

Investigation In the Removal of Toxic Pollutants from Water

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Abstract

The presence of toxic pollutants in water sources poses a significant threat to human health and the environment. In this study, we conducted an investigation into the removal of toxic pollutants from water using adsorption as a treatment method. Adsorption involves the attachment of pollutants onto the surface of an adsorbent material, leading to their removal from the water.

We explored the effectiveness of different adsorbent materials, including activated carbon, zeolites, and metal oxides, in removing various toxic pollutants such as heavy metals, organic compounds, and dyes. The adsorption process was examined under different operating conditions, including pH, contact time, adsorbent dosage, and initial pollutant concentration, to understand their influence on pollutant removal efficiency.

Experimental analysis was performed to evaluate the performance of adsorption in removing the target pollutants. Analytical techniques such as atomic absorption spectroscopy, gas chromatography, and UV-visible spectrophotometry were utilized to measure the pollutant concentrations before and after adsorption. The adsorption capacities of different adsorbents were compared, and the process conditions were optimized to achieve maximum pollutant removal efficiency.

Keywords: Toxic, Pollution, Water, Air, Degradable pollutant

Introduction

The agents which cause pollution are called pollutants. A pollutant can be defined as a material or set of conditions that create a stress or unfavorable alteration of an individual organism, population, community or ecosystem beyond the point that is found in normal environmental conditions.

"Environmental pollutants may be defined as the inorganic, organic, radiological or biological substances, noise, odour etc. which tend to degrade the quality of the environment so as to constitute a hazard or impair the usefulness of the environment." Pollutants can be classified in many different ways. On the basis of decomposition, pollutants can be classified into two main groups:

1.1.1 Non-Degradable Pollutants

The pollutants which do not decompose easily in nature are called non-degradable pollutants. They are not cycled in ecosystem naturally. They not only accumulate but are often biologically magnified with their subsequent movement in food chains and biochemical cycles. These are heavy metals, D.D.T., plastics etc.

1.1.2 Degradable Pollutants

The pollutants which decompose easily are known as degradable pollutants. However, when they accumulate, they may create problems. These are domestic sewage, industrial wastes etc. They are decomposed by micro-organisms such as bacteria, fungi, blue-green algae and some protozoans. On the basis of nature, the pollutants are of following types.

- I. Chemical Pollutants:** These are chemicals such as carbon dioxide, carbon monoxide, Sulphur dioxide, oxide of nitrogen, chlorine, fluorine, iodine, soot, dust, grit, metal dusts and vapors, benzopyrenes, benzene smog, peroxy acyl nitrate, pesticides e.g., herbicides, fungicides, weedicides etc. released by industries and automobiles.
- II. Biological Pollutants:** Micro-organisms such as bacteria, viruses, algae, fungi, pollen grains etc., are biological pollutants.
- III. Physical Pollutants:** Heat, noise, radioactive substances etc., are physical pollutants. In addition to these, uncontrolled population growth and inadequate urban planning can also be included in other type of pollutants. On the basis of source of origin, the pollutants may be classified into following two types.
- IV. Point Source Pollutants:** It includes particles such as dust, lead, iron, zinc, mercury, chromium, carbon-monoxide, sulphur dioxide, hydrogen sulphide, fluorine, chlorine, ammonia etc.
- V. Non-Point Sources:** These are mostly sources which result in run-off, seepage and percolation of pollutants to surface and ground waters via diffusion and unidentified routes. The non-point sources include agriculture, silvi- culture, mining, ground water salinity, urban run-off, rural sanitation, land development, heavy construction works etc.

1.2 TYPE OF POLLUTION

Pollution can be divided into different types but air and water pollution are the most important branches of environmental pollution.

1.2.1 Air Pollution

Air is never completely pure because many gases like, CO₂, CH₄, H₂S, CO, SO₂ etc. are released in atmosphere by natural processes i.e., by breath, decomposition of organic matters, volcanic eruption, fire etc., and we cannot control it. In spite of these natural processes many artificial processes cause air pollution which have serious effects on life. Air pollution is caused by exhaust by automobiles, refineries, fertilizer industry, chemical industry, dyestuff industry, pharmaceutical, pulp and paper mills, pesticide industry, burning of organic materials like coke, wood and other synthetic organic materials etc.

Natural pure air is composed of various components (Table 1.1) which are almost constant, but some additional substances are constantly being added in it.

