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TREATABILITY STUDIES OF ELECTROPLATING WASTEWATER

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ABSTRACT

Treatment of plating wastes by chemical and physical means are designed primarily to accomplish three objectives: removal of cyanides, removal of all other metals and oil and grease.

Wastewater discharged from the Egyptian Mechanical Precision Industry (SABI) was the subject of this study. Two schemes of treatment were investigated. In the first scheme, separate treatment of wastewater bearing cyanide and heavy metal salts from the electroplating department was carried out. After which the pre-treated wastewater was mixed with other industrial and sanitary wastes prior combined treatment via chemical coagulation sedimentation using different coagulants namely lime , alum , and ferric chloride in combination with lime.

The second scheme comprises the treatment of the electroplating wastewater, which contains heavy metals and cyanide , through the *formation of non-toxic complex compounds. The supernatant was then circulated over a mat of peat.*

The results obtained schowed that both schemes of treatment are very efficient in removing the organic and inorganic pollutants, cyanide and heavy metals. Complete destruction of cyanide was achieved while more than 99% removal of zinc, nickel and copper were recorded.

INTODUCTION

The cleaning, pickling and processing wastes may contain a variety of chemical compounds, most of which may be toxic to aquatic life in very low concentrations. In higher concentrations, they may be also toxic to humans (1). The discharge of wastewater usually is directed to either surface waters or to a municipal sewage treatment plant. The toxicity considerations and the permissible limits of these toxic compounds in the effluent discharged will be dependent on their effect on aquatic life, that is fish or lower organisms in the water or the bacteria in the sewage treatment plant.

Most heavy metals compounds , such as chromium , zinc, copper nickel and cyanide are toxic to aquatic life . Ammonia would be another cation toxic to fish in low concentrations. For these reasons, the permissible limit for total heavy metals is near the range of 1 ppm maximum (2).

Cyanide and its salts, are extremely toxic especially at low pH. Cyanide compounds formed by the reactions of CN- with heavy metals may by even more toxic substances (3,4). Therefore, control of cyanide and heavy metal salts in the industrial effluents were extremely importants.

Wastewater from the Mechanical Precision Industry Located in North Cairo provide the subject of this study . The company manufactures, taps, door hinges and handles, lockers and torch igniter. Average daily wastewater discharge from this plant is 570 m^3/d, 65% of which is contributed from the electroplating department.

Sanitary wastewater in the company (250 m^3/d) is collected separately in a drainage system and then mixed with the industrial wastewater proir to final discharge to a near-by canal without any treatment.

The main objective of this study is the treatment of wastewater produced from this palnt in order to reduce the concentration of the toxic elements before final disposal.

MATERIAL AND METHODS

Composite samples were collected to obtain a true representation of the industrial waste and the end- of- pipe line as influenced by changes in the daily operations. Characterization and treatment of the industrial wastewater were carried out for almost 8 months. Physico-chemical analysis were carried out according to the American Public Health Association (5).

Treatment of Wastewater

Two treatment schemes were investigated

Scheme1

The first scheme comprised two steps:

1- Destrucion of cyanide salts present in the electroplating wastewater into carbon dioxide and nitrogen gases via alkaline chlorination. (6,7).

2- The pretreated wastewater was mixed with other departmental and sanitary wastes. The mixture was then subjected to chemical coagulation sedimentation using different coagulants namely lime, alum, and ferric chloride in combination with lime at the predetermined optimum operating conditions.

A schematic diagram of the treatment processes is shown in Figure (1).

Determination of the break-point chlorination

To determine the dose of chlorine required to change NaCN to NaCNO, a fixed dose of NaCN (10mg/L as CN) was added to two liter capacity brown bottles with quick fit cover. The pH of the solution was adjusted between 10-11, then different doses of chlorine, ranging from 9.02 to 333 mg/L were added. Sodium hypochlorite was used as a source of chlorine. Residual cholrine was determined after one hour. To change (NaCNO) to carbon and nitrogen, the pH of the pervious samples which contains enough chlorine namely, (9.4 to 112.8 mg/L) was carefully reduced to pH 6.5 then left for 0.5 hour to complete the reaction. Residual chlorine was then determined (7).

