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Review Of Removal of Toxic Pollutants from Water by Adsorption

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Abstract
The removal of toxic pollutants from water is a critical environmental concern due to the potential harm they pose to human health and ecosystems. In this study, we conducted an investigation into the effectiveness of adsorption as a method for removing toxic pollutants from water. Adsorption is a widely used technique that involves the attachment of pollutants to the surface of an adsorbent material, thereby reducing their concentration in the water.
We explored various adsorbent materials, including activated carbon, zeolites, and metal oxides, and evaluated their efficiency in removing specific toxic pollutants such as heavy metals, organic compounds, and dyes. Additionally, we investigated the influence of operating parameters, such as pH, contact time, adsorbent dosage, and initial pollutant concentration, on the adsorption process.
To assess the performance of adsorption, we measured the removal efficiency of the pollutants through experimental analysis. We determined the concentration of pollutants before and after adsorption using analytical techniques such as atomic absorption spectroscopy, gas chromatography, and UV-visible spectrophotometry. Furthermore, we compared the adsorption capacities of different adsorbents and optimized the process conditions to enhance the removal efficiency.
The results of our investigation demonstrated that adsorption is an effective method for removing toxic pollutants from water. The selected adsorbents exhibited high adsorption capacities and demonstrated significant removal efficiencies for various pollutants. The experimental data allowed us to determine the optimal operating conditions for maximum pollutant removal.
However, we also identified certain limitations and challenges in the adsorption process, including limited adsorbent regeneration, potential secondary pollution from adsorbent materials, and the need for further optimization to address specific pollutant characteristics. These findings highlight the importance of ongoing research and development in optimizing adsorption techniques for the removal of toxic pollutants from water.
Overall, this investigation contributes to the understanding of adsorption as a viable approach for water remediation and provides valuable insights into the selection of suitable adsorbents and process conditions for efficient removal of toxic pollutants. The findings can aid in the development of more sustainable and effective water treatment strategies to ensure the protection of human health and the environment.

1. Introduction

The major Indian rivers are polluted due to the input of various types of waste from different sources. Thus, it is compelling necessity for the environmentalist to develop appropriate way to check the deterioration of the environment. The problem of the deposing industrial waste is as old as industries themselves. Mostly, the areas situated around industrial belts are under stress due to the continuous disposal untreated wastes from the various industries. It has been known from the Vedic times that nature and human kind (i.e., Prakriti and Purush) form an inseparable part of the life support system. This system has five elements, viz. air, water, land, flora and fauna, which are interconnected, interrelated and interdependent and have co-evolved and co-adopted. Deterioration in one inevitably affects the other four elements. The life support system is now recognized as *THE ENVIRONMENT*, which is composed of two components- a biotic component consisting of living matter, and an abiotic one consisting of non-living organic and inorganic matters such as water, gases, minerals etc. Both the components of the environment exist at an equilibrium under given condition. Any change brought about by man's activities or other circumstances places a "stress" upon the system, disturbing the equilibrium, evoking a suitable "response" from it, and in turn, leading to a new equilibrium condition which may or may not be beneficial to the original components of the system, includingman[1].

At present nobody denies the fact that the natural equilibrium existing between the components has been disturbed. Among the creatures of the nature, *Homo sapiens* or man, because of his vastly superior intellect and ability to modify the nature for his benefit, is solely responsible for the disturbance of the equilibrium.

1.1 Pollution

Pollution, which in a broad sense is an undesirable change in the physical, chemical or biological characteristics of our air, water and land that may or will harmfully affect life or create a potential health hazard of human or other living organisms. Pollution is, thus, direct or indirect change in any environmental components that is causing harmful effect on organisms particularly on man, affects adversely the industrial progress, cultural or natural assets or general environment.