Table 1.1: Composition of clean air of mean sea level³

Gaseous/Components	Content	
	% of Volume	Volume (ppm)
Nitrogen	78.09	780,900
Oxygen	20.94	209, 400

Argon	0.93	9,300
Carbon dioxide	0.0318	318
Neon	0.0018	18
Helium	0.00052	5.2
Krypton	0.0001	1.0
Xenon	0.000008	0.08
Nitrous oxide	0.000025	0.25
Hydrogen	0.00005	0.50
Methane	0.00015	1.50
Nitrogen dioxide	0.0000001	0.001
Ozone	0.000002	0.02
Sulphur dioxide	0.0000002	0.002
Carbon monoxide	0.00001	0.1
Ammonia	0.000001	0.01

Air pollutants are responsible for a number of hazards viz., depletion of ozone layer, greenhouse effect, acid rain, PAN (peroxy acyl nitrate), climatic changes and a number of disorders not only for human being but also for plant life. Depletion of ozone layer will cause the uv rays to reach the earth, thereby causing the skin cancers. Similarly, peroxy acyl nitrate formations have resulted in death of a number of people in different places. Greenhouse effect is causing the increase in earth's temperature which, if not checked, may cause rise in seawater level endangering the survival of low-lying islands.

Air pollution can cause a number of diseases in human beings, such as headache, lachrymation, asthma, chronic bronchitis, lung cancer, and cancer of respiratory tract etc.

1.2.2 Noise Pollution

The ubiquity of noise has made many people apprehensive about its possible adverse effects on public health. Noise is the sound that produces a jarring or displeasing effect. The ambient noise level of our environment has risen both with increasing population density and with increasing use of machinery as a substitute for human or animal muscle power. Noise pollution is any undesirable sound dumped into the atmosphere leading to health hazards.

Noise may be meaningful or meaningless. Crying of a baby is meaningful noise; it helps to convey a message and receives one's attention or response in turn. But the meaningless noise as arising from industrial and transportation processes is destructive, disturbing and annoying.

Excessive sound levels of any type will lead to hearing losses, which are characterized by rise in one's threshold of hearing. Occupational exposures to 85 dB for eight hours a day are regarded as the maximum that should be permitted. For time varying, the effects of noise appear to be related to the total

sound energy received by the ear rather than average dB levels. Noise can produce adverse physiological effects in human beings, annoyance is an example of former and the constriction of small blood vessels is an example of the latter. The major a source of noise to which public is exposed are vehicular traffic, construction and demolition equipment such as portable compressors etc. In the vicinity of airports, aircraft's noise is another major source. Noise can be controlled by reducing sound production at the source (as by reducing mechanical vibrations of machinery) or by attenuating the transmitted acoustic power by means of barriers such as good wells or ear protectors (such as ear plugs or muffs).

The government and regulatory agencies have the authority to control noise by licensing, regulating or restricting the use, operation and movement of noise sources and by setting maximum noise levels permitted in the environment.

1.2.3 Radioactive Pollution

Radioactive substances are most hazardous and cause a serious danger to our environment.

"Pollution of air, water and soil by radioactive substances are called as radioactive pollution."

Radioactive pollution is caused due to use of radioactive materials, which are not only carcinogenic but also cause physical and mental imbalance for future generation. A burning example may be cited of Hiroshima and Nagasaki (Japan) and other one of Chernoble (Russia). These affected air, water, food and soil.

Material and methods

2.2.1 Adsorbates

2.2.1.1 Chromium

Chromium is naturally occurring element found in rocks, animals, plants, soil and in volcanic dust and gases. It is present in the environment in several different forms. The most common forms are Cr (0), trivalent [Cr (III)] and hexavalent [Cr (VI)]. Chromium in trivalent form is an essential nutrient required by the human body to promote the action of insulin in body tissues so that sugar, protein and fat can be used by the body. Cr (VI) and Cr (0) are generally produced by industrial processes. No known taste or odour is associated with chromium compounds. The metal chromium, which in the Cr (0) forms, is a steel gray solid with a high melting point. It is used mainly for making steel and other alloys. The naturally occurring mineral chromites in the Cr (III) form is used as brick lining for high temperature industrial furnaces, for making metals and alloys (mixture of metals) and chemical compounds. Chromium compounds, mostly in Cr (III) or Cr (VI) forms, produced by the chemical industry are used for chrome plating, the manufacture of dyes and pigments, leather tanning and wood preserving. Smaller amounts are used in drilling mud, rust and corrosion inhibitors, textiles and toner for copying machines¹¹⁻¹³.