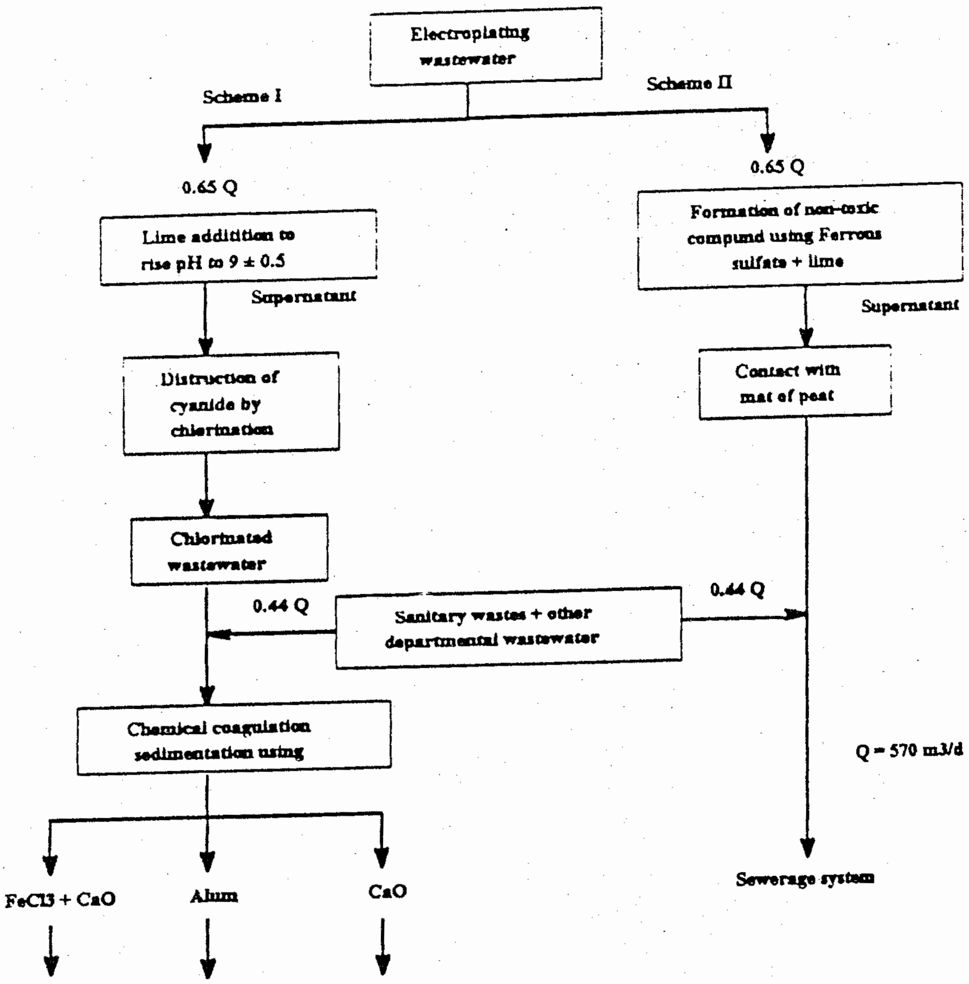

Figure (1) :Schematic diagram of the different treatment processes. (*Q 570 m^3d^{-1}) ·

Scheme II

In the second scheme, the electroplating wastewater bearing cyanide was treated via the formation of non toxic compounds (Figure 1) by adding ferrous sulfate and slaked lime to convert cyanide salts into a non-toxic form.

Calcium ferrocyanide, $Ca_2\{Fe(CN)_6\}$, and ferrous ferrocyanide, $Fe_2\{Fe(CN)_6\}$, are formed. The latter compound was then oxidized to ferric ferrocyanide, $Fe_4\{Fe(CN)_6\}_3$ (1,8).

The reaction was found to be most effective at a pH range from 7.0 to 10.5. Air agitation was applied, after which the wastewater was left to stand for 24 hours. In this study the Fe/CN molecular ratio was 2 : 2.5 (9). The supernatant was then subjected to adsorption with a mat of peat to remove the residual heavy metals.

The adsorbent was treated as follows

Sphagnum peat-moss (obtained from jiffy 7 product Ltd. Norway) was washed with water and dried at 90 °C. Then it was broken up using a hammer mill and finally sieved into (0.3 - 1.3 mm) fractions. It is important to use peat with a moisture content of less than 30% to obtain maximum absorbency and good hydraulic properties of the mat.

The natural capacity of peat to retain cations is related to the pH of the solution. At pH above 8.5 peat itself not stable. At pH below 3.0 most metals will be leached from beat. Between these values, it is known that beat can adsorb most metals in a very efficient way up to 4% of the weight of dry peat (10).

Continuous folw bench-scale unit

A Laboratory continuous flow bench-scale unit was designed (Figure 2) . The beat moss has a thickness of 1 // and a diameter of 13 cm , while the weight of the peat used was 20 gram . The mat was fed with the pretreated effluent by a motor-driven distribute the waste through a plastic plate (10.5 cm) located at the top of the mat at a flow rate of 240 ml/hr.

