ISSN 1063-455X, Journal of Water Chemistry and Technology, 2020, Vol. 42, No. 3, pp. 157–163. © Allerton Press, Inc., 2020.

Study on Removal of Heavy Metal Ions (Pb^{2+}, Cd^{2+} and Cu^{2+}) by *Coriandrum sativum* (Coriander)

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Received October 30, 2017; revised May 18, 2018; accepted January 2, 2019

Abstract—The removal of metallic trace elements from our environment especially in wastewater is now shifting from the use of conventional adsorbents to the use of biosorbents materials which have a big potential application in environmental control and metal recovery operations. It can be considered as an alternative green technology which has been proved as more efficient and economical for metallic trace elements. In this work, we propose to test the ability of *Coriandrum sativum* (Coriander) seeds in the elimination of metallic trace elements (Pb^{2+}, Cd^{2+}, and Cu^{2+}) in water. This study was carried out by electrochemical (differential pulse polarography) and spectroscopic characterization (fourier-transform infrared, FTIR). The *Coriandrum sativum* seeds are powdered and added with different weight (0.1, 0.2, 0.4, 1, and 2 g) to different solutions containing Pb^{2+}, Cd^{2+}, or Cu^{2+} (20 ppm), after filtration with filter paper, all solutions were analyzed by differential pulse polarography technic (DPP) with a dropping mercury electrode (HMDE). The obtained results had shown a significant ability in removing, which achieved a removal efficiency of the 98.05% of Pb^{2+}, 98.1% of Cd^{2+} and 87% of Cu^{2+} at 2 g of optimal mass of *Coriandrum sativum* powder. The obtained results indicate that the *Coriandrum sativum* is a good support for elimination of toxic metals. The metallic trace elements Pb^{2+}, Cd^{2+}, and Cu^{2+} are mainly interacted by the chelation between metallic ions and the carboxylate anion as the conjugate base of a carboxylic acid in *Coriandrum sativum* particles.

Keywords: Coriandrum sativum, trace metals, elimination, Pb^{2+}, Cd^{2+}, Cu^{2+}

DOI: 10.3103/S1063455X20030029

INTRODUCTION

Metal trace elements rejected to the environment from various sources (natural or industrial) are mostly toxic even at very low concentrations. In order to preserve the environment and in particular the water resources of this pollution, efforts must be made in all sectors of activity [1].

Industrial activities have contributed to the development of countries but they have also generated several types of pollution. Many industries use and reject large quantities of heavy metals such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, electronic component industry, paint industries and pigments, etc. which making them a real threat to the environment. These pollutants have a strong toxicological impact on our water sources [2, 3].

The toxic metals lead, mercury, chromium, cadmium, copper, nickel and arsenic are characterized by their persistence, toxicity and accumulation in the natural environment. Consequently their presence in the environment can be detrimental to several varieties of living species. For this purpose, several scientific researchers have been developed in order to minimize their concentrations [4].

Generally, trace metallic elements are present in the liquid effluents in their highly mobile cat-ionic. Conventional methods applied to their separation and recovery only distinguish them by their electrical charges and often do not make it possible to restore the raw materials and the reagents used. In order for recovery to be effective, efforts should be made to develop efficient and reliable industrial wastewater regeneration processes [5].

Many methods that are being used to remove heavy metal ions include chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, naturel supports, etc. [6].

Among the most suitable current methods, membrane techniques such as osmosis, electrodialysis, ultrafiltration, microfiltration or nanofiltration are methods of choice for treatment an effluent charged with metal ions. However, these techniques also have the disadvantage of being poorly selective and largely consuming energy [7].

The *Coriandrium sativum* (coriander) is used for treating of different physiological disorders because of its active and very much vital natural nutrients and harmless nature for human body, the herb has a vast application for treating different dysfunction in humans. The *Coriandrium sativum* has proved its worth as an important medicinal herb as studied by different herbal scientists the herb has a great importance in treating disorders like diabetes, increased cholesterol, arteries blockage leading to high blood pressure, ulcers, urinary tract problems, anti anxiety, anti-bacterial and anemia prevention, skin Problems, swelling prevention, anti-osteoporosis, liver diseases, etc. [8, 9].

In the present study, we propose to use a natural support *Coriandrum sativum* to eliminate the metal trace elements (Cu^{2+}, Pb^{2+}, and Cd^{2+}). The coriander seeds or the dry fruits of coriander are powdered and added to the different solutions which contain the metal trace element. This study was carried out by electrochemical and spectroscopic characterization.