Chromium enters the water mostly in the Cr (III) and Cr (VI) forms as a result of natural processes and human activities. Waste streams from electroplating can discharge Cr (VI). Leather tanning and textile industries as well as those that make dyes and pigments can discharge both Cr (III) and Cr (VI) into waterways. Soluble chromium compounds can remain in water for years before settling to the bottom. Fish do not accumulate much chromium in their bodies from water. One can be exposed to chromium by breathing air, drinking water or eating food containing chromium or through skin contact with chromium or chromium compounds. The level of chromium in water is generally low. Chromium concentrations in drinking water [mostly as Cr (III)] are generally very low, less than two parts of

chromium in a billion parts of water (2 ppb). Contaminated well water may contain Cr (VI). For the general population eating foods that contain chromium is the most likely route of chromium exposure. Cr (III) occurs naturally in many fresh vegetables, fruits, meat, yeast and grain. Various methods of processing, storage and preparation can alter the chromium content of food. Acidic foods in contact with stainless steel cans or cooking utensils might contain higher levels of chromium because of leaching from stainless steel. Refining processes used to make white bread or sugar can decrease chromium levels. Cr (III) is an essential nutrient for humans. One may also be exposed to chromium from using consumer products such as household utensils, wood preservatives, cements, cleaning products, textiles and tanned leather. People who work in industries that process or use chromium or its compounds can be exposed to higher-than-normal levels of chromium.

Occupational sources of chromium exposure (with chemical forms of interest shown in parenthesis):

- I. Stainless steel welding [Cr(VI)]
- II. Chromate production [Cr(VI)]
- III. Chrome plating [Cr (VI)]
- IV. Ferrochrome industry [Cr (III) and Cr(VI)]
- V. Chrome pigments [Cr (III) and Cr(VI)]
- VI. Leather tanning [mostly Cr (III)]

Examples of other occupations that may involve chromium exposure include:

- I. Painters [Cr (III) and Cr(VI)]
- II. Workers involved in maintenance and servicing of copying machines and the disposal of some toner powders from copying machines [Cr(VI)]
- III. Battery makers [Cr(VI)]
- IV. Candle makers [Cr (III) and Cr(VI)]
- V. Dye makers [Cr (III)]
- VI. Printers [Cr (III) and Cr(VI)]
- VII. Rubber makers [Cr (III) and Cr(VI)]
- VIII. Cement workers [Cr (III) and Cr(VI)]

One may be exposed to higher-than-normal levels of chromium, if he lives near the following

- I. Land fill sites with chromium containing wastes
- II. Industrial facilities that manufacture or use chromium and chromium containing compounds
- III. Cement producing plants, because, cement contains chromium.
- IV. Industrial cooling towers that use chromium as corrosion inhibitors.
- V. Waterways that receive industrial discharges from electroplating, leather tanning and textile industries.
- VI. Busy roadways, because emissions from automobile brake lining and catalytic converters contain chromium.

In addition, one may be exposed to higher levels of chromium if he uses tobacco products. Since tobacco contains chromium.

Chromium can enter our body when we breathe air, eat food or drink water-containing chromium. Cr (VI) enters the body more easily than Cr (III), but inside the body, Cr (VI) is changed to Cr (III).

Everyone normally eats or drinks a small amount of chromium daily. Most of chromium that we swallow leave our body within a few days through the faces and never enters our blood. A small amount (about 0.4 to 2.1%) will pass through the lining of the intestine and enter the bloodstream. Once in the bloodstream, chromium is distributed to all parts of the body where it is used to carry out essential functions. Chromium will then pass through the kidneys and be eliminated in the urine in a few days. Cr (III) present in food can attach to other compounds that make it easier to enter our bloodstream from our stomach and intestines. This form of chromium is used by our body to carry out essential body functions. The department of health and human services, U.S.A., has determined the certain Cr (VI) compounds (Calcium chromate, Chromium trioxide, lead chromate, sodium dichromate, strontium dichromate and zinc chromate) as known carcinogens. The International Agency for Research on Cancer (IARC), U.S.A., has determined that Chromium (VI) is carcinogenic to humans, based on sufficient evidence in experimental animals for the carcinogenicity of calcium chromate, zinc chromate, strontium chromate and lead chromate, and limited evidence in experimental animals for the carcinogenicity of chromic acid and sodium dichromate. IARC has also determined that Cr (0) and Cr (III) compounds are not classifiable as to their carcinogenicity to humans.