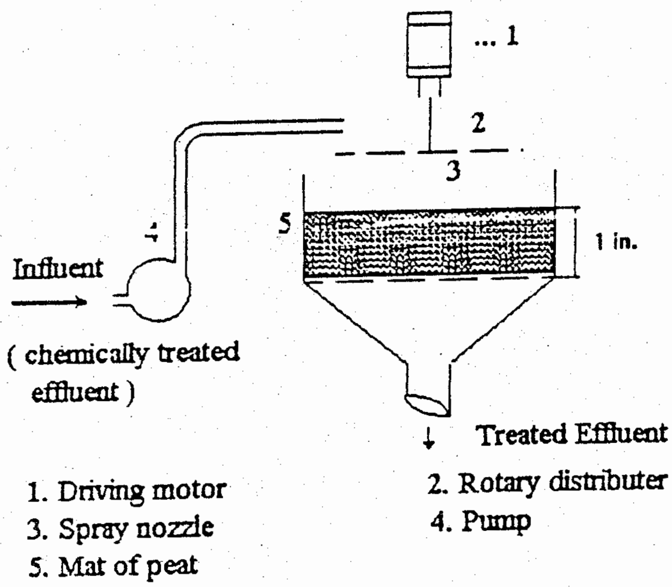

Figure (2) Schematic diagram of continuos flow bench scale unit.

RESULTS AND DISCUSSION

Characterization of wastewater

Variation in the quality of the electroplating wastewater are given in Table (1) and illustrated in Figure (3 a, b). From the data, it can be seen that the variation in zine and nickel concentrations in the wastewater from the electroplating department were ranged between 8 and 35 mg/l and from 4 to 8 mg/1, respectively. Average values of copper and chromium varied from 2.8 to 3 mg/1, respectively.Cyanide was found in concentration ranged between 2.9 and 30 mg/1. Oil and grease concentration up to 17 mg/l was recorded.

Physico-chemical analysis of the end-of-pipe waste is shown in Table (1) and Figure (4a,b). This waste is slightly alkaline. The pH ranged between 7.4-9.3. Chemical oxygen demand varied from 237 to 517 mg/1 with an average value of 346 mg / L. Average concentrations of oil and grease, cyanide and total heavy metals were 110, 26 and 37 mg/1, .respectively. Appreciable concentrations of oil and grease were detected in wastewater discharged from almost all the departments due to lubrication of the machines.

Table (1) : Characterization of the electroplating and the end of pipe waste from the plant.

Waste	Electroplating wastewater		End- of -pipe waste	
Parameters mg/L	Range	Average*	Range	Average*
pH	7.4 - 9.8	8.8	7.4 - 9.3	-
Chemical Oxygen demand	26 - 86	50	237 - 517	346
Suspended solids	38 - 90	64	86 - 306	200
Iron	1 - 6	4	3.6 - 10	6.8
Oil & grease	6 - 17	10	23 - 110	47
Total Cr	0.46 - 8.5	3	0.5 - 3.5	1.3
Nickel	4 - 8	6	2 - 6	3
Copper	1.4 - 5	2.8	1 - 4	10.6
Zinc	8 - 35	16	3.5 - 24	9
Cyanide	2.9 - 30	11	2.2 - 26	7.4
Aluminum	Zero - 1.6	0.23	N.D.	N.D.

*Average of 5 results

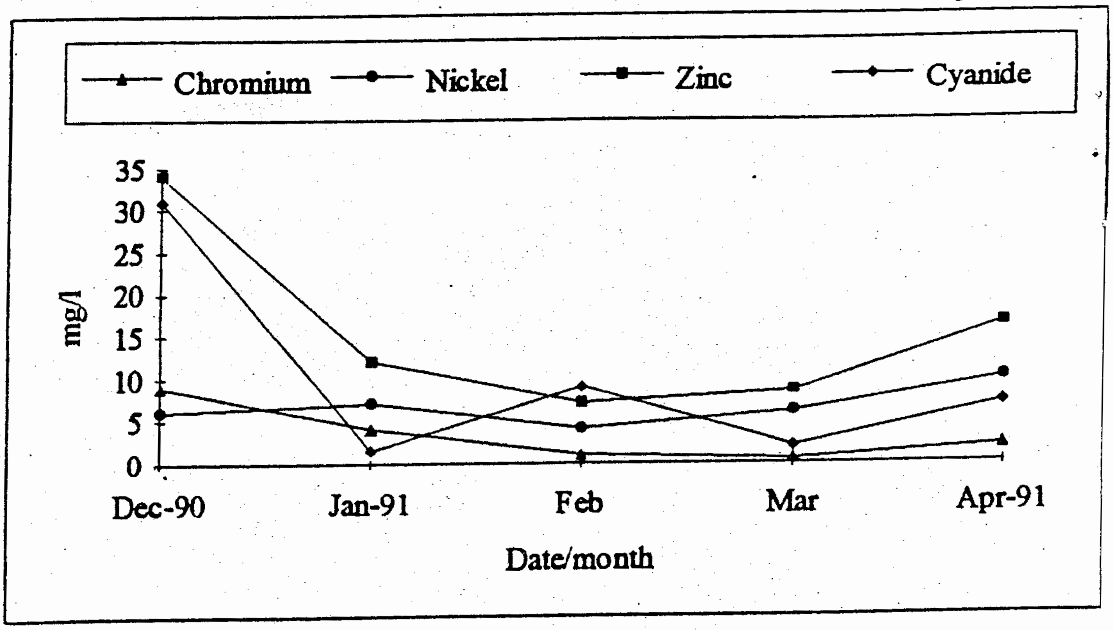

Figure (3a) : Physico - chemical parameters of rinse water from electroplating department.

