Treatment of Heavy Metal Pollution of Industrial Effluent using a Green Biosorbent Lemon Peel (*Fructus limonis*)

Rizwan Ali, Roha Imran, Hoor-ul-Ain, Rowaiba Muqadas,
Ali Abbas*, Zafar Iqbal
Department of Chemistry: Government Islamia
Graduate College, Chiniot.

* Corresponding Author
Dr. Ali Abbas

Introduction

Even though water is abundant on earth, because of high salt concentration 97% of the water is not suitable for drinking or industrial purposes. About two-thirds of the remaining 3% is in the form of ice and snow, so there is only 1% of the total water is fresh water. About 98% of this freshwater account for groundwater there is only 2% of surface water. Thus 0.02% of the total amount of water present on earth is available in lakes and streams. That's why such limited sources are very precious and there is a need to be conserved1 (Warren et al., 1999). These limited sources are polluted day by day which is one of the severe problems.

The effluents released from textile and paper industries as well are complex mixtures whose composition varies over time as well as from one mill to another. High concentrations of suspended solids, metals, NPEs, and other organic substance are present in untreated P&TMEs. They also betray diverse pH variations and elevated temperatures. A variety of chemical products such as detergents, surfactants, plasticizers, mineral oils, dyes, dye carriers, and auxiliary products are used in textile and paper mill operations. A large proportion of these products end up in freshwater in the form of organic pollutants. NPEs, which are found in detergents, emulsifiers, wetting, and dispersing agents, are also discarded into the wastewater. Toxic metals such as **arsenic, cadmium, chromium, mercury, zinc, nickel lead,** etc. can also be found in P&TMEs. (Minister of the Environment, Canada, 2001) These metals and chemicals are hazardous to human and aquatic life as well.

Elma Šabanović and her coworkers researched the parameters for the simultaneous removal of metals like Cd (II), Co (II), Cr (III), Cu (II), Mn (II), Ni (II), and Pb (II) from aqueous solution using lemon-peel based material. The removal of these seven metals was found to be suitable at pH 5 with 300 mg/50 ml within 60 min at 25°C with an adsorption capacity of 46.77mg g–1 (Elma Šabanović et al; 2020). Sladana Meseldzija and coworkers studied to check the possibility of lemon peels as material for the removal of Fe^{2+}, Zn^{2+}, and Mn^{2+} from aqueous solution and mining wastewater. They also investigated to check the reusability of lemon peels by using 0.1M of CH3COO4, HCl, and HNO_3 solution. (Sladana Meseldzija et al; 2020).In 2023 Duru Chinonye and coworkers made use of waste lemon peels as a source of bioremediation to remove the lead from sludge. The result of this study showed a 90.5% efficiency of lemon peels in removing lead from sludge (Duru Chinonye et al; 2023). Villen-Guzman and his coworkers in 2021 used lemon peels as biosorbent to remove nickel and cadmium from industrial effluents. They used alkali-modified lemon peels to study the competitive adsorption of Ni (II) and Cd (II) by using batch adsorption experiments (Villen-Guzman et al; 2021). Muniraj, K and his coworkers 2020 used citrus lemon leaf powder (CCLP) as a biosorbent to remove hazardous metals from wastewater of textile industries by using a batch process (Muniraj, K et al.; 2020). Ganesan, in 2021 used waste fruit cortexes (banana, mango, and oranges) for the removal of toxic metals from wastewater. Maximum adsorption occurred at PH between 2 and 6.0(Ganesan, S et al; 2021). In 2020 Kumar, N, and his coworker applied a bio-sorption technique to remove heavy or toxic metals from water or waste water. They compared the efficiency of various natural substances wastes (Kumar, N et al.; 2020). Aboli, E and his coworkers studied the removal of ions of toxic metals like Pb (II), Co (II), and Ni (II) by preparing activated carbon from leaves of Citrus limetta from the synthetic aqueous system(Aboli, E et al; 2020).

We used to analyze the industrial wastewater to determine its composition and concentration of different heavy metals such as lead, cadmium, and nickel. We tried to remove these heavy metals from industrial (paper &textile) effluents by using lemon peels as bio-sorbent through the process of bio-sorption. Firstly we collected samples of effluents from the paper and textile industry and analyzed them by Atomic Absorption Spectrometry (AAS). After analysis, these samples were treated with bio-sorbent and treated effluent again analyzed by AAS. The difference in concentration of heavy metals before and after treatment is noted.

