



Preliminary Study of Zinc Removal from Cyanide-free Alkaline Electroplating Effluent by Precipitation using Oxalis Plants

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<http://dx.doi.org/10.13005/ojc/300215>

(Received: April 05, 2014; Accepted: May 15, 2014)

ABSTRACT

The aim of this study is the reduction of Zinc from the cyanide-free alkaline zinc-plating effluent. Various methods utilized for removing or recovering the heavy metals are adsorption, chemical precipitation, sedimentation filtration, reverse osmosis etc. We are interested in using oxalis plant as a potential chelating/settling agent for the treatment of electroplating effluent collected from a local industrial unit. *Oxalis pes-caprae* has an exceptionally high content of oxalic acid which is known as moderate and weak chelating agent. The efficiency of the performance oxalis powder (KITININ) was estimated and the optimum dose was determined using conductivity, volumetric, atomic absorption spectroscopy and pH measurements. The results show the performance of oxalis in treating Zn plating effluent effectively. In effect, a white crystalline precipitate of zinc oxalate is easily extracted (98,52 % elimination of Zn) and a high settling rate is observed. The maximum zinc uptake by Oxalis in batch systems is estimated to 6,44 mg/g.

Key words: Oxalis, precipitation, Zinc, Electroplating effluent.

INTRODUCTION

Today, developed industries can use more than 40% of total water, leading to more water quality problems. The metal pollutants can originate from a variety of sources: Metal finishing and electroplating processes. The plating baths contain high concentrations of potential polluting metals. The rinse water has a low concentration of heavy metals but, can contribute to significant load

because of their large volumes. In addition only 30-40% of all metals used in the electroplating process can be effectively plated onto the articles¹. Its residual waste effluents are responsible for the supply of toxic and corrosive heavy metals to the environment. So, a number of treatment techniques have been developed and are utilized for heavy metal removal or recovery², because of the slow natural process of metal formation (metals are considered to be a nonrenewable resource) and

their toxic effects^{3,4}. These points have clearly explained the importance of fixing some limits for these heavy metals in drinking and waste waters. Treatment methods to reach the fixed limit (5ppm) include chemical precipitation and other separation methods⁵⁻¹². In this study we are interested in the treatment of the cyanide-free alkaline zinc-plating effluent, where cyanide may be replaced by complexing or chelating agents such as sodium gluconate, triethanolamine or polymeric amines. The resulting baths present therefore problems with waste treatment. A second generation of organic addition agents eliminated chelating agents was developed in industry and most of the currently available processes have eliminated these problems with the use of an entirely new family of organic reaction products¹³ but zinc removal from dilute solution remains a problem. Many researchers have studied various natural and synthetic chelating agents for their ability to remove heavy metals from electroplating effluents. Chelating agents (organic acids) are the most popular extracting reagents used for soils decontamination^{14,15}. Oxalate compound used to precipitate metal ions from solutions, oxalate-treated activated carbons was also used for the adsorption of Co and Ni from aqueous solutions¹⁶. The aim of the present study is to assess the potential of a natural, low molecular weight organic acid, oxalic acid for zinc removal from electroplating effluent. This aliphatic organic acid exists naturally form relatively stable complexes with metals and has a greater potential to mobilize Zn from aqueous effluent in its insoluble zinc oxalate form. Indigenous to South Africa, *Oxalis pes-caprae* is an invasive plant in many other parts of the world, including Algeria and it can contain up to 16% of the dry weight as oxalic acid, present in both photosynthetic and non-photosynthetic tissues¹⁷. The present study provides general guide lines for the removal of dissolved Zn metal from cyanide-free electroplating effluent using oxalis plant in a powder form (KITININ) estimated as a potential chelating/settling agent.

MATERIAL AND METHODS

The electroplating effluent used in the experiment was taken from a local electroplating unit. It consists of a dilution of a cyanide-free alkaline electroplating bath, where temperature and pH were

determined using pH meter. A suitable volume was taken before the dilution and was analyzed by volumetric method, using complexion III and indicator eriochrom Black T, buffer tampon pH 10. At the equivalence point, color changes from red to net blue. 1 ml complexion III (0.05M) corresponding to 3,2685 mg of Zn¹³.