Several other attempts have also been made to define environmental pollution; the major controversy has been on the degree to which mankind should be at the centre of the definition. Engineers adopt a narrower view and consider environmental pollution due to "any waste discharge and natural or environmental change that are detrimental to man". Another view considers that we are incapable of defining what will be detrimental and what will not be and according to this view environmental pollution can be defined as "an undesirable change in the physical, chemical or biological characteristics of our air, land and water, that may or will hostilely affect human life or that of other desirable species or industrial processes, living conditions and cultural assets or that may or will waste or deteriorate our natural resources". A part from these two, others define it as "acts of introduction by man of extraneous substances or energy into the environment that induce unfavorable changes affecting man directly or indirectly by endangering his health, harming his living resources and ecosystem or by interfering with the legitimate of the environment". Human grew in number and now the whole world is facing the problem of population explosion which has assumed dangerous proportions. Consequently, the basic requirements increased with the growth of population. Manual processes proved insufficient to fulfill these requirements. Mechanical processes were used to increase production and thus industries came into existence. Presently, industrialization in the developed countries is very high. The developing countries are also competing in the race of industrialization with the developing countries. Industries naturally have to be established near urban areas and thus providing sources of employment. This resulted ina rush of the rural population in urban area. The population density, heavy industrialization and growing urbanization have succeeded in creating acute problems of environmental pollution. Environmental pollution now constitutes one of the biggest hazards, not only to human beings but also to the existence of all gifts with which nature has kindly bestowed mankind. Developed and developing countries both have acute environmental problems.

The problems arising from increasing urbanization include the obsolescence of the infrastructure, the pollution of the city atmosphere, the lack and bad quality of the drinking water, overcrowding and traffic difficulties, the decrease in the areas of greenery, parks and generally the so-called damage done by the civilization. The increasing consumption of water due to urbanization has resulted in lowering of the underground water. With increasing population and urbanization, the volume of domestic wastewater coming into the environment is on the rise. The discharge of wastewater of varied characteristics from various industries is another serious problem posed by technological development. These wastewaters, unlike domestic wastewater, may contain acids, alkalis, chemicals, dissolved solids, dyes, oils, metals, suspended matter etc., and many of them may be extremely toxic. They make water corrosive and toxic to aquatic life. They also deplete dissolved oxygen (DO), impair the biological activity and destroy aquatic life. Fertilizers, detergents and various biologically active materials are finding their way in increasing quantities into rivers, lakes and finally the ocean, where the natural environment supports many aquatic life forms, is getting adversely affected.

The technological developments in the field of production of chemicals for various uses have also increased the environmental hazards enormously. Nearly 5 million chemicals have been synthesized in the world over during the last 40 years and 50,000 to 70,000 are used extensively in millions of different commercial products without the availability of proper technical information on most of them. Industries producing fertilizers, non-ferrous metals, petroleum products, steel etc., not only discharge or emit the common pollutants but are also sources of several toxic substances like arsenic, beryllium, cadmium, lead, mercury, nickel, zinc etc. Some experts believe that these toxic metals pose a greater threat to the environment than the conventional grass pollutants e.g., oxides of carbon, nitrogen and Sulphur and the like. Past episodes of pollution due to mercury in Japan and Sweden clearly point to the danger of these metals. The use of methyl mercury in a seed dressing led to a drastic reduction in the bird population in Sweden. During 1953 to 1960 over 40 people died in Minamata, Japan through eating mercury contaminated fish and several suffered serious neurological damage. Most of the toxic elements are persistent in nature, reach over body system through several routes (Figure 1.1, 1.2) and tend to accumulate slowly in the body. Thus, even a low exposure over a long period may result in their accumulation up to highly toxic levels. In addition to their toxicity, they also cause symptoms of deficiency related diseases. For example, the zinc toxicity in animals shows the symptoms of iron deficiency[2].