EXPERIMENTAL

Chemicals and Solutions

All chemicals used in this study were of analytical reagent grade and used without further purification $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 3H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ were from Merck Millipore. The stock solutions of Pb^{2+}, Cd^{2+} and Cu^{2+} were prepared by dissolving the appropriate amounts of their salts in ultrapure water and 0.1 M HNO_3 (Acros Organics), and then diluted to various concentrations.

Protocol of Metal Trace Elements Elimination

The *Coriandrum sativum* seeds are purchased from the local market (BordjBou Arreridj in Algeria), the dry fruits of *Coriandrum sativum* are powdered and added (0.1, 0.2, 0.4, 1, and 2 g) to the different solutions Pb^{2+}, Cd^{2+}, and Cu^{2+} (20 ppm), after 5 min of stirring a filtration was carried out with filter paper, and then all solutions are recovered and analyzed.

Analysis Technics

A polarographic analyzer (Trace Lab) was used for all electrochemical tests, which were performed in a three-electrode cell, with mercury drop electrode (HMDE) as working electrode, platinum wire as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. The analyses were performed after removal of oxygen by bubbling with nitrogen for 10 min. An analytical method used for the determination of metal trace elements is the differential pulse polarography (DPP).

The IR transmittance analysis was recorded using Fourier transform infrared spectroscopy spectrum 1000 (Perkin-Elmer), using KBr pellets containing 0.1 mg of *Coriandrum sativum* powder.

RESULTS AND DISCUSSION

Characterization of Coriandrum sativum

The infrared transmittance spectrum of the *Coriandrum sativum* powder is reported in Fig. 1. The broad band around 3422 cm^{-1} represented the ν O–H stretching, the 3023 cm^{-1} indicated alkenyl ν C–H stretching, the 2923 and 2853 revealed the aliphatic ν C–H stretching, 1764 cm^{-1} is due to ν C=O stretching, 1651 indicated the ν C=C stretching and 1375 cm^{-1} transmittance band is attributed to the ν O–H bending vibration while the bands observed at 2364 cm^{-1} is due to the hydrated KBr [10].

The *Coriandrum sativum* also known as cilantro, is an annual herb belonging to the Apiaceae family that is widely cultivated but is indigenous to southwestern Asia and North Africa [11]. The *Coriandrum sativum* seeds contain 26–29 wt % of vegetable oil [12]. The primary fatty acid (FA) constituent in *Coriandrum sativum* oil that comprises 31–75% of the fatty acid profile is petroselinic (9Z-octade-cenoic) acid, which is an uncommon isomer of oleic acid and is found at high levels in a restricted range of seed oils mostly from the Apiaceae family [13].

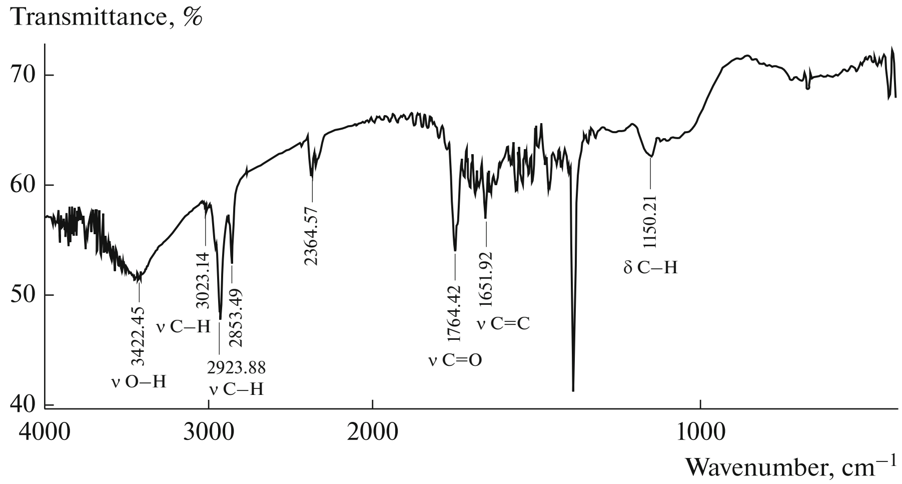

Fig. 1. Spectra FTIR of *Coriandrum sativum* powder.