This research work aims to remove heavy metals from industrial effluent to minimize their concentrations and make sure that these effluents are safe to release in water streams. It's our objective to minimize water pollution and to make it suitable for aquatic life and eventually human beings. As these heavy metals are hazardous and may be carcinogenic so, we should not release these effluents without any treatment. So we want to make a filter by using lemon peels to treat the effluents before releasing them in water streams. After treatment, the effluents will contain a minimum concentration of heavy metals, and other hazardous chemicals will not affect aquatic life and human beings.

Experimental

Sample collection and purification:

We collected samples of industrial wastewater from Haji Mehboob Paper Industry Faisalabad Road Bypass, Chiniot, and Nishat LTD, Lahore. We purified these collected samples by filtration to remove the suspended particles present in the samples. Then we stored the filtered samples under suitable environmental conditions for further analysis.

Preparation of Biosorbent:

We collected fresh lemons and squeezed them. The squeezed lemon peels were dried in sunlight and crushed in the form of powder. The powdered lemon peels were dipped in solution of

10% ethanol for 24 hours for removal o colour. After 24 hours we filtered the dipped lemon peels and dried again. So by following these steps, the biosorbent was prepared.

Treatment of biosorbent with Sample Effluents:

After preparation of biosorbent we treated it with effluents for which we filtered 20ml of effluents and treated them one by one with biosorbent. We treated it under different parameters such as agitation times and different concentrations. For optimizing the concentration of biosorbent we added 0.1, 0.2, 0.3, 0.4, 0.5g of biosorbent in 20ml sample one by one and placed in magnetic stirrer and observe the results, and for optimizing the agitation times we treated the samples for 10, 20, 30, 40, and 50 minutes with 0.25g biosorbent.

Analysis of the Sample Effluents:

For analysis of sample effluents we used atomic absorption spectrophotometer (AAS) (Arti & Mehra, 2023) for which we filtered the samples and placed them in a sample holder which is nebulized with the help of a nebulizer in the form of mist. After nebulization, the sample is atomized under the influence of high temperature by a flame atomizer. The sample in the atomic state absorbs radiations of a particular wavelength emitted by a hollow cathode lamp which is made up of metal of interest and gets excited from ground state to excited state. The radiations are passed through a mono-chromator after passing through the sample which allows the radiations of a particular wavelength to pass and remove the absorbed energy from flame. The intensity of absorbed radiations is detected by the detector from which the concentration of a particular metal present in the sample is estimated. After initial analysis, we treated the samples with bio-sorbent under different agitation times and different concentrations. These samples were treated for 10, 20, 30, 40, and 50 minutes and 0.1, 0.2, 0.3, 0.4, 0.5

grams of biosorbent. After treatment, the samples are analyzed again by AAS similar to those analyzed as before treatment.

Operation Conditions:

For analysis of Cadmium the wavelength is auto-selected at 228.8 nm, 440 V of photomultiplier tube voltage, slit width 1.30 nm, lamp current 7.5 mA, air-acetylene flame, 1.5 l/min fuel flow, 160 kPa oxidant pressure, 15.0 l/min oxidant flow, 5.0 mm burner height, 1.00 s time constant, 0.5 s measurement time, 3 s delay time.

For analysis of Nickel the wavelength is auto-selected at 232.0 nm, 410 V of photomultiplier tube voltage, slit width 0.20 nm, lamp current 12 mA, air-acetylene flame, 1.7 l/min fuel flow, 160 kPa oxidant pressure, 15.0 l/min oxidant flow, 7.5 mm burner height, 1.00 s times constant, 0.5 s measurement time, 3 s delay time.

For analysis of Lead the wavelength is auto-selected at 283.3 nm, 540 V of photomultiplier tube voltage, slit width 1.30 nm, lamp current 7.5 mA, air-acetylene flame, 1.7 l/min fuel flow, 160 kPa oxidant pressure, 15.0 l/min oxidant flow, 7.5 mm burner height, 1.00 s times constant, 0.5 s measurement time, 3 s delay time.

Results and Discussion

First of all the samples were analyzed by atomic absorption spectrometry (AAS) and the initial concentrations of heavy metals present in the samples were determined. Then we used to treat the samples with biosorbent for the sake of removal of these heavy metals. For which we treated the 20ml samples for different agitation time (10 to 50 minutes) and different concentration of bio-sorbent (0.1 to 0.5g), in result of which the heavy metals were removed from the samples efficiently. The efficiency of the bio-sorbent changed with the change in its concentration and contact time (agitation time) with the sample. The efficiency of bio-sorbent ranged from 06.67% to 93.33%.