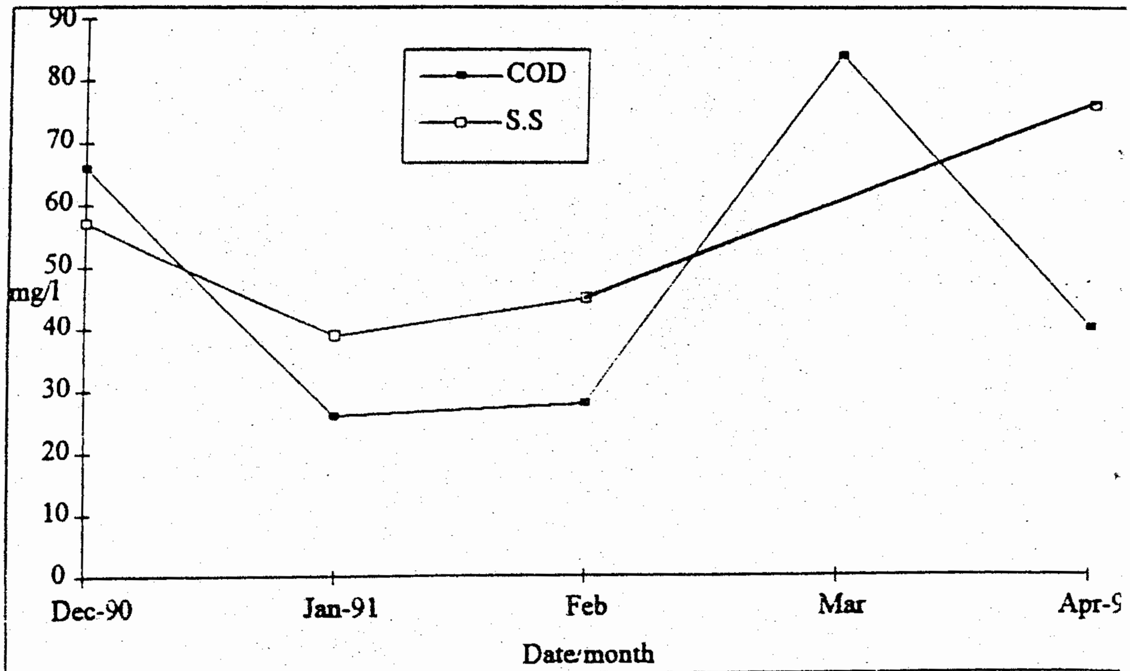

Figure (3b) Physico-chemical parameters of rinse water from electroplating department

