

Eco – Friendly Removing of Some Heavy Metals Via *Morusnigra* Leaves

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Abstract: The main objective of this research is using of *Morusnigra* leaves powder as adsorptive material for remove of some heavy metals ions, practically Pb(ii), Cu(ii), Mn(ii) and Co(ii). The efficiency of *Morusnigra* leaves powder was investigated to remove these heavy metals ions form their solutions and wastewater. The parameters such as weight of adsorptive material (g) and Metal ion concentration are investigated in the constant time and pH. The results showed that as weight of adsorptive material increased the removal% was increased. Therefore, the higher removal% for Pb(ii), Cu(ii), Mn(ii) and Co(ii) was found to be 91, 85, 83 and 67 respectively.

Keywords: Adsorption Isotherm, *Morusnigra*, Eco-Friendly Removing

1. Introduction

Local name is Creole (mi); English (mulberry, small fruited mulberry, blackmulberry, black Persian); French (Muriernoir, mûres); German (Schwarzer Maulbeerbaum); Hindi (tut, shah-tut); Indonesian (murbei); Italian (gelsonero); Javanese (besaran); Spanish (moranegra, morero, moreranegra); Swahili (mforsadi); [1] trade name (tut); Vietnamese (dâu tam). *Morusnigra* is a deciduous tree, slender but with numerous branches. Grows to 6-9 m in height, but it tends to be a bush if not trained when young. Leaves rough on upper surfaces and pubescent underneath [2], 7-12.5 cm long, often producing leaves of several different shapes, with 1 or more lobes, multilobed leaves often appearing on the same branches as lobeless ones; abnormally shaped leaves usually produced from stem shoots or sucker growths, and frequently by very vigorous young branches. Flowers held on short, green, pendulous, nondescript catkins that appear in the axils of the current season's growth and on spurs on older wood. The flowers appear in 1.3 cm scaly clusters, female flowers ripening quickly into 1.3-2.5 cm blackberry-shaped edible fruits. Botanically, the fruit is not a berry but a collective fruit; the fleshy bases of pollinated flowers begin to swell and

ultimately become completely altered in texture and colour, becoming succulent, fat and full of juice [3]. In appearance, each tiny swollen flower roughly resembles the individual drupe of a blackberry. The colour of the fruit does not identify the mulberry species. It has been suggested that the generic name of the mulberry [4], *Morus*, was derived from the Latin 'mora' (delay), from the tardy expansion of the buds. An alternative explanation is that it comes from the Celtic 'mor' (black), referring to the colour of the fruit. The specific name refers to the dark colour of the fruit.

Trees are either dioecious or monoecious, and sometimes will change from one sex to the other. *M. nigra* trees do not begin to bear much fruit before 15 years of age. They are wind pollinated, and some cultivars will set fruit without any pollination, for example in California, USA. The self-fertile trees commonly produce 2 crops a year [5] [7] [8].

Several technologies have been proposed to treat wastewater contaminated with metal species. Among several technologies, the extraction of metal ions using solid materials such as modified silica, alumina [9] [10], activated carbon, and resins has been extensively investigated [11]. These materials have been subjected to functionalization reactions to anchor molecules containing Lewis bases in its structure, which acts as a metal collector [12] [13]. In the case of silica, the main advantages are its high surface reactivity,

the possibility to anchor molecules with desirable selectivity toward metal ions [14, 15] and the high stability of legend molecules on the silica surface, enabling the matrix to be used over a number of cycles. Despite these advantages, preparing modified silica gel with organic molecules is expensive because high-purity chemicals are required to enhance the efficiency of the reaction; moreover, the solvents used in the modification reaction are usually toxic [16] [17]. This standpoint, therefore led to natural solid material that can be considered more attractive, besides being aligned with the concepts of green chemistry. Natural products usually considered waste, such as sugar cane bagasse, peanut shells, and apple waste, have been employed to extract metals from water [18] [19]. This is possible due to the presence of acid groups such as carboxylic and phenolic groups [20]. This type of product can also be used in metal speciation, as in the case of Cr(VI) sorption by coconut coir [19].

2. Materials and Methods

2.1. Materials

All chemicals used were of analytical reagent grade (AR), were obtained from Sigma Chemical Co. (St. Louis, MO). Nitric acid, Copper II Nitrite, Manganese (ii) nitrate, Cobalt (ii) nitrate, lead (ii) nitrate, Sodium Hydroxide, industrial wastewater, Deionized water and *Morusnigra*.

