

Biosorption of Chromium(VI) and Mercury(II) from Aqueous Solutions by *Eriobotrya japonica* (Rosaceae)

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A method was developed to investigate the potential removal of chromium(VI) and mercury(II) from aqueous solutions through biosorption by *Eriobotrya japonica* (Rosaceae). The results obtained shows removal of Cr(VI) by 68.4 % and for Hg(II) by 97.4 % for 100 mg/L solutions of Cr(VI) and Hg(II), with biomass of 3 g. However, both solutions containing Cr(VI) and Hg(II) were reached the equilibrium within 1 h. The optimum pH value used for both elements was pH 5. The biosorption of Cr(VI) and Hg(II) was studied using FTIR. The spectra suggested that the presence of Cr(VI) ions in the biomass effects the bands corresponding to the carboxyl groups. Similar result was achieved for Hg(II) ion at optimum pH 5. The results obtained by the method indicated that *Eriobotrya japonica* (Rosaceae) is appropriate material for biosorption of Cr(VI) and Hg(II).

Key Words: Biosorption, Chromium(VI), Mercury(II), *Eriobotrya japonica* (Rosaceae).

INTRODUCTION

The presence of mercury and chromium in the environment causes a toxic effects. The important sources of mercury to the environment were the effluents from chloro-alkali plants, dentistry and military operations and in units manufacturing organo-mercurial compounds. The main sources of chromium specially hexavalent oxidation state were from mining, leather tanning, electroplating and production of steel and other metal alloys.

Determination of low concentrations of trace elements in natural waters required a sensitive instrument or a preconcentration and separation methods. Several methods have been applied for treatment of water to remove trace elements prior to analysis including ion exchange or chemical precipitation^{1,2}.

Recently, plant was used for removal of heavy elements from aqueous solutions. A number of chemical treatment methods employing plant for removal of mercury and chromium from aqueous solutions have been used. Metal accumulating fungi³ and *Azolla filiculoides*, an aquatic fern⁴ were indicated as metal biosorbers. However, aquatic higher plants including water hyacinth (*Eichhornia crassipes*)⁵, duckweed (*Lemna minor*)⁶ and water velvet (*Azolla pinnata*)⁷ were found to have the ability to

remove various heavy metals from solutions. Some other types of sorbents have been used are cotton⁸, coffee grounds⁹, wool fiber¹⁰, apple waste¹¹, waste rubber¹² and barks of trees¹³.

Fourier transform infra red spectroscopy (FTIR) has been used to studying compositional changes in plant¹⁴. Dokken *et al.*¹⁵ used FTIR to determine the effect of some chemical materials on the structure of sun flower plants, while other workers used it for analyses of plant cell wall¹⁶.

In this work, the biosorption of mercury(II) and chromium(VI) from aqueous solutions by the leaves of *Eriobotrya japonica* (*Rosaceae*) as well as the changes in the structure of functional groups which are presented in the leaves of *Eriobotrya japonica* were studied.

EXPERIMENTAL

The pH measurements were achieved with pH ion analyzer during the experiments. 21D Milton Roy spectrophotometer was used with matched silica micro cells of 10 mm path length. In order to determine the functional group responsible for metal uptake, unreacted leaves sample and pretreated leaves with 100 mg/L chromium and mercury, solutions were analyzed using fourier Fourier Transform Infrared Spectrometry (FTIR) Bruker IFS-25 instrument.

Preparation of biosorbent: Leaves of *Eriobotrya japonica* (*Rosaceae*) was collected from different places in Tripoli-Libya and used as biosorbent material for removal of chromium(VI) and mercury(II) ions. The leaves was washed extensively in running tap water to remove all the adhering soil particles after that the leaves washed again with deionized water and boiled in double distilled water repeatedly to remove colour materials. The washed and boiled leaves were oven dried at 40 °C in the convention heating oven for 36 h and finally the leaves is grounded separately in a mortar and sieved through a 125-150 µm mesh.