Table 1 First of all we noted the concentrations of both samples under analysis.

Characteristics	**A**	**B**
Colour	Violet	Light Brown
Lead	0.029 ppm	0.029 ppm
Cadmium	0.015 ppm	0.014 ppm
Nickel	0.024 ppm	0.046 ppm

Effect of Agitation Time on Adsorption

As we know that adsorption is a surface phenomenon, so by changing the contact time between bio-sorbent and metals to be removed the efficiency of adsorption also changes. The efficiency of adsorption of lead increases from 10.34 to 37.93% &20.69 to 68.96% by increasing the contact time (agitation time) from 10 to 50 minutes. Similarly, the efficiency of adsorption of cadmium increases from 13.33 to 93.33% & 28.57

to 71.43% as well as adsorption of nickel also increases from 16.67 to 66.67% & 28.26 to 47.83%.

We treated the sample with the biosorbent for removal of lead. We used to increase the contact time between the biosorbent and lead and noted the efficiency of biosorbent.

Table 2 Effect of agitation time on the adsorption of Lead by Lemon Peel (*Fructus limonis*)

Sample	**Agitation Time (min)**	**Concentration before adsorption (ppm)**	**Concentration after adsorption (ppm)**	**% Efficiency of Adsorbent**
A	10	0.029	0.026	10.34
	20	0.029	0.022	24.13
	30	0.029	0.020	31.03
	40	0.029	0.018	37.93
	50	0.029	0.018	37.93
	10	0.029	0.023	20.69

	20	0.029	0.021	27.59
B	30	0.029	0.015	48.28
	40	0.029	0.013	55.17
	50	0.029	0.009	68.96

We treated the sample with the biosorbent for removal of cadmium. We used to increase the contact time between the biosorbent and cadmium from 10 to 50 minutes and noted the efficiency of biosorbent.

Table 3 Effect of agitation time on the adsorption of Cadmium by Lemon Peel (*Fructus limonis*)

Sample	**Agitation Time (min)**	**Concentration before adsorption (ppm)**	**Concentration after adsorption (ppm)**	**% Efficiency of Adsorbent**
	10	0.015	0.013	13.33
	20	0.015	0.012	20.00

A	30	0.015	0.011	26.67
	40	0.015	0.002	86.67
	50	0.015	0.001	93.33
	10	0.014	0.010	28.57
	20	0.014	0.006	57.14
B	30	0.014	0.005	64.28
	40	0.014	0.004	71.43
	50	0.014	0.004	71.43

We treated the sample with the biosorbent for removal of nickel. We used to increase the contact time between the biosorbent and nickel from 10 to 50 minutes and noted the efficiency of biosorbent.

Table 4 Effect of agitation time on the adsorption of Nickel by Lemon Peel (*Fructus limonis*)

Sample	Agitation Time (min)	Concentration before adsorption (ppm)	Concentration after adsorption (ppm)	% Efficiency of Adsorbent
	10	0.024	0.020	16.67
	20	0.024	0.019	20.83
A	30	0.024	0.018	25.00
	40	0.024	0.017	29.17
	50	0.024	0.008	66.67

B	10	0.046	0.033	28.26
	20	0.046	0.029	36.96
	30	0.046	0.027	41.30
	40	0.046	0.024	47.83
	50	0.046	0.024	47.83

Effect of Concentration on Adsorption

By increasing the concentration of bio-sorbent, the surface area for adsorption also increases, so the degree of adsorption increases and hence the efficiency of biosorbent also increases. By increasing the concentration of bio-sorbent from 0.1g to 0.5g the efficiency of adsorption for lead increased from 6.90 to 37.93% &20.69 to 79.31%. The degree of adsorption of nickel increased from 25 to 75% &17.90 to 58.70% and of cadmium also increased from 6.67 to 40% & 14.28 and 57.14%.

We treated the sample with the biosorbent for removal of lead. We used to increase the surface area for adsorption by increasing the concentration of biosorbent from 0.1 to 0.5g for 20ml sample and noted the efficiency of biosorbent.