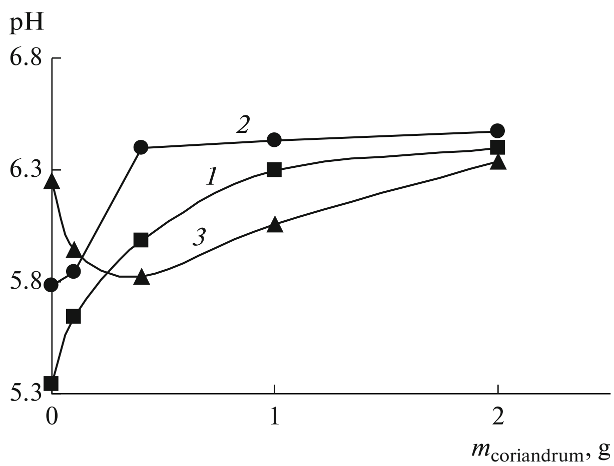

Fig. 2. Evolution of pH with *Coriandrum sativum* powder weight: Pb^{2+} (*1*), Cd^{2+} (*2*), Cu^{2+} (20 ppm) (*3*).

Effect of Coriandrum sativum Addition on pH

Figure 2 shows the evolution of pH in function of coriander powder mass which was added to 20 ppm of Pb^{2+}, Cd^{2+}, or Cu^{2+} solutions. We observe that the initial pH values were 5.34 for Pb^{2+}, 5.78 for Cd^{2+} and 6.25 for Cu^{2+} and then the pH increases until it reaches a value of 6.40 for Pb^{2+} 6.34 for Cu^{2+} and 6.47 for Cd^{2+} the solutions at 2 g of added *Coriandrum sativum* powder. We can say that coriander possess a buffering capacity which stabilizes the pH and which becomes almost neutral for all studied solutions.

Electrochemical Analysis

The calibrations curves for analyte ions Pb^{2+}, Cd^{2+} and Cu^{2+} are shown in Fig. 3. The standard solutions of different metal trace elements were prepared with concentrations (1, 5, 10, 20 and 40 ppm) and recorded over a potential range from –0.4 to –0.6 V/SCE for Pb^{2+}, –0.2 to –0.8 V/SCE for Cd^{2+} and 0 to –0.5 V/SCE for Cu^{2+}, in 0.1 M HNO_3 electrolytic support by using the differential pulse mode. The peak potentials were –0.467 V/SCE for Pb^{2+}, –0.637 V/SCE for Cd^{2+} and –0.222 V/SCE for Cu^{2+}. All peaks are attributed to the reduction of different metal trace elements cations. All calibration curves show

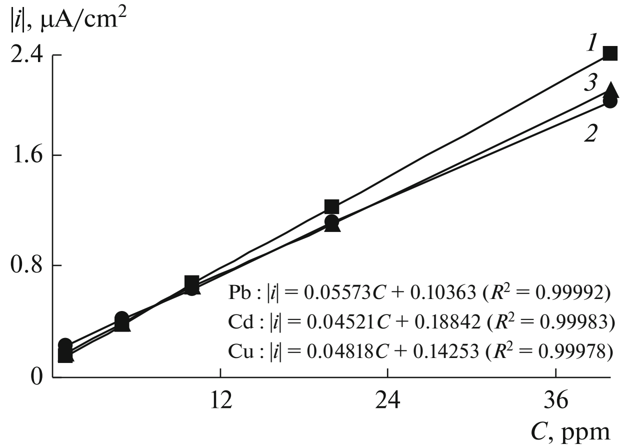

Fig. 3. Calibration curves of Pb^{2+} (*1*), Cd^{2+} (*2*) and Cu^{2+} (*3*).

a linear dependence of current with Pb^{2+}, Cd^{2+} and Cu^{2+} concentrations. The correlation coefficient of all curves was in order of 0.999 and this can be expressed by the following regression equations:

$$|i| = 0.05573C + 0.10363 \text{ for } Pb^{2+};$$

$$|i| = 0.04521C + 0.18842 \text{ for } Cd^{2+};$$

$$|i| = 0.04818C + 0.14253 \text{ for } Cu^{2+}.$$

As we can observe that the sensitivity of Cd is lower than Cu and Pb. This can be attributed to the different diffusion coefficients of Pb^{2+}, Cd^{2+}, and Cu^{2+} in the electrolyte solution.