2.2. Procedures

2.2.1. Samples Collection

Morusnigra Leaves were collected from Gasor ben basher, Libya. Taxonomic authentication of the plant has been carried out in the Botany Department - Faculty of Science Trhona University - Libya.

Industrial Wastewater

The used industrial wastewater was collected from Trablus industry for food materials - libya.

2.2.2. Preparation of *Morusnigra* Leaves as Adsorbent Medium

A 500g of *morusnigra* were weighed and washed well with distilled water then the leaves were dried at 80°C for 24 hours [15].

2.2.3. Preparation of Standard Solutions of Heavy Metals Solutions

Lead nitrate, Copper (ii) Nitrite, Manganese (ii) nitrate and Cobalt (ii) nitrate salts were used to prepare standard solutions of (10 and 50 ppm) in 100mL volumetric flasks, according to standard methods of preparations of standard solutions.

2.2.4. Preparation of the Raw Industrial Wastewater Sample

The sample of industrial wastewater was subjected to a digestion procedure to oxidize organic substances such as humic acids, that bind metal ions in solution and influence

the pre - concentration results. In this procedure, concentrated HNO₃ (5mL) was added an aliquots of 50 mL of wastewater in a beaker. The mixture was then subjected to evaporated on hotplate. The colour of the solution became dark. Further HNO₃ conc (5mL) was added and the mixture was heated for 1 h at 95°C. The pH of the digested extract was adjusted to 5.5, the sample's volume was adjusted to 100 mL in a volumetric flask [20].

2.2.5. Treatment of Standard Solutions of Heavy Metals Via *Morusnigra* Leaves (Adsorption Process)

Morusnigra leaves (0.5g) was placed in clean Erlenmeyer flask. Prepared wastewater (100mL) was added through the leaves for adsorption of ions concentration. Then standard solutions of Pb(ii), Cu(ii), Mn(ii) and Co(ii) (10 and 50 ppm) were being added separate through different *Morusnigra* Leaves (0.5g). The pH was adjusted at (5.5). Then the solution was stirred for 2 hours. the above steps were repeated with deferent *Morusnigra* Leaves weight (1, 1.5, 2, and 3).

2.2.6. Investigation of Ion Concentrations

The marked ion concentrations were investigated in industrial wastewater before and after treatment by *Morusnigra* Leaves and in the standard solutions of heavy metals ions using Atomic Absorption Spectrophotometry technique (AAS).

3. Results and Discussion

The percentage yield of dry banana peel is shown in Table 1.

Table 1. Yield of Dry *Morusnigra* Leaves.

Weight of <i>Morusnigra</i> Leaves (g)	Weight of dry leaves(g)	percentage yield (% g/g)
500	150.73	30.1

The percentage yield of dry leaves is higher than percentage yield of renata *et al* since 2011 [20], they found that the percentage yield of dry Brazil *Morusnigra* Leaves is 22.4%. The comparison between obtained result of percentage yield in the current study and renata *et al* results is shown in Figure 1.