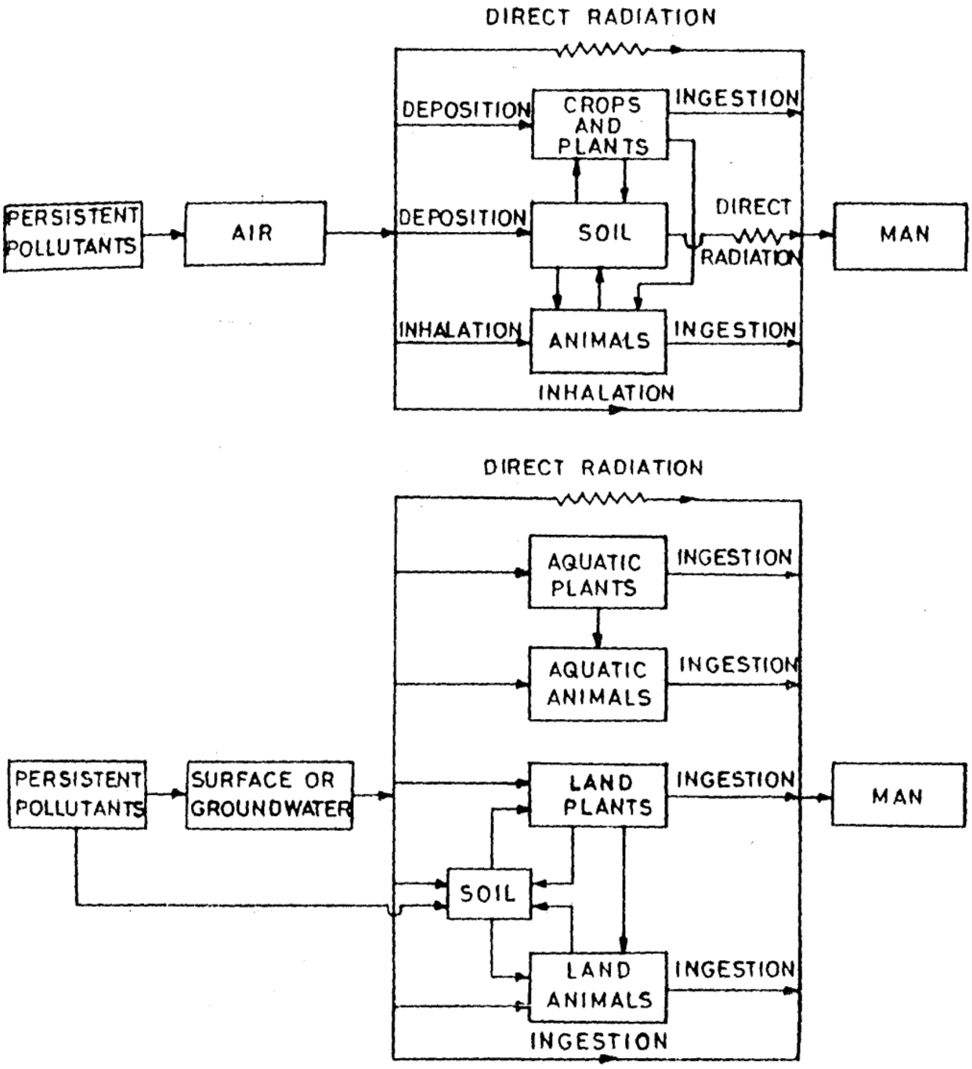

Figure 1.1: Exposure pathways for persistent pollutants.

Now-a-days, water pollution is the biggest hazard for all form of life. The environmental pollution has been the most remarkable side effect of rapid industrialization and growing population of the world. Environmental pollution is a serious day-to-day problem faced by the developing and developed nations in the world. Water, air and solid waste (Plastics) pollution due to the anthropogenic sources contribute to a major share to the overall imbalance to the ecosystem. Today, almost all the things, which are most necessary to the human being, are more or less contaminated by toxic substances. Industries discharge waste water containing various pollutants such as heavy metals, organic and inorganic impurities including coloring materials etc. depending on type of industries, raw materials and processing conditions used. The major Indian rivers are polluted due to the input of various types of waste from different sources. Thus, it is compelling necessity for the environmentalist to develop appropriate way to check the deterioration of the environment. The problem of the deposing industrial waste is as old as industries themselves. Mostly, the areas situated around industrial belts are under stress due to the continuous disposal untreated wastes from the various industries.