Figures 4a–4c shows differential pulse polarograms corresponding to the determination of Pb^{2+}, Cd^{2+} and Cu^{2+} concentrations respectively in different solutions. At first, a stock solution was prepared containing 20 ppm of each metal trace element and then a different mass (0.1, 0.2, 0.4, 1, and 2 g) of *Coriandrum sativum* powder was added to 100 mL of stock solution, after stirring and filtration, the recovered solution was analyzed by differential pulse polarography technic.

As can be seen, a well-defined polarographic peaks were obtained at –0.467 V/SCE for Pb^{2+}, –0.637 V/SCE for Cd^{2+} and –0.222 V/SCE for Cu^{2+} solution, which correspond to the reduction of these metal trace elements [14]. After the addition of *Coriandrum sativum* powder to the stock solution, the intensity of the cathodic peaks decrease by increasing the mass of *Coriandrum sativum* powder, this is attributed to the decrease of metal trace elements concentrations in solution.

The differential pulse polarograms of Pb^{2+} (a), Cd^{2+} (b), and Cu^{2+} (c) (see Fig. 4) in 1 M HNO_3 containing different mass of *Coriandrum sativum* powder (0.1, 0.2, 0.4, 1 and 2 g) confirm an important elimination for all studied metals. This elimination is due to the accumulation of the different elements in *Coriandrum sativum* particles.

To evaluate the effect of *Coriandrum sativum* mass, we studied the elimination of Pb^{2+}, Cd^{2+}, and Cu^{2+} in the stock solution by plotting the elimination curve of metal trace elements shown in Fig. 5. The initial concentration of metal ions was 20 ppm and then begins to decrease after treatment. The removal efficiency increased significantly with weight of added *Coriandrum sativum*. Using the equation of the previous calibration curve to investigate the removal efficiency of different metal ions, a remarkable percent of elimination were obtained at 2 g of *Coriandrum sativum*, 98.05% for Pb^{2+}, 98.1 for Cd^{2+} and 87% for Cu^{2+}.

Mechanism of Accumulation

As known the *Coriandrum sativum* seeds are rich in fatty acid (FA) as the principle component in biodiesel fuels the petroselinic acid. Most of the remaining fatty acid profile consisted of common 18 carbon constituents such as inoleic, oleic and stearic acids [15]. The vegetable oils are generally composed of five common fatty acids, which are palmitic, stearic, oleic and linolenic acids [16].The probable accumulation

