

Original Article

Irrigating *Melissa officinalis* L. Medicinal Plant with Chromium Wastewater Treated by Electrocoagulation

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Abstract

In recent decades, enormous use of chromium in different industries as well as water and soil pollution by those industries caused serious concern. Toxic impact of chromium on the growth of plants includes changes in the process of germination and root, stem and leaves' growth. Chromium also has harmful impact on the plants' physiological processes such as photosynthesis. On the other hand, iron is one of the essential elements for the growth of plants without which enough chlorophyll would not exist in the cells, consequently; making leaves pale. *Melissa officinalis* L. is an herb with 30 to 120 cm long. This plant is sensitive to iron deficiency. Electrocoagulation is a method to remove heavy metals. One of the advantages of this method is low consumption of power and high efficiency in removing pollutants. In this study chromium removal with 500 mg/l concentration from artificial wastewater containing chromium (III) was examined and removal efficiency of 97% was achieved. Here also the impact of pH on efficiency of chromium removal and amount of produced iron was tested and voltage parameter was examined to achieve optimal condition. In regard to efficiency of chromium removal, the optimal pH of tests was 6 and the amount of iron was 8.14 mg/l.

Key words: Chlorophyll, Chromium, Electrocoagulation, Iron, *Melissa officinalis* L.

Introduction

Development of industrial activities and enormous use of chromium compounds has made chromium as a serious environmental pollutant. Chromium (III) compounds within the nature enjoy more resistance and less toxicity in comparison with the chromium (VI) [1,2].

Chromium compounds especially Hexavalent chromium are very toxic for the plants, causing harmful impact on their growth. Though crop plants grow better in chromium of lower concentration, higher concentration is toxic and harmful for most plants. Chromium is an unnecessary element for plants which enjoy no especial mechanism for the adsorption. Thus; the adsorption of this heavy metal occurs by catching conveyers of the plants' necessary elements. The very first physiological process affected by chromium is germination [1]. To Pralta and et al, the ability of a seed for germination under chromium toxicity indicates the plant's level of

tolerance to chromium. They found out the germination ability of alfalfa seeds reduces 23% under the chromium of 40 mg/L concentration [3]. One of the most important impacts of chromium toxicity on the plants is growth reduction of the plants' roots. The growth of plants' shoots, leaves and numbers of leaves also would reduce due to chromium toxicity. This process leads to reduction of photosynthesis and of harvest [1]. In Sharma test, 0.5 Mm increase of trivalent chromium in nutrient solution led to 50% reduction of wheat's leaves [4].

Melissa officinalis L. is an herb with 30 to 120 cm long growing as an automotive and wild plant in many regions of Iran. It has small and ramiform root with leaves of 3 to 8 cm long and dark green color. *M. officinalis* L. is aborigine of central and southern Europe, North Africa and West Asia.

The leaves and the young shoot of this plant used in medicine to heal wounds and rheumatism and to cure neurological and heart diseases and stomachache. Desirable soil's pH for *M. officinalis* L. ranges

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from 4.8 to 8. This plant is sensitive to lack of iron and it is necessary to add iron fertilizer to the soil of no rich iron [5-11]. So far, 16 elements have been considered necessary for the plants' growth. Carbon, oxygen, hydrogen, nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, iron, manganese, zinc, copper, boron, molybdenum and chlorine are all sixteen necessary elements for the plants [12-18]. Iron is an essential element for the plants' growth [19-21]. Without which, enough chlorophyll would not exist in the cells, consequently; making leaves pale [22-25]. Lack of iron highly reduces photosynthesis [12-17]. Many plants are sensitive to lack of iron and in the event that the amount of iron in the soil is less than 5 mg/l, iron fertilizer or other methods must be used to increase iron [26]. Iron compounds are effectual when used in the form of spray on leaves [27,28]. Iron transfers to the soil in the form of Fe^{+3} by diffusion and movement, as soon as it penetrates into rhizosphere of the plants, it reduces in the form of Fe^{+2} and then absorbed by root [12-17]. The amount of iron within the plants' tissues changes from 40 to 200 mg/l; however it must be over 100 mg/l in well-grown plants [29]. The plants which suffer from lack of iron contain less than 30 mg/l iron in their leaves [21]. Some nutrients and elements required for plants shown in table 1.