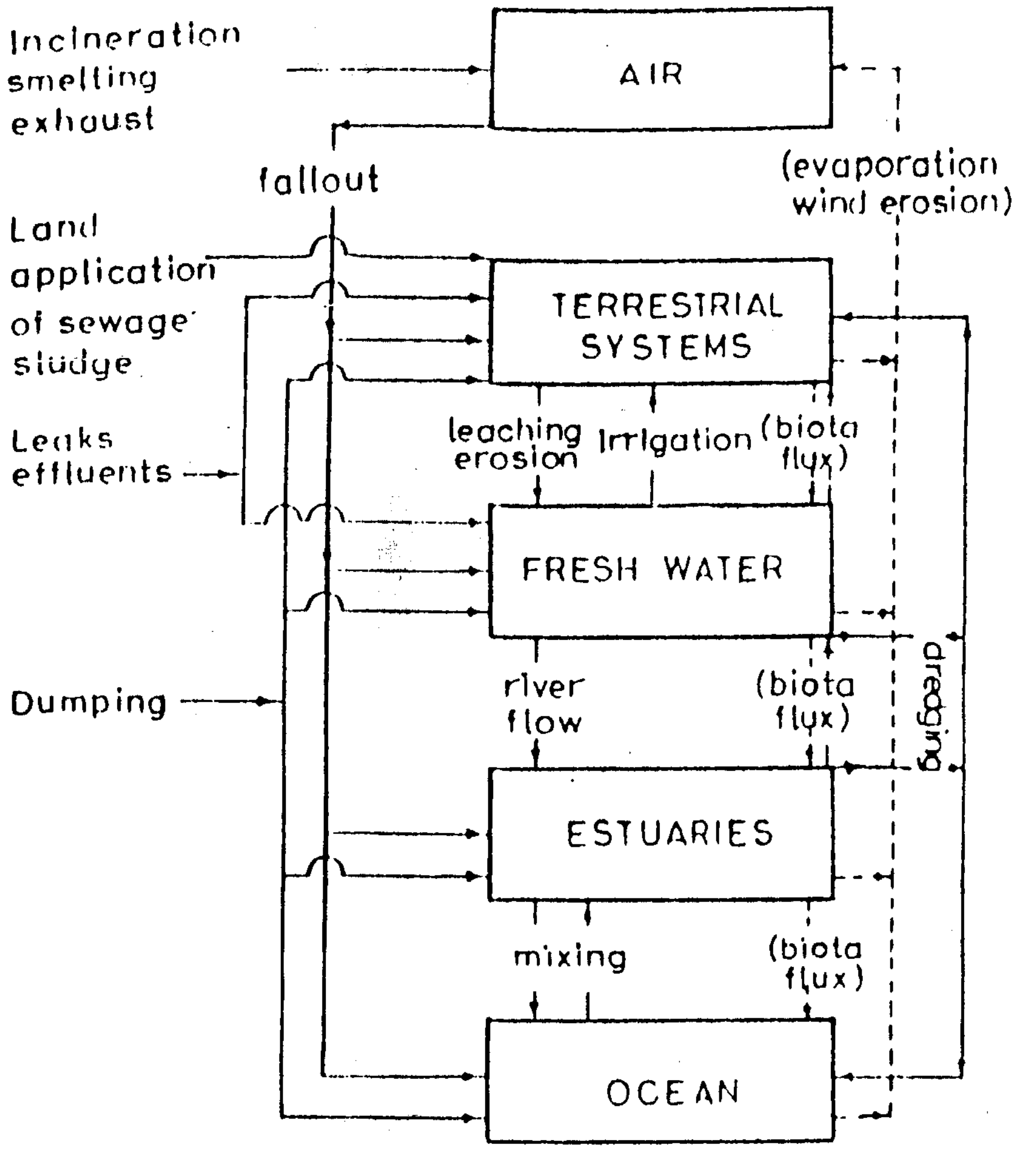

Figure 1.2: General routes of metal pollutants into the environment

2. Literature review

F. **Renault et al.** [1] In order to increase the density or to remove these colloidal particles, coagulation treatment strategies are carried out. The effectiveness of coagulation depends upon the types of the coagulant used, the dosage of coagulant, pH, temperature, alkalinity, mixing conditions. In this process, chemical reagents or inorganic flocculants like Al2(SO4)3, Fe2(SO4)3 and FeCl3 and derivatives of these materials such as poly aluminium chloride and poly ferric chloride were used as flocculants in the wastewater treatment process.

G. **Chang et al**. [2] Flocculants are added which agglomerates the destabilized particles to form larger particles with the help of mixing or stirring. Straining or flotation and filtration are employed to separate these larger particles. new type of macromolecule flocculants like mercaptoacetyl was prepared by reacting chitosan with mercaptoacetic acid.

H. **L. Yu, M. Han et al**. [3] which reports that it can remove heavy metals along with turbidity. Other flocculants like poly aluminium zinc silicate chloride are used in oil wastewater treatment, achieved the removal rate of turbidity and COD is about 98.9% and 71.8%. The examples of complex coagulant and flocculant are CAX and anionic poly acrylamide increase the removal efficiency of oil in wastewater.