Oxalis pes-caprae were harvested from the field, stored and dried at room temperature. After complete drying of the plant, it was grounded to fine powder. Next, the obtained powder was washed by an appropriate solvent to eliminate chlorophyll. Finally, the particles which supposed to be poor of oxalic acid were separated by a mechanical method. Content of oxalate anion was analyzed by volumetric method with potassium permanganate 0,1 N at 80°C, in the presence of sulfuric acid 4N under magnetic stirring. At equivalence point, the solution became colorless. 1 mL KMnO₄ 0,1 N corresponds to 4,4 mg of C₂O₄²⁻[2]. The pH-metric titration of the raw and treated oxalis powders were carried out for the estimation of the oxalate anion and the free oxalic acid content and to confirm mechanic purification efficiency.

After dilution of the electroplating bath solution with demineralized water, Zn concentration metal content was 140 mg/L. Three liters of this solution were prepared and stored for experiments. A volume of 100 mL was then taken in a beaker (250mL) and 10% suspension of treated oxalis powder (KITININ) was added gradually with agitation at a speed of 50 rpm at room temperature. After treatment, Zn was measured by Atomic Absorption Spectroscopy.

RESULTS AND DISCUSSION

The electroplating cyanide-free alkaline solution bath taken from a local electroplating unit was analyzed for the quantitative determination of Zn metal and sodium hydroxide contents. Zn was found to be 25 g/L and the concentration of NaOH rang of 125 g/L. A quantity of this concentrated solution was diluted by adding demineralized water to 140 mg/L of Zn metal and the final pH was 11,09. The residual concentration of cations in electroplating effluent can be taken into account apart from 50-100 mg/L up to 5-6 g/L according to

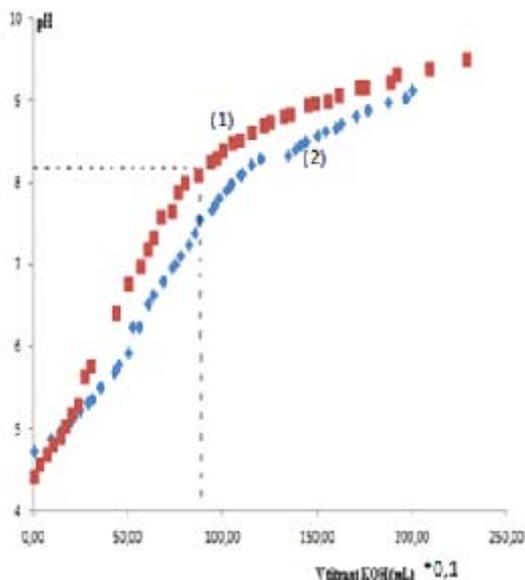


Fig. 1: pH-titration curve of 2g Oxalis powder (KITININ) (1) and 2g raw oxalis powder (2) in 100mL distilled water with KOH(0,4 N)