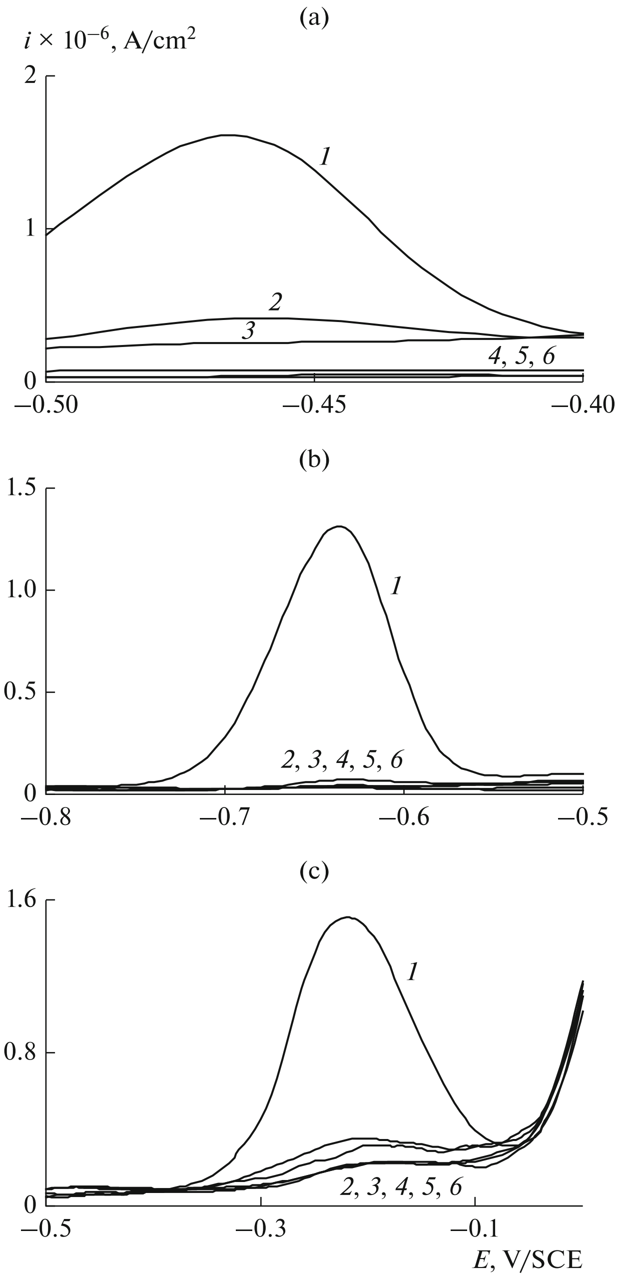

Fig. 4. Evolution of differential pulse polarograms of Pb^{2+} (a), Cd^{2+} (b) and Cu^{2+} (c) solutions containing 20 ppm of cation (*1*) and different mass of *Coriandrum sativum* powder (0.1 (*2*); 0.2 (*3*); 0.4 (*4*); 1 (*5*) and 2 g (*6*)).

mechanism is shown in Fig. 6. The metal ions mainly interacted with the particles by chelation between the metal ions (M^{2+} : Pb^{2+}, Cd^{2+} or Cu^{2+}) and the carboxylate anion (–COO–).

CONCLUSIONS

The results of this study shows that metallic trace elements (Pb^{2+}, Cd^{2+}, and Cu^{2+}) have been eliminated by the *Coriandrum sativum* particles significantly. The proposed mechanism indicates that the metal ions are mainly interacted with the particles by chelation between metallic ions and the carboxylate anion. However, after the addition of *Coriandrum sativum* the removal efficiency of Cu^{2+} is less than the Cd^{2+} and Pb^{2+}. The experimental results obtained are encouraging for the present work and opens up a number of

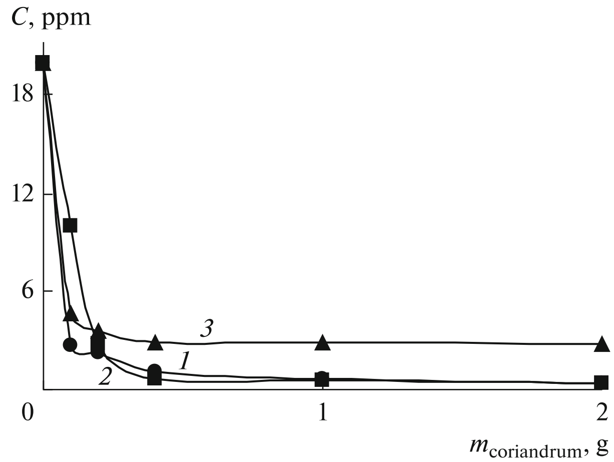

Fig. 5. Evolution of Pb^{2+}—98.05 (*1*), Cd^{2+}—98.1 (*2*) and Cu^{2+}—87% (*3*) concentration in solution with *Coriandrum sativum* quantity and the removal efficiency until 2 g.

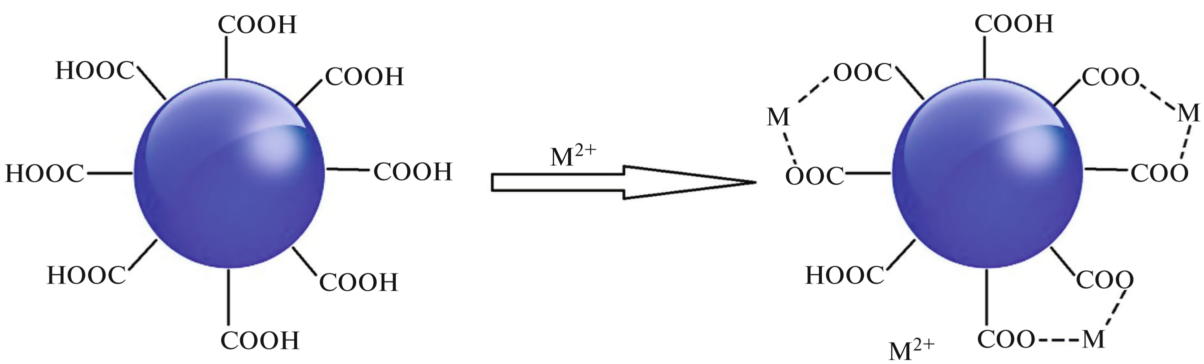

Fig. 6. Mechanism of accumulation of metal ions (M^{2+}) on *Coriandrum sativum* particles.

perspectives for a possible improvement and continuation of work on adsorption of metallic trace elements on *Coriandrum sativum* particles.

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