Table 1 Elements required for plants (27)

Element	Amount (mg/l)
Iron	5
Zinc	8
Copper	0.5
Manganese	1-1.8
Magnesium	0.3

Since chromium is harmful, there are many methods to remove this pollutant from water and wastewater for plants' irrigation. Among these methods, electrocoagulation is a novel one, using direct current to remove pollutants from solution [30-35]. In recent decade, this technology was used to treat industrial wastewater containing metals [36,37]. In this process, the coagulant produced by electrolytic oxidation of an anode of suitable kind and then charged ion, metals and other materials remove through following mechanisms:

- Reaction to an ion with opposite electrical charge
- Composition with metal hydroxide flocs formed in the wastewater [38].

Studies on wastewater treatment of dairy industry [39,40], wastewater treatment of tannery on the

stages of liming and hide for tanning [41, 42], wastewater treatment of olive firm and refinery of herbal oil [43, 44], wastewater treatment of textile (45, 46) and wastewater treatment of wood and paper mill [47] show the efficiency of electrocoagulation for removing turbidity, suspended solids, heavy metals, sulphide, sulphate, organic materials, fat, color, COD and BOD pollutants.

This study examined performance of electrocoagulation on chromium (III) removal by iron electrodes. The role and effect of pH in the chromium removal and the amount of produced iron have been also tested.

Material and Methods

Initially, the artificial wastewater containing chromium (III) ion of 500 mg/l was poured into electrocoagulation tank made of Plexiglass in order to remove chromium pollutant. 500 mg/l concentration was suggested due to quality of tanning wastewater containing variable amount of chromium which ranges from 400 to 1700 mg/l (48). In this study, basic chromium sulphate ($Cr_2(SO_4)_2(OH)_2 \cdot 16H_2O$) with basicity of 33-35% made by Rock Chemical Co. was used.

Reaction conditions were as follows:

Optimal time was 25 min and samples were agitated by magnetic stirrer at 100 rpm

Required time for settling produced flocs and achieving transparent solution was 30 min. Total chromium is determined by atomic absorption spectrophotometry according to standard methods of testing water and wastewater [49].

1- IKA magnetic stirrer with RCT Basic, made in Germany, was used.

2- DAZHENG DC POWER SUPPLY PS-305D converting current, was used.

3- 691 pH meter Metrohm, made in Switzerland, was used.

Features of electrocoagulation reactor are as follows:

- A cubic tank made of Plexiglass
- A number of 10 metal plates made of iron measuring 11×7 cm, 2 mm thick, with surface area of 77 Square meter placed inside of the tank with fixed gap of 2 cm. Electrodes placed 3 cm away from the bottom of the tank.

Fig. 1 shows schematic form of electrocoagulation reactor, in this reactor, electrodes of two poles as well as parallel single pole array were used.

- A transformer was used to convey AC to DC

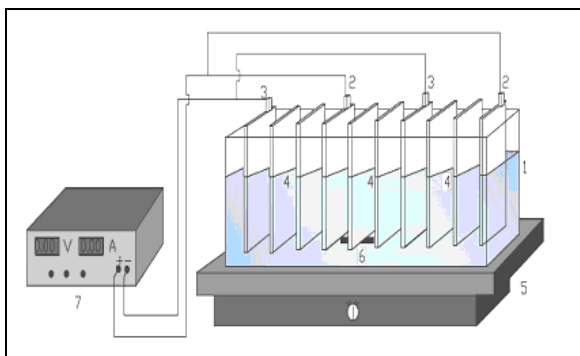


Fig 1 Schematic design of electrocoagulation reactor with single, two pole and parallel array electrodes 1- Electrical coagulation cell 2- Anode (Iron) 3- Cathode (Iron) 2,3- Monopolar electrodes 4- Bipolar electrodes 5- Magnetic stirrer 6- Magnetic bar- stirrer 7- Direct current (DC) source

In this technique, metal ions are made by anode dissolution.

pH was adjusted in the range 2 to 8 with 2 units of discrepancy for the purpose of suggesting optimal pH.

pH was adjusted with sulfuric acid and sodium hydroxide.

After every test; blades were washed by hydrochloric acid of 50% in order to remove oxide layer formed on the electrode surface in the process of electrocoagulation.

Results and Discussion

In this method an electric current passed through two electrode plates and caused metal oxidation to its cation. Simultaneously the water reduced to hydrogen and hydroxide ions, thus; EC process led to production of metal cation by electrochemical method and by using consumable anodes.