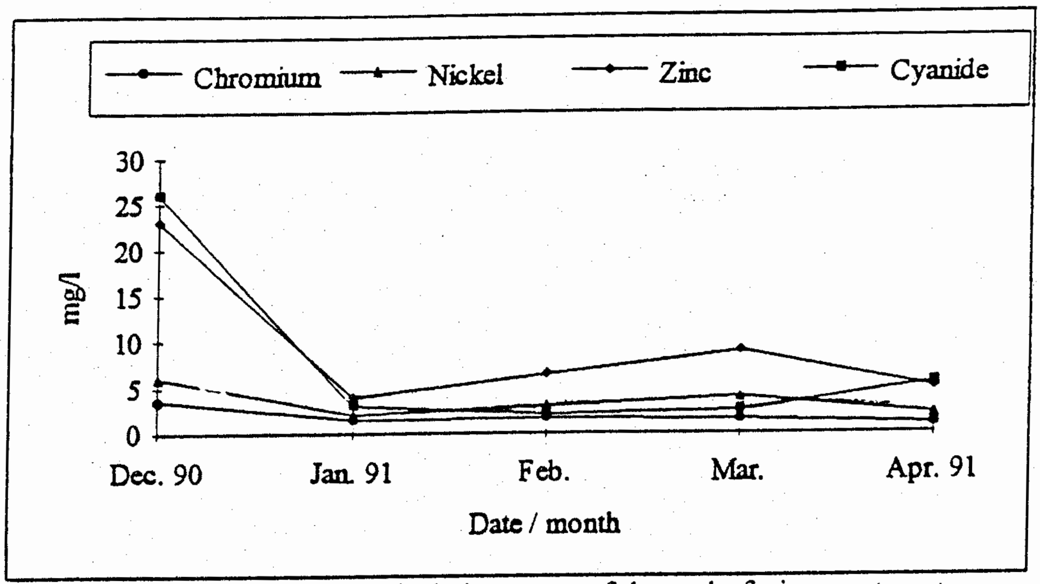

Figure (4a) Physico-chemical characters of the end-of-pipe wastewater

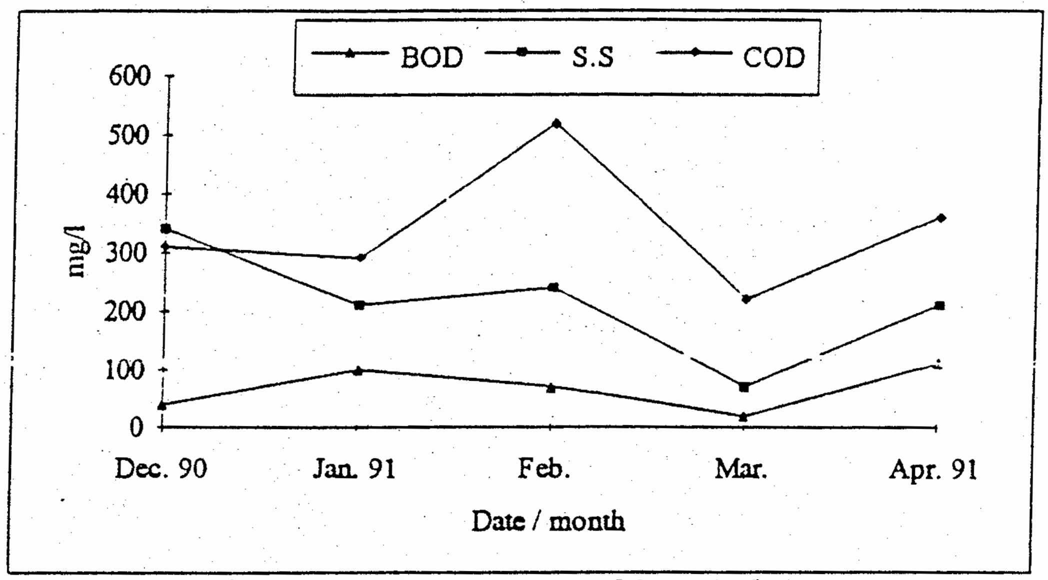

Figure (4b) Physico-chemical characters of the end-of-pipe wastewater

Treatability Studies

Treatment of Wastewater Bearing Cyanide (Electroplating Wastes)

Alkaline chlorination of cyanide was carried out in two steps . The results obtained in Figure (5) indicated that oxidation of cyanide to cyanate ion required 2.7 to 2.8 parts (by weight) of chlorine and 3.1 parts of sodium hydroxide per one part of cyanide as CN. Complete destruction of cyanate to nitrogen and carbon dioxide gases at pH 6.5 was carried out . The results obtained in Figure (6) indicated that each part of cyanide required (7.3 ± 0.2) parts of chlorine for complete destruction . These results are in agreement with the theoretical requirements (7) .

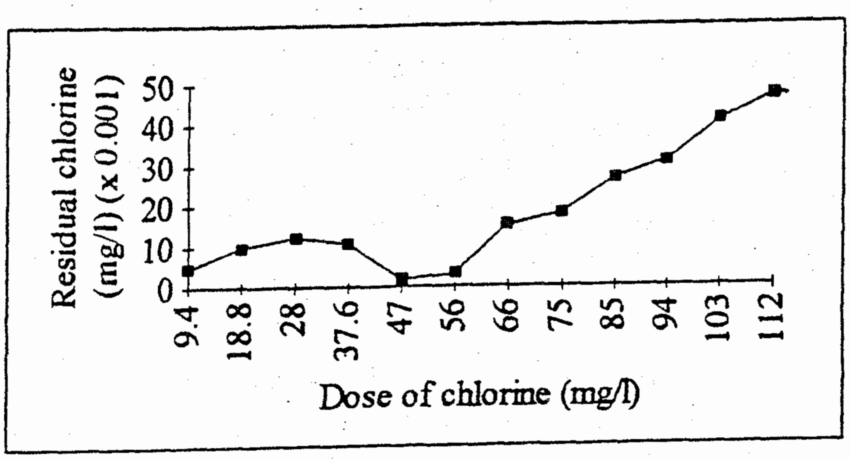

Figure (5) Oxidation of cyanide to cyanate .(Initial CN concentration = 10 mg / 1,pH 10 - 11)

After destruction of cyanide , chemical coagulation using lime at pH10 produced a good quality effluent . The use of lime was more advantageous in removing the organic and inorganic contaminates Table (2) . Average residual COD, and suspended solids were 7.0 mg/l and 17 mg/l , respectively . Percentage removal of Oil and grease was 92% . Also , it was found that the best removal values of the heavy metals under consideration were achieved at pH 10 . Above pH10 negative stable colloid exists (11) .