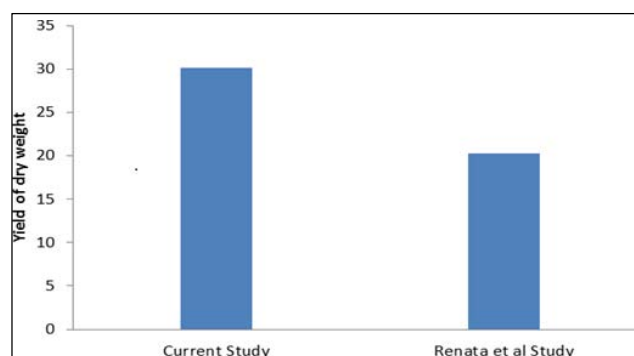


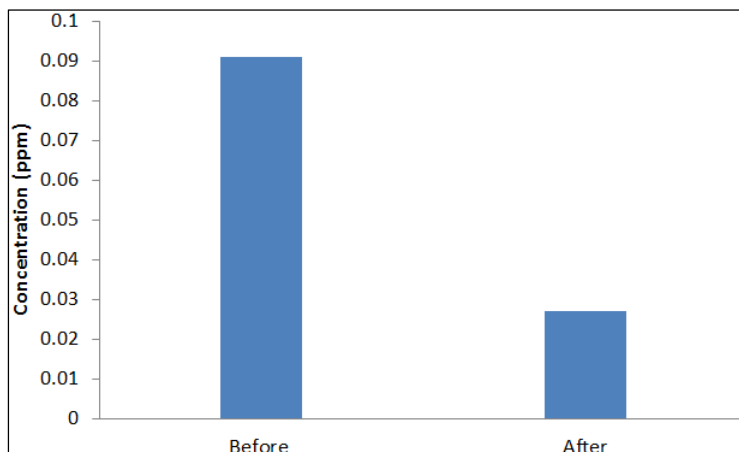
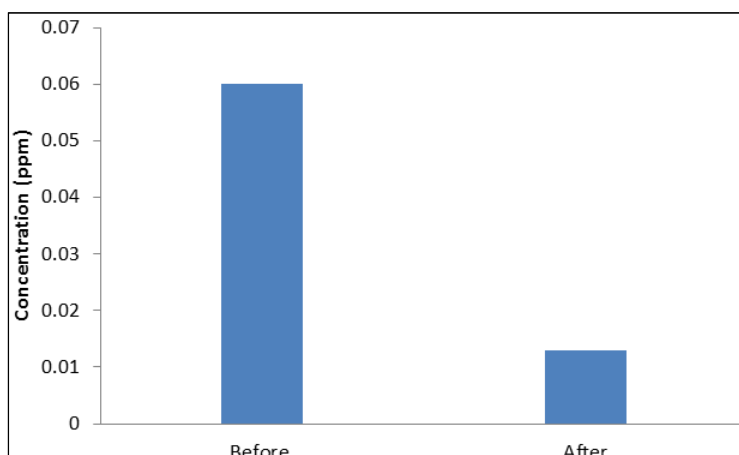
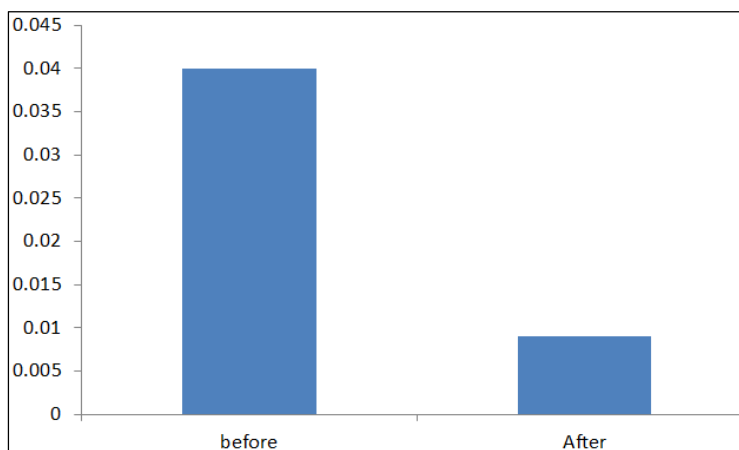
Figure 1. Comparison Between Current Study and Renata et al Results.

Table 2. The Concentration of Pb(ii), Cu(ii), Mn(ii) and Co(ii) in Industrial Wastewater Before and After Passing on *Morusnigra* Leaves.

Metals	Before Passing on leaves	After Passing on leaves
Lead	0.091	0.027
Copper	0.060	0.013
Manganese	0.04	0.009
Cobalt	0.87	0.03

The obtained results revealed that the *Morusnigra* leaves

have shown high abilities of adsorption of lead, copper, manganese ion from industrial wastewater, the concentration of lead and copper in wastewater after passing on leaves medium were found to be lower than American Society for Testing and Materials ASTM limits. The comparison between the concentration of lead, copper, manganese and Cobalt in industrial wastewater before and after passing on *Morusnigra* leaves are shown in Figure 2, 3, 4 and 5. Respectively.

**Figure 2.** Concentration of Lead in Industrial Wastewater Before and After Treatment by *Morusnigra* Leaves.**Figure 3.** Concentration of Copper in Industrial Before and After Treatment by *Morusnigra* Leaves.**Figure 4.** Concentration of Manganese Ion in Industrial Wastewater Before and After Treatment by *Morusnigra* Leaves.