Dominant hydroxide species were formed by the hydrolysis of cation with pH solution. Generally, mutual reactions between species occurred differently within solution and finally led to removal of the pollutants as follow:

- Immigration of produced ions species toward an electrode with opposite electric charge and formation of floc due to charge neutralization
- Metal cation along with OH^- ion formed a hydroxide of high adsorption capacity which bonds to pollutants. Aforementioned mechanism played an important role in removal of organic compounds.
- Hydroxides formed network structure and swept up pollutants within liquid (38).

Iron oxidation within an electrolytic system causes production of $\text{Fe}(\text{OH})_n$.

$\text{Fe}(\text{OH})_{n(s)}$ formed in water flow left in the form of gelatin suspension.

This gelatin suspension can remove pollutant from wastewater through complex construction method or electrostatic absorption and frequently coagulation.

Results from electrocoagulation test and percent of chromium removal in wastewater in initial pH with different voltage shown in Table 2 and Fig 2. Test temperature was 25°C , samples were agitated at 100 rpm, test time was 25 min, and settlement time was 30 min. As shown in Fig. 1, the optimal voltage was decided to be 30 V.

pH tests shown in table 2 indicate that in low voltage the percent of chromium removal is trivial and final pH is lower than pH in high voltage. The reason is that in low voltage enough hydroxide is not produced for the iron and chromium co-settlement; consequently; less amount of chromium will remove. Higher voltage would increase production of metal cation and make this production quicker; therefore reaction of cation hydrolysis would occur several times leading to high percent of chromium removal.

Table 2 The amount of initial and final pH, before and after the process of electrocoagulation in different voltage, initial chromium of 500 mg/l

Voltage(V)	Initial pH	Final pH
10	2.18	3.86
20	2.19	4.62
26	2.22	4.91
30	2.23	5.06

Fig 3 shows the amount of chromium removal with initial concentration of 500 mg/l in different pH. To find optimal pH the tests got done under temperature of 25°C , 100 rpm in the 25 min and 30 min time for settlement and 30 V.

Table 3 shows the amount of final and initial pH and released iron in regard to the amount of chromium removal after the process of electrocoagulation.

As shown in Table 3, higher pH was caused higher removal efficiency. The reason is that in lower pH the amount of produced metal hydroxide dissolves in the acidic environment, so that the acidic factor reduces in the cathode, then iron hydroxide forms and traps chromium particles and cause chromium and iron co-deposit, frequently; final pH increases as coagulation time is passing, in consequences, less chromium would get trapped in comparison with higher pH. In this study, optimal pH was about 6 and in pH 6, initial and final pH were quite equal since produced hydroxide formed gelatin settlement of iron hydroxide and then iron and chromium co-deposit took place.

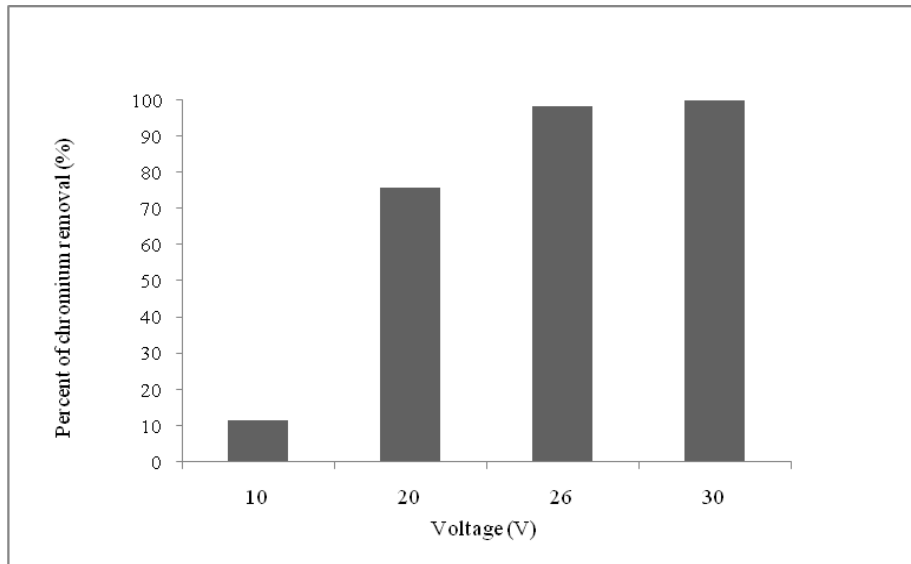


Fig 2 Comparison between percent of chromium removal in different voltages by electrocoagulation method

