Adsorptive Removal of Some Pollutants from Industrial Effluent Using Eco-Friendly Biomaterial

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Abstract: The effluent samples were collected from selected manufacturing units established nearby Gwalior, Madhya Pradesh, India. The study found that COD and heavy metals namely Fe, Cr, Pb and Zn were present in the sample and their concentration exceeds the permissible limit sometimes as prescribed by BIS. These pollutants cause serious health problems in human beings when they enter through food chain. Therefore, to minimize health problems, the effluent treatment using Neem leaf adsorbent was done. The percentage removal depends on the factors like pH, conc. of pollutants, amount and particle size of adsorbent, contact time etc. The maximum COD removal was observed up to 68.66%, whereas the maximum removal of Fe, Cr, Pb and Zn was observed up to 60%, 48.48%, 63.72% and 59.13% respectively. The findings before and after the adsorption treatment indicate that the pollution level minimized considerably when compared to the permissible limit of BIS.

Keywords: Effluent, COD, Adsorbent, Human being

1.Introduction

It is common that the industrial effluent released directly from manufacturing units under investigation in water bodies through runnels and also in the open or agricultural land without any prior treatment. These untreated effluents contaminate soil by accumulating various toxic substances in it and ground water by percolating through soil bed. Once pollutants enter into soil, the concentration of toxic chemicals increases in the course of time, which further transfer in plants and human beings via food chain, especially heavy metals are the important contaminants that can be found in tissues, surface of fresh fruits, vegetables and also water creature like fishes³⁷. Prolonged consumption of such contaminated food that has unsafe concentration of heavy metals, may lead to the disruption of numerous biochemical and biological processes in the human body. The accumulation of heavy metals give rise to toxic concentration in the body, while some metals like Cr, Cd act as carcinogenic and others like Pb, Hg are caused mental abnormalities in Children³⁵⁻³⁷. The high value of TDS and COD proliferate various abdominal problems in humans. Therefore, an intense need for researchers from all over the world has been observed and they developed a number of methods to minimize water pollution. The different methods such as sedimentation, coagulation, filtration, ion exchange, solvent extraction, electrolysis, chemical oxidation, adsorption etc. can be used for the removal of waste water pollutants. Although, these methods have their own shortcomings and limitations^{1-2, 4-5}. Among the possible techniques for waste water treatment, 'adsorption' process is the most efficient and widely used method for the treatment and removal of inorganic and organic contaminants from industrial wastewater because of convenience, easy operation and simplicity of design and low cost⁶. In recent years, the search for low-cost and eco-friendly adsorbents that have pollutant binding capacities has intensified³²⁻³³. In the study, Neem leaves¹⁹⁻²¹ used as adsorbent to minimize heavy metal contents along with the organic and inorganic load in industrial effluents. The selection of adsorbents based on its availability, cost, eco-friendly nature and efficiency in removal of water pollutants.⁷. The aim of this work is to study the removal of organic content and toxic heavy metal ions by Neem leaves from industrial waste water and to offer this biosorbent as local replacement for existing commercial adsorbent materials ²².

2.Method and material - Preparation of Neem leaves adsorbent

The mature fresh Neem leaves were collected from Neem trees and were washed repeatedly with water to remove dust and soluble impurities and were allowed to dry at room temperature in a shade. Then, the leaves were dried in an hot air oven at $60-70^{\circ}$ C for 30 h, when the leaves became crisp and brittle, the crisp leaves were ground in a mechanical grinder to obtain a fine powder. The Neem leaf powder was sieved and fractionated using a series of sieves. The 0.25 to 0.5 mm fraction was separated and taken as the adsorbent. This fraction was washed several times with double distilled water till the washings were free of color and turbidity. The washed powder was dried for several hours at room temperature and was preserved in glass bottles ²⁵⁻²⁶.