Table 5 Effect of concentration on the adsorption of Lead by Lemon Peel (*Fructus limonis*)

Sample	**Concentration (grams)**	**Concentration before adsorption (ppm)**	**Concentration after adsorption (ppm)**	**% Efficiency of Adsorbent**
A	0.1	0.029	0.027	06.90
	0.2	0.029	0.023	20.69
	0.3	0.029	0.021	27.59
	0.4	0.029	0.019	34.48
	0.5	0.029	0.018	37.93
	0.1	0.029	0.023	20.69

	0.2	0.029	0.021	27.59
B	0.3	0.029	0.014	51.72
	0.4	0.029	0.006	79.31
	0.5	0.029	0.006	79.31

We treated the sample with the biosorbent for removal of cadmium. We used to increase the surface area for adsorption by increasing the concentration of biosorbent from 0.1 to 0.5g for 20ml sample and noted the efficiency of biosorbent.

Table 6 Effect of concentration on the adsorption of Cadmium by Lemon Peel (*Fructus limonis*)

Sample	**Concentration (grams)**	**Concentration before adsorption (ppm)**	**Concentration after adsorption (ppm)**	**% Efficiency of Adsorbent**
	0.1	0.015	0.014	06.67
	0.2	0.015	0.013	13.33

A	0.3	0.015	0.011	26.67
	0.4	0.015	0.009	40.00
	0.5	0.015	0.009	40.00
B	0.1	0.014	0.012	14.28
	0.2	0.014	0.009	35.71
	0.3	0.014	0.008	42.86
	0.4	0.014	0.007	50.00
	0.5	0.014	0.006	57.14

We treated the sample with the biosorbent for removal of nickel. We used to increase the surface area for adsorption by increasing the concentration of biosorbent from 0.1 to 0.5g for 20ml sample and noted the efficiency of biosorbent.

Table 7 Effect of concentration on the adsorption of Nickel by Lemon Peel (*Fructus limonis*)

Sample	**Concentration (grams)**	**Concentration before adsorption (ppm)**	**Concentration after adsorption (ppm)**	**% Efficiency of Adsorbent**
A	0.1	0.024	0.018	25.00
	0.2	0.024	0.016	33.33
	0.3	0.024	0.013	45.83
	0.4	0.024	0.008	66.67
	0.5	0.024	0.006	75
B	0.1	0.046	0.038	17.39
	0.2	0.046	0.032	30.43
	0.3	0.046	0.022	52.17

	0.4	0.046	0.020	56.52
	0.5	0.046	0.019	58.70

Bukhari, A., and his coworkers 2022 worked on the treatment of water that was polluted by synthetic dyes by using lemon peels as biosorbent. The adsorption process was affected by factors like time of contact, sorbent dosage PH, etc. They applied different ranges of parameters like 10-80 min agitation time, 0.1g to 2.0g of biosorbent, and PH from 2 to 8. Parameters that showed maximum adsorption were 2PH, temperature 30 °C, contact time of 60min, stirring rate of 150 rpm, and 0.5g of biosorbent(Bukhari, A. et al; 2022). Begum, B.A in 2021 focused on problems caused by heavy metal contamination of water and its solution. She selected Citrus aurantifolia as a biosorbent. To check adsorption capacity, she changed parameters to 2-10 PH, 10 to 50°C temperature, the biosorbent dose from 0.1g to 3g, and contact time of 60 to 180 min. Efficiency increased considerably at 30°C temperature, 8 PH, contact time of 180 min, and 1g of sorbent than other applied parameters (Begum, B.A et; 2021).M. Lahieb Faisal and his coworkers in 2020 converted orange peels into sorbent to eliminate toxic metals from artificially generated wastewater. That research showed the highest efficiency of 91.0 % and 93.44% for Cd and Ni respectively. Optimum parameters for maximum capacity were found to be from 2.5gm to 3gm amount of sorbent at PH 6, 298K temperature with 180 min of contact time (M. Lahieb Faisal et al.; 2020). Ugya, A.Y. and his coworkers 2019 removed metals like iron and lead from tannery wastewater by using the method of bio-sorption and used fruit wastes as biosorbent. Great efficiency was found to be at PH 2, contact time of 80 min, and sorbent dosage of 5g (Ugya, A.Y. et al.; 2019).

Acknowledgement

We would like to express our heartfelt thanks to **Nishat Ltd, Lahore (A)** and **Mehboob Paper Industry (B), Chiniot** for their support and cooperation in providing samples for our analysis. Their willingness played a crucial role in success of our research work. The project would not have been possible without their contributions. Thank you for your support and collaboration.