The percentage removal values of nickel and copper were 90% and 96% respectively Their corresponding residual values were 0.28 and 0.08 mg/l , respectively. - More than 99% removal of zinc was achieved with corresponding residual value of 0.13 mg / l . Complete removal of cyanide was obtained. The quality of the treated effluent was complying with the National Regularity Standard required for wastewater disposal into surface water . However , the pH must be adjusted before the final disposal of the treated effluent.

Chemical treatment of the wastewater using 37.5 mg / l alum at pH6.9 produced an effluent similar to that obtained with lime , but no significant removal of metal was obtained Table (2) .

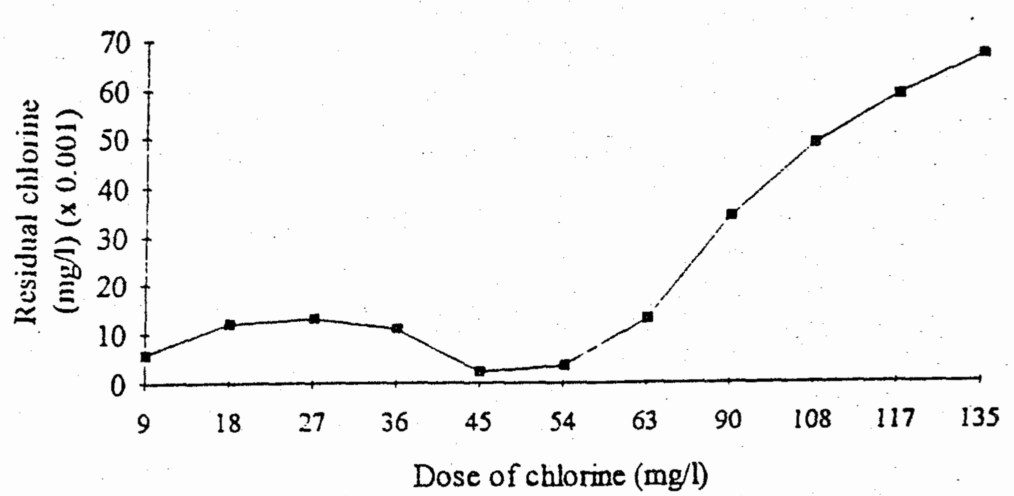

Figure (6) Destruction of NaCNO to Nitrogen and Carbon Dioxide (Initial CN concentration = 10 mg / l , pH 6.5)

The addition of lime with ferric chloride has a dual effect . Lime is used to raise the pH value and also as a coagulant aid . The dose of lime used was 30 mg / l , ferric chloride dose was around 25 mg / l at a pH 7.8 . Tatal COD and SS removal values were 98.5% and 66.7% , respectively . However, total heavy metals concentration in the final effluent was more than 1 ppm . This effluent can be discharged to public sewerage network .

The use of lime as a coagulant is recommended due to its local availability and high efficiency in nickel, chromium and zinc removals .

In case of wastewater disposal into surface water , further treatment should be applied in order to eliminate any residual toxic compounds prior to final discharge .

Table (2) Treatment of wastewater via chemical coagulation after destruction of cyanide .

Coagulant	Lime*		Alum*		Lime + Ferric chloride	
Dose of coaguiant mg/l	250		37.5		30+25	
Parameters mg/l	T.E**	%R	T.F**	%R	T.F**	%R
pH value	10		6.9		7.8	
COD	7	98	19.8	94	5.6	98.5
Suspended solids	17	84	Nil	100	40	66.7
Oil and grease	2.4	92	2.8	91	2.8	91
Iron	0.3	88	Nil	100	2.2	38.1
Cyanide	Nil	100	Nil	100	Nil	100
Copper	0.08	96	0.6	69	0.2	89.7
Zinc	0.13	99	1	73	0.1	97.8
Nickel	0.28	90	1.7	20	1.65	20
Chromium	< 0.1	80	0.3	40	0.2	60

*Average of five results .

** Treated Effluent .

Scheme II

In this scheme , cyanide was changed to non - toxic compounds , while heavy metals were precipitated as well . From the data obtained in Table (3) , it can be seen that most of organic and inorganic constituents were removed . Complete removal of cyanide was recorded . Residual values of total heavy metals were more than 4.75 ppm. The residual concentration of heavy metals still high.

Therefore , adsorption of heavy metals on peat was carried out. At pH above 8.5 peat moss is not stable . Then the experiments was applied at pH 8.2 to form the non toxic compound . The pretreated effluent was then circulated over a mat of peat to remove the residual heavy metals .