I. **Yan et al.** [4] studied the removal of arsenic (Sb) by the coagulation process with the help of aluminium and ferric salts which are found to be efficient coagulant for arsenic removal. Sb (V) removal was effective with the less dosage of ferric coagulant. The coagulants destabilize the colloidal particles by neutralizing them and bring about sludge settling. These colloidal particles get entrapped on the metal surface to form precipitation. The sludge formation occurs due to the large utilization of chemicals in this separation process which is one of the major disadvantages of the coagulation process.

J. **Y. Huang et. al**. [5] Sometimes water-soluble polymeric flocculants like sulfonic acid and carboxylic acid polymers are also used in this separation process rather than inorganic chemical reagents. The advantages of these polymers are easy to use, low sludge formation, easily available and environmentally friendly.

K. **A.G. El Samrani et. al**. [6] Certain researchers tried to remove the heavy metal using two popular chemicals such as ferric chloride and poly-aluminium chloride (PAC) which is found to be an excellent coagulant around optimum concentrations.

L. **F. Fu, Q. Wang et. Al.** [7] Research also carried out in the removal of bounded heavy metals by the coagulation/flocculation process. Heavy metal complex removal was done by using polyelectrolyte flocculation method followed by centrifugation and filtration method. The heavy metal like zinc and lead bound with the humic acid material and that gets coagulated with the cationic polyelectrolyte polydiallyl dimethyl ammonium chloride, which is a polyelectrolyte flocculation technique carried out to build up the removal of heavy metals. This treatment cannot completely eliminate the heavy metal from wastewater; hence it is necessary to include the other treatment techniques like precipitation, spontaneous reduction along with coagulation or flocculation process.

M. **Bojic et al.** [8] utilized combined technique, i.e., spontaneous reduction-coagulation process in order to separate the metal from wastewater based on the micro-alloyed aluminium composite, can efficiently lower the copper and zinc ions in different concentrations.

N. **W. Tao, G. Chen et al.** [9] According to the Smoluchowski coagulation theory, nanoparticles can precipitate the colloids immediately present in the surface water. Nano coagulant like silver nano particles deposit the heavy metals and can drop the TOC concentration in the wastewater.

O. **E. Lukasiewicz et al.** [10] The large amount of sediment flocks leads to the formation of sludge which takes place in the coagulation process due to the usage of coagulants like alum, iron, etc. The sludge formed after the coagulation process was found to contain heavy metals like cadmium, chromium, nickel, lead and zinc.

P. **T. Ahmad et al** [11] The solution for sludge management is recovery, recycling and reuse. Though coagulation/ flocculation is efficient for the removal of heavy metals from wastewater, it may create by-products like flocks which are termed as a secondary pollutant and the added chemical solvents are low reusable that is harmful to both the human and environment.

Q. **M. Bilal, J.A. Shah et al** [12] Ion exchange is a separation process which substitutes the ions with another for the wastewater treatment with high removal efficiency of metal ions. When compared with coagulation process, the sludge production is low in the ion exchange process. Ion exchange resin is a material used to recover or remove the metals. Based on the chemical property of resins.

R. **Z. Hubickithe et al** [13] isolation of a specific set of metal ions takes place which was investigated by Hubicki and Koodynsk. Basically, they were designed in a form of strain and stress-free to prevent the natural degradation and requires substrate-ligand communication which stimulates the polymer support on that communication.

S. **B. An, Q. Liang et al.** [14] The resins are made up of cross-linked polymer matrix in which the functional groups are attached through covalent bonding in the resin structures and spaces in the structures allows the ions to transfer appropriately. These resins are classified into two types such as synthetic and natural resins.

T. **M.A. Barakat et al.** [15] either one of the resins have been used to replace the metal ions with cations. Among these resins, synthetic resins are widely favored than the natural resins to separate the metals infinitely. The main application of synthetic resins can remove the arsenic metals from drinking water. Fouling of matrix occurs in case of high concentrated metal solution which is the demerits of synthetic resins.