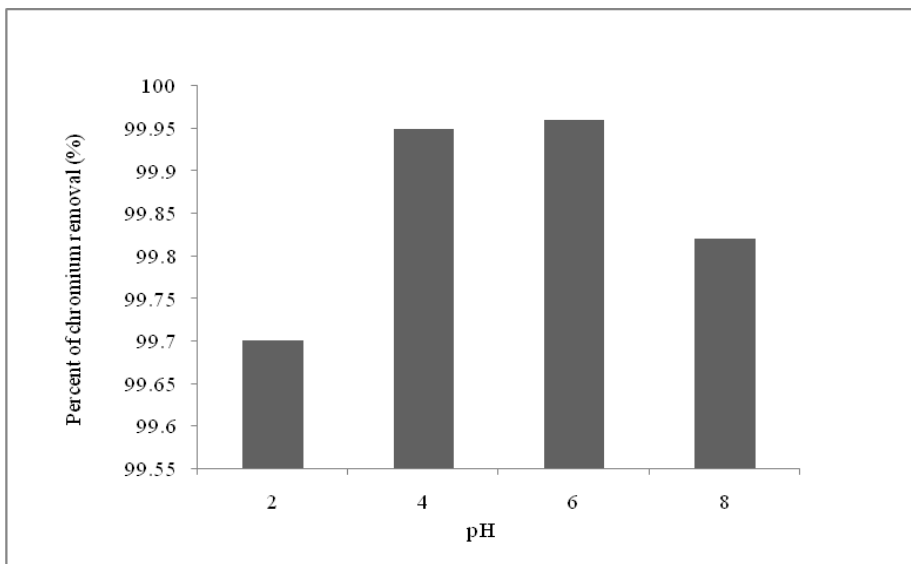


Fig 3 Comparison between percent of chromium removal in different pH by electrocoagulation method

Table 3 Percent of chromium removal, the amount of released iron and final and initial pH after and before the process of electrocoagulation

Initial chromium (mg/l)	Percent of chromium removal (%)	Released iron (mg/l)	Initial pH	Final pH
500	99.7	40.1	2.23	5.06
500	100	22.2	3.99	5.52
500	100	8.14	5.8	5.60
500	99.8	4.5	8.01	10.94

On the other hand in pH 8, existence of excess hydroxide make formation of metal ion's settlement more quickly, an event which lessens ion's flow, thus; less chromium will get trapped in comparison with pH 6. Making potential discrepancy releases iron ions within system giving iron hydroxide along with

produced hydroxide in the solution. In regard to lower initial pH and since the amount of produced hydroxide is low, more amounts of iron left in the solution and higher pH led to settlement of metal ions within the solution with hydroxide ion, thus; the amount of iron ion lessened within solution.

The results of tests on copper, chromium and nickel removal from metal plating wastewater by electrocoagulation proved that metal removal will rise up by increasing flow density, pH and electrical conductivity. In this test 100% removal of three aforementioned metals was achieved in 20 min [31]. Kobya and et al tested arsenic removal from drinking water by electrocoagulation. Optimal time in this test was 12.5 min and pH was suggested 6.5 for iron electrodes resulted in 93.5 % arsenic removal [32].

The results of tests in aforementioned studies conform to this research.

Conclusion

Plants need essential elements such as iron, to grow up and chromium compounds are very toxic for them causing harmful effects on plants' growth. *M. officinalis* L. is a medicinal plant which is very sensitive to lack of iron. Wastewater containing chromium can be treated by electrocoagulation and then be used for irrigation of this plant. The best pH for the test was determined to be 6, since enough metal hydroxide can be emerged and then iron and chromium co-deposit occurs. On the other hand in pH 6 the released iron ions exist enough within the solution and it is when in lower pH the amount of existing iron within treated wastewater is more than what is required. The reason of an increase in final pH is production rate of the coagulant and existence of the left hydroxide. In this test pH impacts directly on the reactions of this process. Also an increase in voltage would cause more metal ions to be released more quickly, thus; metal hydroxide would be produced more and caused an increase in the removal efficiency.

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