The results obtained showed that this treatment is very efficient in removing organic pollutants , cyanide and total heavy metals . Complete destruction of cyanide was achieved while more than 99% removal values of zinc , and copper were recorded (Table 3) , with residual values of < 0.05 mg / l , and < 0.1 mg / l. respectively .

Natural adsorbent proved to be very efficient in removing heavy metals . The results are similar obtained by Abou - Elela and EL - Dib (12) .

Table (3) Treatment of wastewater containing heavy metals .

Parameters mg/l	Raw wastewater	Treated Effluent		
		1*	2*	3*
pH	7.5	9.8	8.2	7.85
COD	44.4	14.4	23.2	60
SS	90	83	88	32
Oil and grease	17.2	0.8	Nil	Nil
Iron	4.4	1.4	2.4	Nil
Cyanide	7.2	Nil	Nil	Nil
Copper	3.5	1.6	1.7	< 0.1
Zinc	16.8	< 0.05	0.5	< 0.05
Nickel	8.0	3.0	4.6	Nil
Chromium	1.5	< 0.1	< 0.1	Nil

*1. Adjustment of pH in the range of 9.8 with lime and adding Ferrous sulfate and settling .

*2. Adjustment of pH at 8.2 with lime and adding Ferrous sulfate and settling .

*3. Adjustment of pH at 8.2 with lime and adding Ferrous sulfate and settling . The supernatant was adsorbed with peat .

CONCLUSION

In order to satisfy the National Regulatory Standards for discharging industrial wastewater to agricultural drains , oil and grease in the final effluents should not exceed 10 mg / l , BOD and COD values ; less than 60 and 100 mg / l , respectively are also required . The permissible limit for total heavy metals is near the range of 1 ppm maximum . Laboratory experiments revealed that an oil trap is necessary before applying both of techniques under considerations .

Although both schemes of treatment produced a good quality effluent , however , scheme (I) is recommended . This scheme comprises the destruction of cyanide by alkaline chlorination followed by chemical coagulation precipitation using lime . The produced effluent can be discharged safely into the public sewerage network which is underconstruction .

Although scheme (II) of treatment was more efficient in removing heavy metals , but the sludge produced (containing cyanide) can represent a great problem to the ground water .

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دراسة أنسب الطرق لمعالجة المخلفات السائلة لشركة الصناعات الميكانيكية الدقيقة

(سابى)

تقع الشركة المصرية للصناعات الميكانيكية الدقيقة (سابى) فى منطقة مسطرد بشبرا الخيمة وتختص هذه الشركة بسباكة وطلاء بعض المنتجات المعدنية الدقيقة من المسح الميدانى للشركة وجد أن المصدر الرئيسى للتلوث هو قسم الطلاء حيث يمثل حوالى ٩٨٪ من حجم الصرف الصناعى الكلى بالشركة (٣٢٠ م٣ / يوم) وبذلك يقدر إجمالى المياة المنصرفة من الشركة بحوالى ٥٧٠ م٣ / يوم . من التحاليل المتاحة وجد أن المخلف النهائى يحتوى على تركيزات من المواد العضوية ممثلة فى الإحتياج الأكسوجينى الكيميائى وصل تركيزها إلى ٣٤٦ مجم / لتر . كذلك اتصفت هذه المخلفات بإحتوائها على تركيزات عالية من الزيوت والشحوم تراوحت بين ٢٣ - ١١٠ مجم / لتر . وجدير بالذكر أن هذه المخلفات تحتوى على المعادن الثقيلة أيضا مثل الكروم والنيكل والنحاس والزنك علاوة على وجود السيانيد .

اما مخلفات قسم الطلاء فقد احتوت على تركيزات عالية من الزنك وصلت فى بعض الاحيان الى ٣٥ مجم / لتر ، فى حين وصل تركيز النيكل الى ٨ مجم / لتر . اما متوسط تركيزات النحاس والكروم فكانت ٢٫٨ و ٣ مجم / لتر على التوالى . ومما سبق يتضح ان قسم الطلاء هو مصدر التلوث الاساسى بالشركة ، علاوة على ان صرف مخلفات بهذه المواصفات يخالف تماما النصوص الواردة باللائحة التنفيذية للقانون رقم (٤٨) لسنة١٩٨٣ .

تهدف عمليات معالجة مخلفات مياه الصناعة إلى إمكانية التخلص من هذه المخلفات بحيث لا تسبب أى تلوث لمصادر المياه أو أضرار الصحة العامة وبناءاً على ذلك فإن درجة المعالجة المطلوب لمياه الصرف الصناعى يتوقف على الإمكانيات المتاحة للتخلص من هذه المياه بعد المعالجة وهذا بدوره يحدد اختيار طرق المعالجة المناسبة .