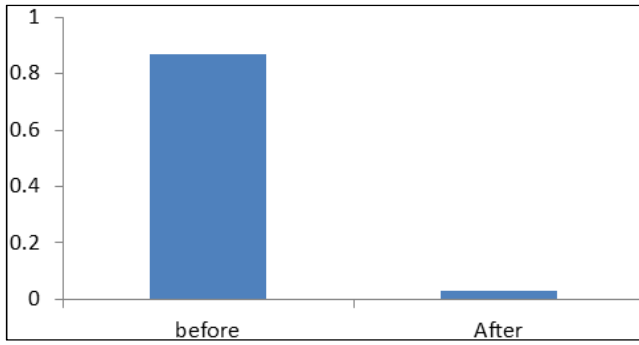


Figure 5. Concentration of Cobalt Ion in Industrial Wastewater Before and After Treatment by Morusnigra Leaves.

Effect of *Morusnigra* leaves weights on the removal percentage of marked heavy metals are shown in Table 3.

Table 3. Effect of *Morusnigra* Leaves Weights on the Removal Percentage of Marked Heavy Metals.

Metal Ion	Weight of Leaves	Removal Percentage (%w/w)
Cu (ii)	0.5	77.54
	1	79.88
	1.5	80.89
	2	83.00
	3	85
Mn(ii)	0.5	72.33
	1	73.65

Metal Ion	Weight of Leaves	Removal Percentage (%w/w)
Pb(ii)	1.5	75.00
	2	79.00
	2.5	83.00
	0.5	74.54
	1	78.50
Co(ii)	1.5	80.01
	2	81.73
	3	91.00
	0.5	63.00
	1	63.88
	1.5	64.78
	2	66.89
	3	67.00

The data obtained (Table 3) revealed that the positive correlation between weight of leaves and the removal percentages were reported with all analyzed heavy metals. The higher extraction capacity of heavy metals can be explained by the fact that carboxylic acid groups [20], which are considered hard bases, have a stronger affinity for hard or intermediate acids such as Cu(II) ions. Pb (II) and other metal ions that are considered soft due to their large ionic radius and high polarizability, which cause their extraction to occur to a higher extent. The leaner shape between removal percentages and weight of leaves for Cu, Mn, Pb and Co ions are shown in Figure 6, 7, 8 and 9 respectively.

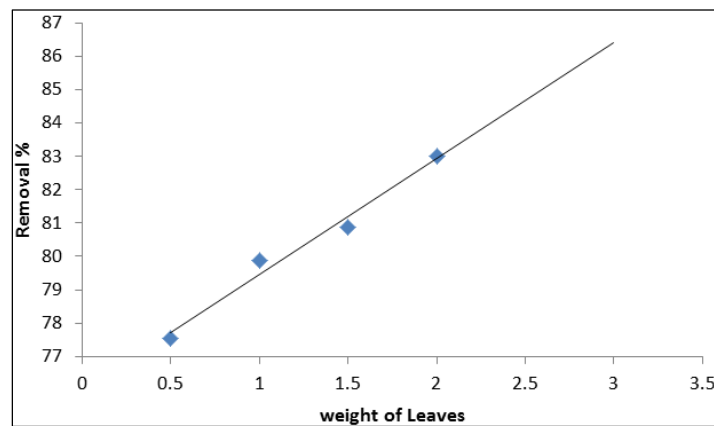


Figure 6. The Leaner Shape Between Removal Percentages and Weight of Leaves for Cu(ii) Ion.

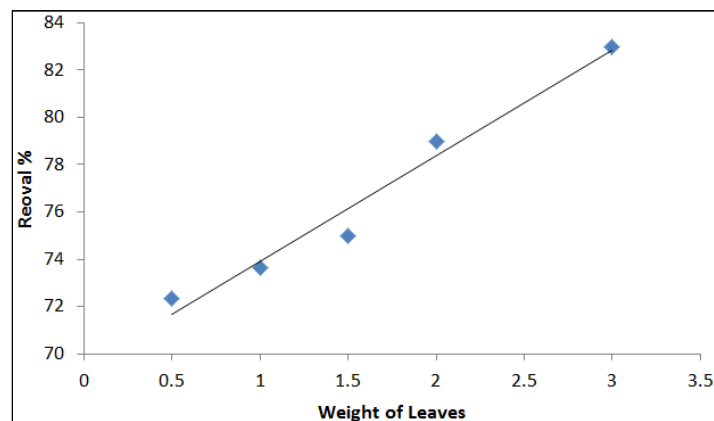


Figure 7. The Leaner Shape Between Removal Percentages and Weight of Leaves for Mn(ii) Ion.