Preparation of stock solutions: An aqueous solution of 1000 mg/L mercury and chromium were prepared. 0.1 N hydrochloric acid and sodium hydroxide were used for adjusting the pH of solutions after the addition of the biosorbent.

Procedure: A solution of Cr(VI) and Hg(II) containing different concentration ranged between 10-100 mg/L and dried biomass ranged between 1-40 g/L were added to Erlenmyer flasks (250 mL). The mixture was stirred at a constant temperature in a shaker at 120 rpm, the flask content was filtrated by vacuum filtration using Whatmann filter paper No. 1. The filtrate containing the residual was analyzed spectrophotometrically for determination of chromium and mercury at wavelength 540 and 488 nm, respectively after complexation with 1,5-diphenyl-carbazide for chromium and diphenylthiocarbazone (dithizone) for mercury.

For determination the rate of metal biosorption from 100 mL at concentrations of 10, 20, 50 and 100 mg/L, the supernatant was analyzed for residual of Cr(VI) and Hg(II) after period of 15, 30, 60, 120, 130, 240 and 300 min.

The effect of pH on ions sorption was investigated at different pH values of 2, 3, 4, 5, 6,7 and 8.

RESULTS AND DISCUSSION

Effect of pH: The effect of pH on the up take of Hg(II) and Cr(VI) by the sorbent was investigated. The results obtained for mercury (Fig. 1) showed that 95 % or more was removed at pH ranged between 4 to 8. It has been observed that the sorption of mercury reached a maximum (> 95 %) around pH 4 and remained constant till pH 8. Similar results was obtained for both inorganic and methyl mercury¹⁷. However, the results obtained for Cr(VI) (Fig. 2) indicated that most of the chromium was removed at pH ranged between 2-6. Chromium exhibits different types of pH depending on the equilibrium in the aqueous solutions. By shifting the pH the equilibrium will shift. Ions such as HCrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are in the equilibrium at pH ranged between 2-6. At pH lower than 2, $\text{Cr}_3\text{O}_{10}^-$ and $\text{Cr}_4\text{O}_{13}^{2-}$ are formed¹⁸. Ismael *et al.*¹⁹ studied the biosorption of Cr(VI) from aqueous solutions by fungal biomass and noted that the highest adsorption was at pH 2 and 4 for *C. neoformans* and *helminthosporium sp.*, respectively. Other workers²⁰ studied the adsorption of different elements using different types of tree leaves and found that the best pH were ranged between 5-6.

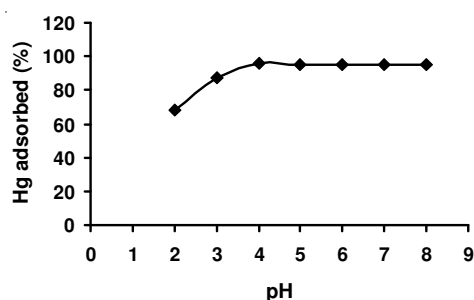


Fig. 1 Effect of pH on the biosorption of Hg(II) ion

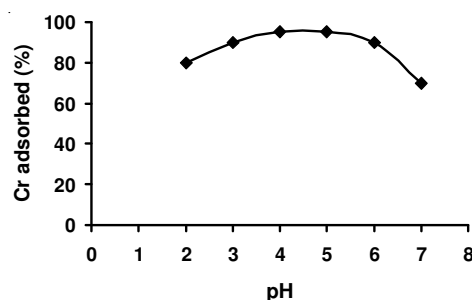


Fig. 2. Effect of pH on the biosorption of Cr(VI) ion

Rate of adsorption: The adsorption of mercury and chromium by *Eriobotrya japonica* was studied using different concentrations of hydrochloric acid, 1 mg of Hg(II) and Cr(VI) were added to two 500 mg of sorbent material and shaken in a 10 mL solutions of HCl. After filtration the mercury and chromium content in the filtered supernatant was determined. The results obtained indicated that desorption of Hg(II) was increased with increasing the concentration of HCl. However, 95 % desorption was achieved after HCl concentration of 4 mol/L. Karunasagar *et al.*¹⁷ noted that complete desorption for Hg^{2+} was occurred with 6 M HCl.