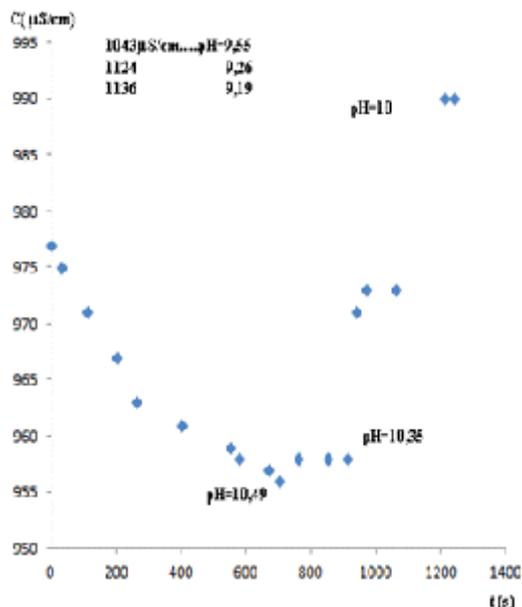


Fig. 2: Evolution of conductivity and pH versus added oxalis powder mass

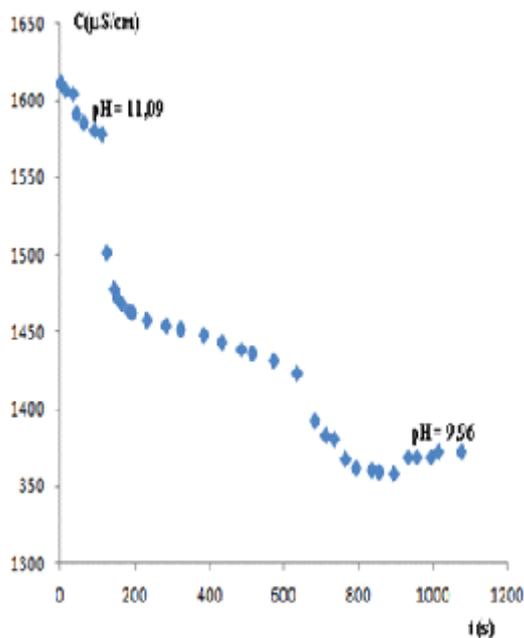


Fig. 3: Evolution of conductivity versus added oxalis powder mass

reference 2. On the other hand, after washing the prepared oxalis powder (KITININ) with an appropriate solvent, the green color corresponding at chlorophyll molecules was successfully eliminated. After drying, the powder was yellow color and particles supposed to be poor of oxalic acid were separated by mechanical method on basis of density. Content of oxalate anion in treated oxalis powder was analyzed by volumetric method with potassium permanganate, and concentration of 130 mg/g was obtained. A pH-metric titration with KOH (0,4N) of the raw and treated oxalis powder was carried out (figure 1). When free oxalic acid is titrated with a strong base (KOH), the titration curve has two equivalence points. These correspond to the removal of each successive proton from the diacid, and occur at pH 2.71 and pH 8.36.

From the titration curves it is clear that the oxalic acid is in its monometallic form (mono potassium salt) as the initial pH corresponds to the end of the first half-neutralization. The pH of a suspension of 2 g of treated oxalis powder becomes more acidic than the crude oxalis powder, but the equivalent volume is almost the same. According to the equivalent volume around 9 mL, the concentration of mono potassium oxalate in the

treated powder oxalis (KITININ) is estimated at 12%. The oxalic acid content in oxalis plant was usually about 16% of the dry weight according to reference¹⁷.

Up on the addition of oxalis suspension, the flockscoalesced and settled down immediately and the Zn elimination was monitored with conductivity measurement. In effect, if the divalent Zn interacts with oxalic acid present in there soluble form and adsorbed by the plant tissues, it is compulsory that the conductivity decreases. The latter was decreased with added mass of oxalis powder, due to the mobilization of Zn as oxalates as shown in figure 2. The main part of heavy metal (Zn) was removed from the sludge, the suspensions were centrifuged at 3000 rpm for 5 min and the supernatant was then filtered for Zn analysis using absorption spectrometry (AAS). The results show about 98,56 % of zinc removal.

In our experiment zinc was removed by precipitation as metal insoluble complex, and oxalis powder can be considered as a flocculent agent. Determining the effectiveness of our bio-chelating agent for Zn removal from electroplating cyanide-free effluent has commonly been accomplished in one-step batch extractions at the laboratory-scale. Such extractions often encounter some limitations and difficulties :reverse reactions and delayed precipitation.

In a first test (Figure 2) the optimum dose has been exceeded in order to neutralize the effluent after zinc mobilization. But the addition of an excess of powder oxalis had a low effect on pH adjustment as the pH in the vicinity of the optimum dose was decreased from 11 to 10.49. By adding advantage of oxalis powder, the conductivity of the treated oxalis powder increased gradually to 1043, 1124 and 1136 $\mu\text{S}/\text{cm}$ for a pH reduction only equal

to 9.55, 9.26 and 9.19 respectively. Therefore a correction of the pH was necessary using a mineral acid, such as hydrochloric or sulfuric.

The effect of the pH on the removal of Zn must be examined because the waste water from plating factory was of various pH values. In our study, effluent samples were used without pH adjusting. Usually, the optimum pH values for Zn precipitation range is 8-10. From the experimental figure 3 of conductivity versus oxalis powder dose, it was evident, that pH 10 was optimum for complexation of Zn with oxalic acid and 5-6 g/L of KITININ is sufficient for the treatment of zinc electroplating cyanide-free effluent concentration ranging from 100 to 150 mg/L of Zn metal.

ACKNOWLEDGMENTS

We Acknowledgment assistance from the AFAK CONTROL Laboratory, Oran-Algeria for AAS analysis

CONCLUSION

A simple and cost effective treatment procedure was proposed for the removal of zinc from zinc plating industry effluent using oxalis plant in its powder form. The most important thing is that the Zinc recovery ions process with 98,52% efficiency. The low zinc oxalate solubility product value is an advantage for the treatment by complexation/flocculation/settling and filtration of waters with zinc ion content. Using this method, it is not only possible to remove the Zinc from the cyanide-free alkaline electroplating effluent but also to recover the transitional metal (Zn). Zinc oxalate adsorbed on organic plant oxalis powder could be turn into oxide. This work is an attempt to develop new bio chelating/flocculent agent for heavy metals removal from dilute solutions and to the reduction of zinc, chrome, lead etc to very low concentration less than 5ppm.

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