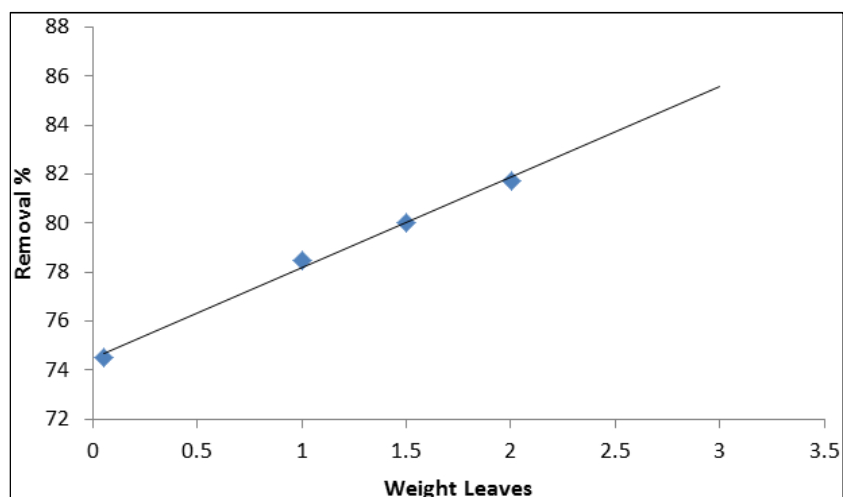


Figure 8. The Linear Shape Between Removal Percentages and Weight of Leaves for Pb(ii) Ion.

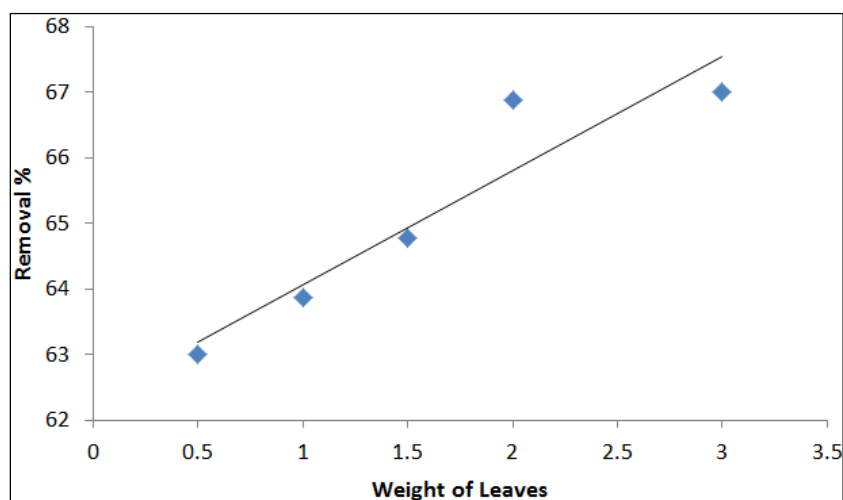


Figure 9. The Linear Shape Between Removal Percentages and Weight of Leaves for Co(ii) Ion.

The highest removal percentage of *Morusnigra* Leaves has been recorded for Pb ion after used 3 g of leaves.

Effect of ions concentration of used heavy metals on removal percentage are shown in Table 4.

Table 4. Effect of Ions Concentration of Used Heavy Metals on Removal Percentage.

Metal Ion	Concentration (ppm)	Removal Percentage%	Concentration (ppm)	Removal Percentage%
Cu	10	90	50	92
Mn	10	83	50	85
Pb	10	98	50	96
Co	10	75	50	78

The obtained results in above table have been showed that the positive correlation between ion concentrations and removal percentage except for lead ion that has been showed

negative correlation. The comparison between ion concentration and removal percentage for Cu, Mn, Pb and Co are represented in Figure 10, 11, 12 and 13, respectively.

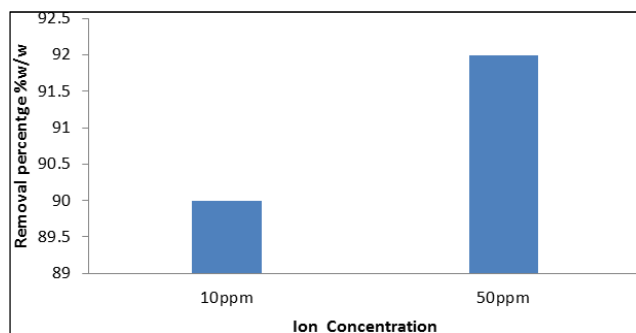


Figure 10. The Comparison Between Ion Concentrations and Removal Percentages for Cu(ii) Ion.