For chromium the results obtained indicated that > 95 % desorption was occurred at concentration of 3 mol/L.

FTIR: The functional groups presented in *Eriobotrya japonica* was responsible for sorption of mercury and chromium were studied by analysis untreated and treated *Eriobotrya japonica* samples with 100 mg/L Hg(II) and Cr(VI) solutions. The

representative FTIR results are shown in Figs. 3-5. From the spectra obtained for both elements with and without sorbent material suggested that presence of Cr(VI) in the biomass at pH 5 effects the bands corresponding to the carboxyl group. However, the spectra for mercury at pH lower than 3 does not showed any difference while repeating the FTIR analysis for Hg ions at pH 5 similar results obtained for Cr(VI) was indicated. Taniguchi *et al.*²¹ studied the functional groups presented in the *Eriobotrya japonica* and found that *Eriobotrya japonica* contains a carboxylic and hydroxyl groups. The structure obtained is shown in Fig. 6. Other workers showed that carboxylic acid groups played a major role in the binding of the mercurial species¹⁷.

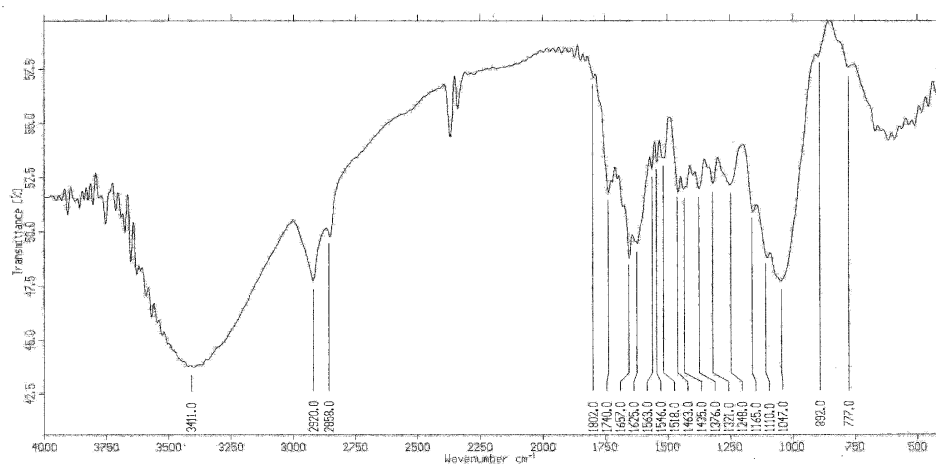


Fig. 3. FTIR spectra for *Eriobotrya japonica*

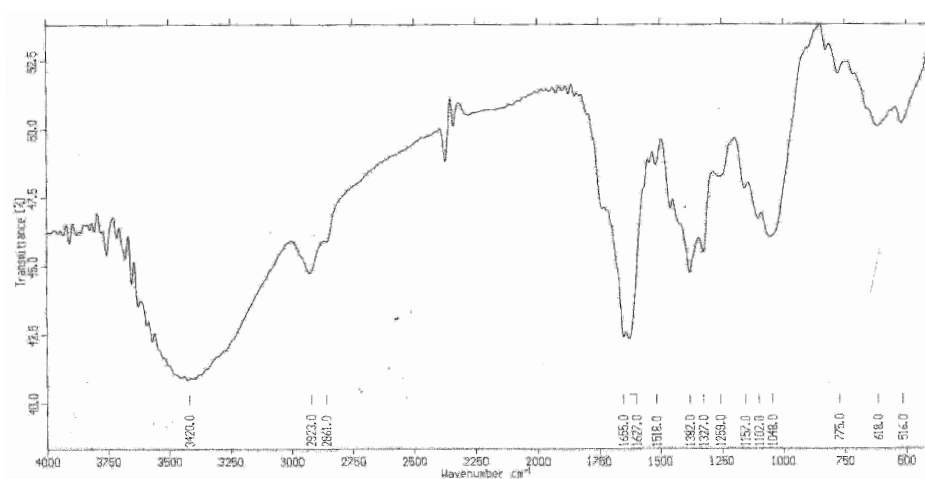


Fig. 4. FTIR spectra for *Eriobotrya japonica* with 100 mg/L Cr(IV) at pH 5

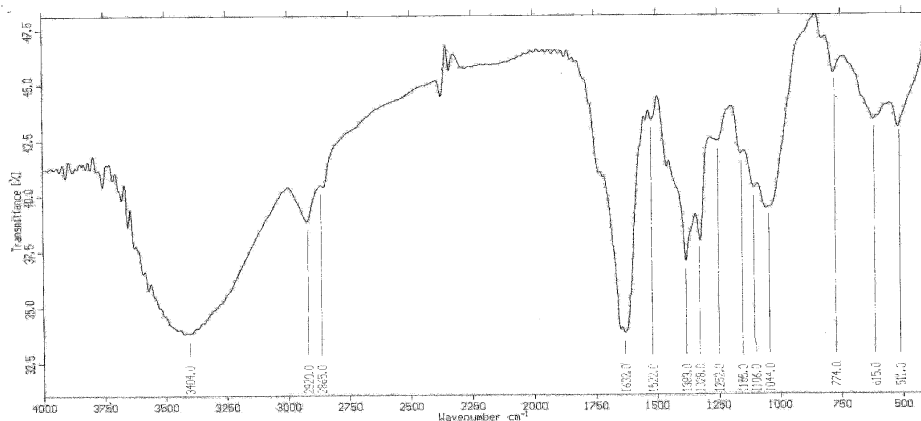


Fig. 5. FTIR spectra for *Eriobotrya japonica* with 100 mg/L Hg(II) at pH 5

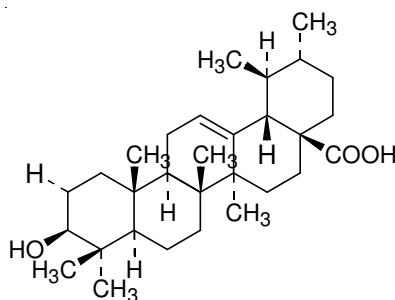