Figure: Fresh Matured Neem Leaf and its Powder

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Characterization of Neem (Azadirachta indica) leaves adsorbent

The fresh Neem leaf has a moisture content of 59.4%, carbohydrates 22.9%, protein 7.1%, fibre 6.2%, minerals 3.4%, fats 1% and many other chemicals. It also has certain important chemical ingredients such as azadirachtin, salannin, meliantriol, nimbin and nimbidin. These belong to a general class of natural products called "triterpenes", or more specifically limonoids. These

chemical compounds were found to have a great metal binding tendency towards Pb, Zn, Cr and Ni ²³⁻²⁴.

Scanning Electron Microscopy (SEM) is an important tool to study the surface topography of a solid material. Scanning electron microscopic image of the neem leaf powder showed that the surface of adsorbent appears as a fibrous material with irregular macropores and some expanded cavities which may allow for the diffusion of the atoms or molecules through the macropores of the adsorbent ²⁹.



Figure: SEM and FTIR image of Neem Leaf Powder

IR spectroscopy is one of the major tools used for obtaining information on functional groups on a solid surface. The principle of IR spectroscopy is based on molecules vibrating with specific frequencies associated with internal vibrations of groups of atoms. These frequencies occur in the IR region of the electromagnetic spectrum, i.e. ~ 200 to ~ 4000 cm⁻¹. When a sample is placed in a beam of IR radiation, the sample absorbs all radiations corresponding to those of molecular vibrational frequencies, and transmits all other frequencies. Identification of functional groups is possible because differences in the chemical structure give rise to characteristic vibrations and yield unique IR spectra.. The IR spectra show the presence of C-H bending (985.56 -1472.55 cm⁻¹), C-H Stretching (2845.77 - 2909.42 cm⁻¹), O-CH₃ (1475.42 cm⁻¹), C=C, Ketone (1575.73 – 1748.35 cm⁻¹), Carboxylic (1319.22 – 1717.49 cm⁻¹), Amides (1575.73 cm⁻¹), aromatic (754.12 – 762.79 cm⁻¹), C-O-C stretching (1164.92 cm⁻¹), sulphur compounds (1097.42 – 1339.47 cm^{-1}), alcohols and phenols ($1271 - 3627.85 \text{ cm}^{-1}$) ¹). Also, $-OH (3597 - 3600 \text{ cm}^{-1}), -NH_2 (3399 \text{ cm}^{-1}), \equiv CH$ (3297 cm^{-1}) , >C=N- (1656 cm^{-1}) , \equiv C-C \equiv , \equiv C-N< and \equiv C-O- (1160cm⁻¹), >C=O (1633, 1656, 1672, 1688, 1714cm^{-1}), >C=C< (1656 cm $^{-1}$), and >C=S (1105 cm $^{-1}$) functional groups on the surface of neem leaf powder ^{28, -} ²⁹. The FTIR spectrum of the Neem Leaf Powder has also been shown to contain a number of fatty acids like oleic acid, stearic acid, palmitic acid, linoleic acid, etc. The presence of polar groups on the surface has been shown to be responsible for considerable cation exchange capacity

Effluent Collection

The effluent samples were taken from some selected industrial points of manufacturing plants around the city in pre-cleaned bottles. The selection of industrial points based on the physico chemical analysis of such units for a period of three years and most polluted samples were considered to adsorptive removal of major pollutants.

Bioadsorptive removal of COD, Fe, Pb, Cr and Zn with Neem Leaf Powder

According to Environmental Protection Agency, USA, the metals As, Pb, Hg, Cd and Cr (VI) are included in the toxic substances. Hence, in this part of work, Fe, Pb, Cr, Zn and COD were chosen for study with respect to removal from the industrial effluent samples by a natural adsorbent. The first step of the study consisted of the assessment of industrial effluent in reference of COD, Fe, Pb, Cr and Zn, whereas, during the second step, adsorption was applied to reduce COD, Fe, Pb, Cr and Zn from released waste water which is taken as a sample. The one part of effluent was treated with Neem leaf Powder as adsorbent, termed as treated effluent and another remaining part was termed as untreated effluent. The treated and untreated effluent samples were analyzed for COD, Fe, Pb, Cr, and Zn.