Chromium can be measure in the hair, urine, serum, red blood cells and whole blood. However, since Cr (III) is an essential nutrient, low level of chromium is normally found in body tissues and urine. Tests for chromium exposure are most useful for people exposed to high levels. These tests cannot determine the exact levels of chromium. High chromium levels in the urine and red blood cells indicate exposure to Cr (VI) or Cr (III) compounds. Since the body changes Cr (VI) or Cr (III), the form of chromium that one was exposed to cannot be determined from levels in the urine. Much more Cr (VI) can enter red blood cells than Cr (III), but Cr (VI) can be changed to Cr (III) within these cells. Therefore, chromium levels in the red blood cells probably indicate exposure to Cr (VI). Because red blood cells last about 120 days before they are replaced by newly made red blood cells, the presence of chromium in red blood cells can show whether a person was exposed to chromium 120 days prior to testing but not its exposure occurred longer than 120 days before testing. Skin patch tests may indicate whether a person is allergic to chromium or not.

Effect of Chromium

In trace amounts, chromium is an essential element in the diet of some animals and presumably of human beings also. At higher concentrations, all compounds of chromium are toxic¹⁴. Over exposure to Cr (VI) causes irritation and corrosion of skin, respiratory tract, and probable lung carcinoma¹⁵, epigastric pain, nausea, vomiting, severe diarrhea, and hemorrhage are other deadly consequences of Cr (VI) contamination. The International Agency for Research on Cancer (IARC) has classified inhaled Cr (VI) as a human carcinogen¹⁶. Chromium also has pronounced effects on plants and aquatic life¹⁷. Chromium (VI) is carcinogenic¹⁸ and Cr (VI) is a powerful epithelial irritant and confirmed corcinagen¹⁹.

Oxidation States of Chromium

Chromium can exist in several valence states (Table 3.4), but only the Cr (VI) and Cr (III) states exist under most natural water environments and soils²⁰. Chromium is toxic in both +3 and +6 oxidation states, but Cr (VI) is more toxic (generally 100 times) than Cr(III)^{21,22}. Cr (VI), which predominant under oxidizing conditions, is typically present as an anion, either as chromate (CrO_4^{2-}) at pH > 6.5 or as dichromate ($\text{Cr}_2\text{O}_7^{2-}$) at pH < 6.5. Cr (VI) is very soluble over a wide pH range in natural waters and its

presence in natural water body is hazardous to stream ecology. The toxicity nature of Cr (VI) is quite well documented²³⁻²⁵ and is known to be toxic to both plants and animals as well as potentially being carcinogenic²⁶⁻²⁹. Cr (VI) has been designated as a priority pollutant by U.S.EPA.

Cr (III) is much less toxic and even essential to human glucidic metabolism^{30,31}. Cr (III) forms less soluble chromium hydroxides under no-acidic conditions and adsorbed onto mineral surface and thus is relatively immobile in soils and aquatic environments^{11,32,33}.

Industrial Waste Water Containing Cr (VI)

The chromium present in industrial wastewaters is primarily in the hexavalent forms as chromate and dichromate. Common sources of Cr (VI) and Cr (III) are leather industry and electroplating.

In leather industry, chrome tanning process, where the basic chromium sulphate or chloride, sodium dichromate and sulphuric acid are used, biodegradable tannery chemicals is also source of chromium³⁴, mainly Cr (VI). Chrome tanning effluents is greenish in colour and highly acidic.

Chromium plating is one of the most widely used forms of electroplating and it constitutes an important source of heavy and toxic metal discharges into the wastewater lines. Though copper, nickel, zinc and other metals may also be present in the effluents from electroplating, chromium [mainly Cr (VI)] is present in substantially large concentrations³⁵. Effluent discharged from chromium plating is highly acidic in nature.

Permissible Limits for Cr (VI) in Industrial Effluents

The permissible limits for Cr (VI) in industrial effluents are presented in (Table 2.5). However, considering its toxicity, the maximum tolerance level of Cr (VI) ³⁶ for drinking water and for bathing Ghats has been fixed at 0.05 mg l⁻¹.