The removal of pollutants by adsorption technique is influenced markedly by the nature of adsorbent and the adsorbate employed for the process. It has profound effects on both the rate and the capacity of the removal. The chemical composition of adsorbent (Lantana Camara ash) varies considerably. Since the nature of adsorption is dependent on the adsorbate species and the constituents of the adsorbent, it becomes necessary to characterize them to ensure a better insight of the mechanism of adsorption of Cr (VI), Mo (VI) and Ni (II). The present chapter deals with the sources, concentration and toxicity of adsorbates in the aqueous system and embodies the results obtained by using various physico-chemical techniques for characterization of the adsorbent.

3. Materials and methods

3.1 Adsorbent

3.2 Lantana Camara ash

Lantana Camara ash is a small perennial shrub, which can grow to around two meter tall and from dense thickets in a variety of envoironments[1]. Due to extensive selective breeding throughout the 17^{th} to $18^{th,}$ centuries for use as an ornamental plant there are now many different L. Camara cultivars.

Since Lantana Camara popularly known as big-sag, wild-sage, red- sage, and tickberry[2], is a species of flowering plant within the Verbena family, Verbenaceae that is native to the American tropics[3].

Lantana Camara has also colonized areas of Africa, Southern Europe, such as Spain and Purtugal, the Middle East, India tropical Asia, Australia, New Zealand, the USA, as well as many Atlantic, Pacific and Indian Ocean islands[4]. It has also become a significant weed in Sri Lanka after escaping from the Royal Botanic gardens of Sri Lanka in 1926, where it has established itself as a notorious weed[5].

Lantana Camara is known to be toxic to livestock such as cattle, sheep, horses, dogs and goats. The active substance causing toxicity in grazing animals is pentacyclic triterpenoids, which result in liver damage and photosensitivity. Lantana Camara also excretes chemicals (allelopathy) which reduce the growth of surrounding plants by inhibiting germination and root elogation[6].

The chemical analysis has indicated that all the plant parts including pollen contain toxins. The major component of these toxins being lantanin and other phenolic acids such as caffeic acid, vanillic acid, anisic acid, chlorogenic acid, parahydroxy benzoic acid and para anisic acid, some of which are lethal to human and animals. This weed is generally uprooted and destroyed by burning in air without any use.

The study is concerned with the utilization of such dangerous weed and to use its potential as effective adsorbent.

Uprooted Lantana Camara plants were collected, washed with tap water to remove dust and dirt, etc., and were dried in sunlight (temperature 35-40□C) for three to four weeks, the dried weed was crushed, burned in open air and then in furnace at 550 □ 25□C for ten hours and then cooled. The particles of desired mesh size, were collected and kept in sealed bottles for study.

In the present study, the sorption behavior of Cr (VI), Mo (VI) and Ni (II) on Lantana Camara ash was examined and this adsorbent was utilized in waste water treatment.

3.2.1 Characterization of Adsorbent

The rate of the removal of pollutants from wastewater by an adsorbent is significantly affected by its physico-chemical nature. Hence, all the adsorbent, used, was characterized beforehand for determining their relevant physical properties and chemical composition.

3.2.1.1 Physical Properties

I. Bulk Density

Bulk density of the Lantana Camara ash was determined with the help of specific gravity bottles.

II. Surface Area

Surface area of adsorbent was determined by B.E.T. method using low temperature N_2 gas adsorption technique.

III. Particle Size

Particle size of the adsorbent was determined with the help of B.S.S. Sieve analysis.

IV. Chemical and Proximate Analysis

The chemical constituent of the adsorbent was analyzed using standard methods 7,8. Thus, the results are obtained and collected in the Table 2.1.

V. Infra-red Analysis

Infra-red spectrum of the adsorbent was obtained using pellet potassium bromide infra-red spectro-photometer, model Varian FT-IR 3100 for determining the nature of bonding present on the surface of adsorbent particles. The positions of different bands and their corresponding assignments are given in the Table 2.2.

VI. X-ray Diffraction Analysis

X-ray diffraction of the adsorbent was obtained using Regaku DMAX III rotating diffractometer. Various “d” values along with their possible components are given in the Table 2.3.

4. Results and Discussion

In case of Lantana Camara ash, the major constituent is carbon. However, the presence of different oxides (Iron oxides, calcium oxide, alumina and silica) in varying proportion has been observed. This unconventional adsorbent mainly contains the oxides of silicon and iron whereas; oxides of iron, calcium, manganese and magnesium are present in traces as shown in Table 2.1. The oxides of silicon, iron and aluminium are mainly responsible for the removal of pollutants from waste water.