Fig. 6. Chemical structure suggested by Taniguchi *et al.*²¹ for (16 mg/g dry weight) intact leaves of *Eriobotrya japonica*

Previous literature showed that sorption of metal ions in both specific and non specific sorbents has been known to be pH dependent²².

Determination of Hg and Cr in aqueous solution: After the optimum conditions were chosen for removal of Hg(II) and Cr(IV) from aqueous solution, the per cent recovery for both elements was investigated for addition of 100 mg/L solutions of Hg(II) and Cr(IV) to 3 g of absorbent (Table-1).

TABLE-1
PER CENT RECOVERY FOR REMOVAL OF Hg(II) AND Cr(IV)

Element	pH	Recovery (%)
Mercury	5.0	97.4
Chromium	5.0	68.4

The results showed a 97.4 % removal of Hg(II) and 68.4 % removal of Cr(IV) indicating that efficiency of *Eriobotrya japonica* is excellent for the removal of Hg(II) from the aqueous solution but it is not enough for removal of total Cr(IV) from the same type of solution.

Conclusion

The sorbent *Eriobotrya japonica* was found to sorb all Hg(II) from aqueous solutions with excellent efficiency, but for Cr(IV) is not good enough. The degree of removal of both elements Hg(II) and Cr(IV) was found to ranged between pH 4-8 and 2-6, respectively. The FTIR analysis indicated that the carboxylic groups could be mainly responsible for the sorption of Hg(II) while for Cr(IV) the same group's dose not showed a high efficiency.

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