Conclusion

As Lead, Cadmium and Nickel are removed from the samples with greater efficiency the adsorbent used i.e. Lemon Peel (*Fructus limonis)* is considered as best Bio-sorbent for removal of heavy metals from industrial effluents. We removed lead from paper industrial effluent up to 79.31% and 37.93% from textile industry. Similarly, cadmium was removed up to 93.33% from textile industry and 73.43% from paper industry and Nickel up to 75% from textile and 58.70% from paper industry. So it can be concluded that by treating the industrial effluent with lemon peels as bio-sorbent, a large quantity of heavy metals can be removed which is very necessary to reduce the hazardous effects of effluent and to avoid water pollution. So, we must treat the water before discharging in water bodies in order to secure our limited water resources.

References

Aboli, E., Jafari, D., & Esmaeili, H. (2020). Heavy metal ions (lead, cobalt, and nickel) biosorption from aqueous solution onto activated carbon prepared from Citrus limetta leaves. *Carbon Letters, 30,* 683-698.

Arti, & Mehra, R. (2023). Analysis of heavy metals and toxicity level in the tannery effluent and the environs. *Environmental Monitoring and Assessment*, *195*(5), 554.

Begum, B. A. (2021). *Study of biosorption and desorption process of Cu (II), Cr (VI), Pb (II) and Zn (II) ions by using peels of Citrus aurantifolia.*

Bukhari, A., Ijaz, I., Zain, H., Gilani, E., Nazir, A., Bukhari, A., Raza, S., Hussain, S., Alarfaji, S. S., Naseer, Y., & Aftab, R. (2022). Removal of Eosin dye from simulated media onto lemon peel-based low cost biosorbent. *Arabian Journal of Chemistry, 15*(7), 103873.

Duru, C., Ibrahim, F. B., & Dandajeh, A. A. (2023). Waste lemon peel as a circular solution for the remediation of lead-contaminated sludge for land application. *FUDMA Journal of Sciences, 7*(6), 252-260.

Faisal, L., Al-Najjar, S. Z., & Al-Sharify, Z. T. (2020). Modified orange peel as sorbent in removing of heavy metals from aqueous solution. *Journal of Green Engineering, 10*(11), 10600-10615.

Ganesan, S. (2021). Waste fruit cortexes for the removal of heavy metals from water. In *Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water* (pp. 323-350).

Kumar, N. (2020). Application of biosorption technique for removal of heavy metals present in water or wastewater. In *Contaminants and Clean Technologies* (pp. 279-306). CRC Press.

Meseldžija, S., Petrović, J., Onjia, A. E., Volkov-Husović, T., Nešić, A., & Vukelić, N. (2020). Removal of Fe2+, Zn2+ and Mn2+ from the mining wastewater by lemon peel waste. *Journal of the Serbian Chemical Society, 85*(10), 1371-1382.

Minister of the Environment Canada. (2001). *Fact sheet towards better management of textile mills effluents*. Published by Authority of the Minister of the Environment, Minister of Public Works and Government Services Canada.

Muniraj, K., Raju, G., Asha, B., & Manikandan, G. (2020). Citrus lemon leaf powder as a biosorbent for the removal of liquid phase toxic metals from textile effluent. *Desalination and Water Treatment, 196,* 422-432.

Šabanović, E., Memić, M., Sulejmanović, J., & Selović, A. (2020). Simultaneous adsorption of heavy metals from water by novel lemon-peel based biomaterial. *Polish Journal of Chemical Technology, 22*(1), 46-53.

Ugya, A. Y., Hua, X., & Ma, J. (2019). Biosorption of Cr 3+ and Pb 2+ from tannery wastewater using combined fruit waste. *Applied Ecology & Environmental Research, 17*(2).

Villen-Guzman, M., Cerrillo-Gonzalez, M. D. M., Paz-Garcia, J. M., Rodriguez-Maroto, J. M., & Arhoun, B. (2021). Valorization of lemon peel waste as biosorbent for the simultaneous removal of nickel and cadmium from industrial effluents. *Environmental Technology & Innovation, 21,* 101380.

Warren, S. Perkins1999. Oxidative decolorization of dyes in aqueous medium. *Textile Chemist and Colorist and American Dyestuff Reporter, 1*(4), 33-37.