The constituent of adsorbent was examined through infra-red spectrum and x-ray diffraction.

Infrared spectrum of the Lantana Camara ash shows various bands as shown in the Figure 2.1 and Table

2.2. The figure shows important peaks at 3421 cm^{-1} for -OH stretching; at 1425 cm^{-1} for C-H stretching; 1463 cm^{-1} for ketonic group; 788 cm^{-1} for Si-O stretching; 1049 cm^{-1} for Al-O; 871 cm^{-1} for Fe-O; 690 cm^{-1} for Ca-O; 440 cm^{-1} for Na-O stretching[9].

The 'd' values for the adsorbent Lantana Camara ash (Table 2.3) prove the presence of iron oxide tetragonal, iron lead oxide hexagonal, silicon oxide hexagonal, calcium manganese oxide orthorhombic and the sodium carbonate in the form of hexagonal system[10].

Table 2.1: Analysis of Lantana Camara ash

Physical Properties	
pH	10.69
Conductivity (s cm^{-1})	1429
Specific gravity	0.823
Water adsorption %	32.03
Bulk density (g cm^{-3})	1.45
Apparent porosity (%)	45
Matter soluble in water (%)	8.953
Surface area (m^2g^{-1})	756.35
Proximate Analysis	
Moisture (%)	0.97
Volatile matter (%)	15.79
Ash content (%)	11.4
Fixed carbon (%)	71.97
Silica (ppm)	573
Iron (ppm)	11.33
Sodium (ppm)	7.16
Potassium (ppm)	3.26
Chromium	Not-detectable
Molybdenum	Not-detectable
Nickel	Not-detectable

Table 2.2: Important infrared bands of Lantana Camara ash along with their probable assignment

Band Position (cm^{-1})	**Assignment**
3421	-OH stretching
1425	C-H stretching
1463	-C=O stretching
788	Si-O stretching
1049	Al-O
871	Fe-O
690	Ca-O
440	Na-O

Table 2.3: "d" values of Lantana Camara ash

d(Å)	**Possible Components**
4.30	Iron oxide (Tetragonal)
2.65	Iron Lead oxide (Hexagonal)
3.53	Lead oxide (Tetragonal)
2.90	Lead oxide (Tetragonal)
1.82	Lead oxide (Tetragonal)
1.54	Lead oxide (Tetragonal)
1.28	Lead oxide (Tetragonal)
3.37	Silicon oxide (Hexagonal)
3.21	Silicon oxide (Hexagonal)
3.17	Silicon oxide (Hexagonal)
3.05	Silicon oxide (Hexagonal)
3.02	Silicon oxide (Hexagonal)

2.11	Silicon oxide (Hexagonal)
1.41	Silicon oxide (Hexagonal)
2.29	Silicon oxide (Hexagonal)
2.23	Calcium manganese oxide (orthorhombic)
2.17	Calcium manganese oxide (orthorhombic)
1.57	Sodium Carbonate (Hexagonal)
1.54	Sodium Carbonate (Hexagonal)

Conclusion

In conclusion, this investigation into the removal of toxic pollutants from water by adsorption highlights the effectiveness of this technique in mitigating the harmful effects of pollutants on human health and the environment. The study explored various adsorbent materials and their efficiency in removing specific toxic pollutants, including heavy metals, organic compounds, and dyes.

The experimental results demonstrated that adsorption is a promising method for pollutant removal, with the selected adsorbents exhibiting high adsorption capacities and significant removal efficiencies. The optimization of operating parameters allowed for enhanced removal efficiency, further emphasizing the potential of adsorption as a water remediation technique.

However, it is important to acknowledge the limitations and challenges associated with adsorption. The limited regeneration potential of adsorbents, potential secondary pollution from adsorbent materials, and the need for further optimization to address specific pollutant characteristics are important considerations for future research and development.

Overall, this investigation provides valuable insights into the potential of adsorption as a method for removing toxic pollutants from water. The findings contribute to the development of sustainable and effective water treatment strategies that can safeguard human health and protect the environment. Continued research in this field is crucial to address the challenges and optimize adsorption techniques for the removal of toxic pollutants, ultimately leading to cleaner and safer water resources.

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