	45	< 0.1	< 1
4	B_2	78	690	2	< 0.5	< 0.1	< 1

4. Conclusions

According to this experimental work, the following points can be concluded :

1. using (electrical precipitation and adsorption with bentonite clay) for reduce ratio of heavy and toxic metals in wastewater instead of the classical method (chemical precipitation), to preserve the fluvial environment.
2. From the chemical analysis of samples [Table 2], observed the little concentration of chrome metal compared with zinc concentration in samples therefore concentrated Ions (a little amounts from zinc ions) in spite of chrome deposit before zinc because the standard electrode potential for chrome is higher than zinc.
3. The sludge resulting in electrical precipitation were little quantities compared with another method followed which collect their waste in large containers for discarded again.
4. In this studying don't use any chemical material except industrial HCL16% and NaOH10% for electrical precipitation therefore it is consider relatively good economic method.

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