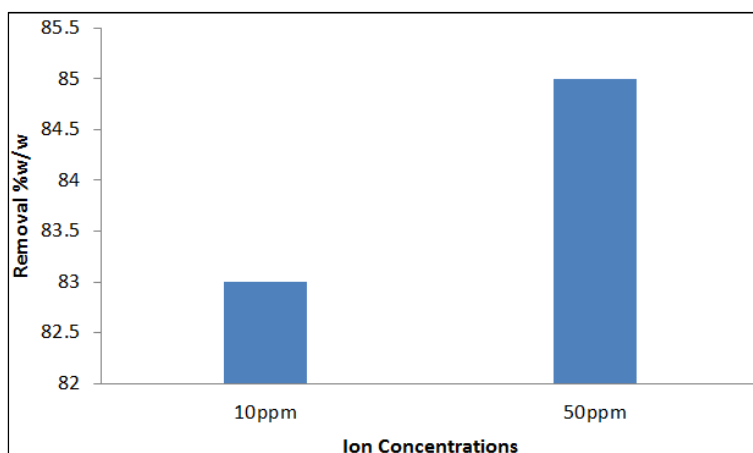


Figure 11. The Comparison Between Ion Concentrations and Removal Percentages for Mn(ii) Ion.

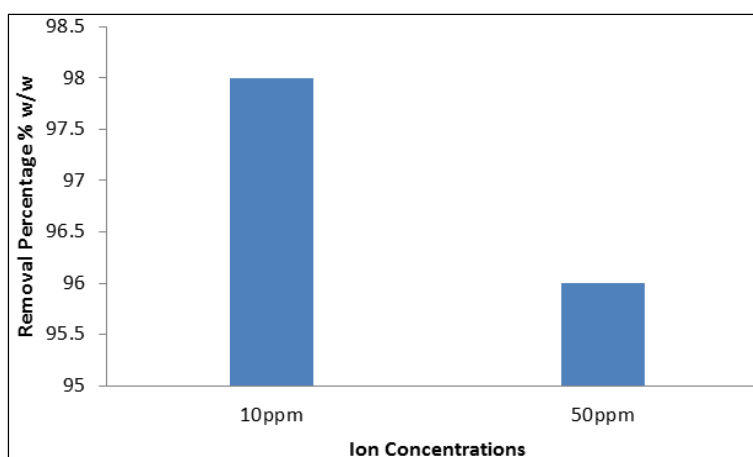


Figure 12. The Comparison Between ion Concentrations and Removal Percentages for Pb(ii) Ion.

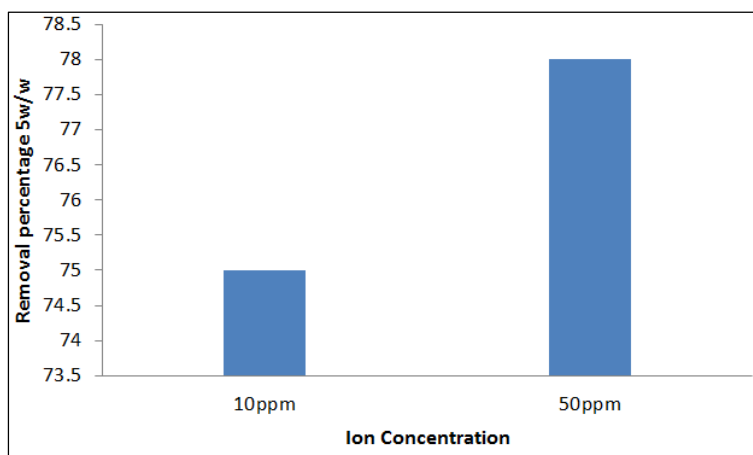


Figure 13. The Comparison Between Ion Concentrations and Removal Percentages for Co(ii) Ion.

4. Conclusion

This research led to the conclusion that minced *Morusnigra* Leaves can be applied in the extraction and pre-concentration of Cu II, Mn II, Pb II and Co II ions in industrial wastewater. The correlation between weight of leaves, Ion concentrations and removal percentage have been studied. The uptake ability of *Morusnigra* Leaves can be

explained by the fact that carboxylic acid groups which are considered hard base, have a strong affinity for interacted with lead and copper ions. The high retention percentage of analyzed ions in acid medium is an important aspect of the adsorption process because it can be applied to the purification of wastewater. In our opinion, this biomaterial is also very attractive due to its low cost and the fact that it does not require modification reactions such as those required by

other materials used in this type of work.

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