ويمكن التخلص من المخلفات السائلة المنصرفة من المصنع بعد معالجتها إما بصرفها

على مصرف مسطرد وهذا يتطلب أن تتفق مواصفات المياه المعالجة والمعايير المنصوص عليها بالقانون ٤٨ لسنة ١٩٨٢ أو يمكن التخلص منها لصرفها على شبكة الصرف الصحى العمومية بالمنطقة . وهذا بدوره يتطلب ضرورة الوصول بنوعية المياه إلى المواصفات التى يحددها القانون رقم ٩٣ الصادر ١٩٦٢ .

وفى كلا الأحوال فإنه يلزم إزالة نسبة كبيرة من كميات الزيوت والشحوم الموجودة بالمخلفات وأيضاً إزالة المعادن الثقيلة والمواد السامة بالإضافة إلى ذلك فإنه يستلزم إزالة عناصر أخرى إذا ما تم صرفها على مصرف مسطرد .

وبناءاً على ذلك فقد تم إيجاد عدة بدائل لمعالجة المخلفات السائلة من الشركة وقد تمت المفاضلة بين تلك البدائل والتى تم على أساسها الوصول بالمخلف إلى المعايير التى تسمح بصرف المياه بعد المعالجة على مصرف مسطرد أو شبكة الصرف الصحى العمومية ، وهذه البدائل هى :

البديل الأول :

التخثير والترويب والترسيب لمخلفات قسم الطلاء متبوع بالكلورة ، ثم تجميع المياه المنصرفة من وحدة المعالجة مع باقى المخلفات المنصرفة من الشركة ومعالجتها بالتخثير والترويب والترسيب بأنواع مختلفة من المجلطات .

وقد أوضحت نتائج التجارب المعملية مايلى :

– التخثير والترويب والترسيب لمخلفات قسم الطلاء قبل الكلورة باستخدام الجير الحى .

– يلزم التخلص من كميات الزيوت والشحوم الموجودة لباقى المخلفات المنصرفة من الشركة قبل خلطها مع مخلفات قسم الطلاء المكلورة لمعالجة خليط المخلفات سواء تم فيما بعد التخلص من المياه المعالجة بالمصرف أو شبكة الصرف العمومية .

– خلط المخلفات الخارجة من وحدة الطلاء بعد الكلورة مع باقى المخلفات الخارجة من الشركة ومعالجة الخليط بالتخثير والترويب والترسيب يلزم لإزالة المعادن الثقيلة سواء

تم التخلص من المياه المعالجة بالمصرف أو شبكة الصرف العمومى ، كما أنه ضرورى للتخلص من الحمل العضوى الموجود بالمخلفات فى حالة الصرف على المصرف .

وقد أوضحت النتائج أن استخدام الجير الحى طريقة فعالة فى إزالة الملوثات العضوية والغير العضوية حيث تم إزالة السيانيد كاملاً فى حين أن نسبة إزالة النيكل والنحاس والزنك فقد وصلت إلى ٩٠ ٪ و٩٦ ٪ و ٩٩ ٪ على التوالى علاوة على ذلك فقد تم إزالة نسبة كبيرة من المواد العالقة وكان متوسط المتبقى منها ١٩ مجم / لتر .

البديل الثانى :

إزالة السيانيد بتكوين مركبات معقدة .

معالجة مخلف قسم الطلاء بتكوين مركبات معقدة غير سامة مع السيانيد وذلك باستخدام كبريتات الحديدوز بنسبة 2 CN : 3 Fe وذلك عند الرقم الأيدروجينى من ٨ر٢ ويراعى إضافة الجير الحى بالوصول إلى إلى هذا الرقم الأيدروجينى مع التقليب الشديد أو التهوية ثم الترسيب لمدة ٢٤ ساعة للتخلص من كل المركبات التى تحتوى على السيانيد

- تجميع المياه المنصرفة من وحدة المعالجة وتمريرها على تربة صناعية (mat of peat moss) لإدمصاص كل العناصر الثقيلة .

- وتوضح النتائج المتحصل عليها مدى كفاءة هذه الطريقة أيضاً فى إزالة الملوثات وخاصة السيانيد والمعادن الثقلية حيث وصلت نسبة الإزالة لكل من الزنك والنحاس لأكثر من ٩٩ ٪ بقيمة متبقية ٠٥ر٠ مجم / لتر ، ٠١ر٠ مجم / لتر على التوالى كما تم التخلص من السيانيد نهائياً .

وقد أوضحت نتائج التجارب المعملية أن هذه الطريقة لها مشاكلها الفنية نظراً لأن التخلص من الرواسب يحتاج إلى احتياطات خاصة لاحتوائه على مركبات السيانيد لذا فإن هناك تحفظ فى استخدام هذا المرادف فى معالجة المخلفات الخارجة من الشركة .