The adsorption measurements were conducted by mixing specified amount of adsorbent (3 g) in 500 mL Borosil Conical flasks containing 250 cm³ of effluent sample. The initial pH of the effluent samples were adjusted to the desired values by adding few drops of 0.1M HCl or 0.1M NaOH aqueous solution. The samples were agitated using a magnetic stirrer for a predetermined time (180 minute) to

of a solid.

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attain equilibrium at constant agitation speed of 300 rpm and room temperature; after which the samples were taken out and allowed to settle and then, the sample was filtered through Whatmann filter paper and filtrate was analyzed by standard testing procedures for COD and metals¹⁷.

The percentage adsorption and substrate's equilibrium adsorption capacity (mg/g) were evaluated using following equations¹⁷

Adsorption or Removal (%) = $\frac{\text{Initial Conc.-Final Conc.}}{\text{Initial Conc.}} \times 100$

3.Result and Discussion

The results obtained from analysis of untreated effluent samples and treated effluent samples were represented in the following table.

Parameter	Sample	Adsorption	
		Before	After
COD (mg/L)	S ₂	876	274
	S ₃	957	314
Fe (mg/L)	S ₁	5.27	2.24
	S ₂	7.2	2.88
	S ₃	7.8	3.2
Pb (mg/L)	S ₁	0.40	0.22
	S_4	0.33	0.17
Cr (mg/L)	S ₃	5.1	1.85
Zn (mg/L)	S ₃	11.5	5.2

For all collected samples adsorbent dose was 12 g/L and samples were run for 180 min. The result shows that about 68.66% and 67.19% removal of COD were obtained for S_2 and S_3 respectively. The obtained results show that maximum COD removal occurred for S_2 , were achieved at pH 8-10 because of better adsorption observed at higher pH attributed to the co-precipitation of the organic matters³⁴. The heavy metals content also showed remarkable reduction after adsorption, Iron in S_1 decreased from 5.27 mg/L to 2.24 mg/L, similarly in S_2 and S_3 reduced up to 60 % and 58.97 % respectively. Lead metal decreased from 0.40 mg/L to 0.22 mg/L in S₁ while in S₄ from 0.33 mg/L to 0.17 mg/L. The initial concentration of Cr and Zn decreased up to 1.85 mg/L and 5.2 mg/L respectively. The obtained readings of all selected parameters after adsorption showed appreciable decrease in their values. The results of the treated and untreated effluent samples and percentage removal of pollutants also represented graphically.



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Chromium (mg/L)





4.Conclusion

In this part of work, an attempt has been made for studying the removal of COD, Fe, Pb, Cr and Zn from industrial effluent using Neem Leaf Powder adsorbent. The result of present work showed that Neem Leaf Powder can be used as an effective low cost bioadsorbent for removal of COD, Fe, Pb, Cr and Zn from industrial effluents. The maximum COD removal was observed up to 68.66 %, whereas the maximum removal percentage of Fe, Pb, Cr and Zn occurred up to 60 %, 48.48%, 63.72 % and 54.78% respectively. The findings before and after the adsorption treatment indicate that the level of water pollution minimized considerably when compared to the permissible limit of BIS ³¹. The adsorption process is influenced by pH of the sample, initial concentration of the metal ions, the amount of adsorbent, particle size, and contact time of adsorbent¹⁰. Therefore, efficiency of adsorption can be further enhanced by adjusting pH of solution, adsorption time, particle size and quantity of an adsorbent.

This present work will not be significant only to the manufacturing industries to minimize cost of COD and heavy metals removal, but also to minimize the impact to the environment for the betterment of mankind. It has also demonstrated that mature Neem leaves, a useless plant waste which are shed regularly each winter, can be converted into an excellent and beneficial adsorbent for organic as well as inorganic pollutants.

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