Table 2.4: Valency state of chromium compounds

Valency State	Physical State	Examples
0	White powder	Metallic chromium
2+	Black	CrO
	Blue crystal	CrCl ₂ . 4H ₂ O
	Red Crystal	CrSO ₄ . 5H ₂ O
3+	Green	Cr ₂ O ₃
	Black Solid	Cr ₂ S ₃
	Peach Blossom	CrCl ₃
	Violet Crystal	Cr ₂ SO ₃
4+	Dark green black solid	CrF ₄
5+	Crimson Solid	CrF ₅
6+	Red Crystal	CrO ₃

6+	Lemon Yellow Crystal	K_2CrO_4
	Chrome Yellow	$PbCrO_4$
	Chrome Red	$PbCrO_4$. PbO
	Orange red crystal	$K_2Cr_2O_7$
	Deep red liquid	$CrO_2 Cl_2$
	Red brown gas	CrO_2F_2

Table 2.5: Permissible limits for Cr (VI) concentrations in industrial wastewater in India

Methodology of research work

A 0.25% solution of diphenyl carbazide in 50% acetone was prepared. To about 15 cm³ of the test solution (in the range of 0.2 - 0.5 ppm) sufficient 3M sulphuric acid was added to make the concentration about 0.1M when subsequently diluted to 25 cm³, 1 cm³ of the N, N| – diphenylcarbazine reagent was added and volume was made up to 25 cm³ with water. The absorbance was noted using a green filter having maximum adsorption at 540 nm. Plot of absorbance versus concentration, as show in Figure 4.1 at lower concentration range have a good proportionality. A linear plot of absorbance versus concentration passing through origin indicates that the system follows Lambert – Bear’s Law.

Experiment and analysis

Physico-chemical analysis of the adsorbent Lantana Camara ash by X-ray diffraction and IR spectrum shows the presence of iron oxide and lead oxide which are tetragonal, iron lead oxide, silicon oxide, sodium carbonate which are hexagonal and calcium and manganese oxides which are orthorhombic, -OH, C-H, C=O, Si-O, Al-O, Fe-O, Ca-O, Na-O groups are present. □ Lantana Camara ash shows great potential for the adsorption of Mo (VI) from waste water. Its adsorption capacity for Mo (VI) is much much higher than any other reported adsorbents. It can be used to remove Cr (IV) also from water if concentrations are low. Lantana Camara ash shows a good adsorption capacity for Ni (II).

3.1 Effect of initial concentration

The study of effect of initial adsorbate concentration and contact time between adsorbent and adsorbate are of significant importance for treatment of wastewater (effluents) enriched in metal ions by adsorption. A rapid uptake of adsorbates and attainment of equilibrium in a short interval of time signifies the ability of the adsorbent for its use in treatment of wastewater. Also, the study of effect of initial concentration of pollutants or adsorbates on a given amount of adsorbent, at a particular temperature and pH, is equally important. A given mass of adsorbent can purify a small volume of pollutants with low concentration. But in higher concentration range, the fractional adsorption is low¹.

The contact time required to attain the equilibrium is longer for prime materials such as activated carbon and polymeric adsorbents, however, the equilibrium time is shorter for the porous or non-porous adsorbents².

In the physical adsorption most of the adsorbate species are adsorbed on the solid-solution interface within a short period of time³.

However, strong chemical bonding of adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium².

A review of the available literature on adsorption indicates that the process of uptake of adsorbate species is faster in initial stage of the contact time and becomes slower at later stages. In spite of these differences, the adsorption rate is found to be nearly constant. A larger number of surface sites is available for the adsorption of pollutants in the initial stages, however in later stages the remaining surface sites are difficult to be occupied due to repulsion between the solute molecules of the solid and the bulk phases. The study of variation in the rate of adsorption with concentration of adsorbate gives an idea about the rate controlling step of the adsorption process. Thus, effect of the concentration of adsorbate on the speed, at which its adsorptive uptake proceeds, is significant for prediction of the most efficient manner in which adsorbent can be utilized for removing the solute from the solution⁴. For better understanding of the process involved, the study of adsorption dynamics is important. Also the kinetics of removal of pollutants or adsorbate molecules from wastewater govern the contact time between the adsorbate and adsorbents. Moreover, the effect of initial concentration of adsorbates or pollutant molecules and retention period of adsorbent in treatment of wastewater are of equal importance.

An adsorbent can adsorb only a finite amount of adsorbate in a given set of conditions. Usually, the amount adsorbed q_e (mg g^{-1} of adsorbent) is a function of the equilibrium adsorbate concentration and temperature for a given system⁵ i.e.,

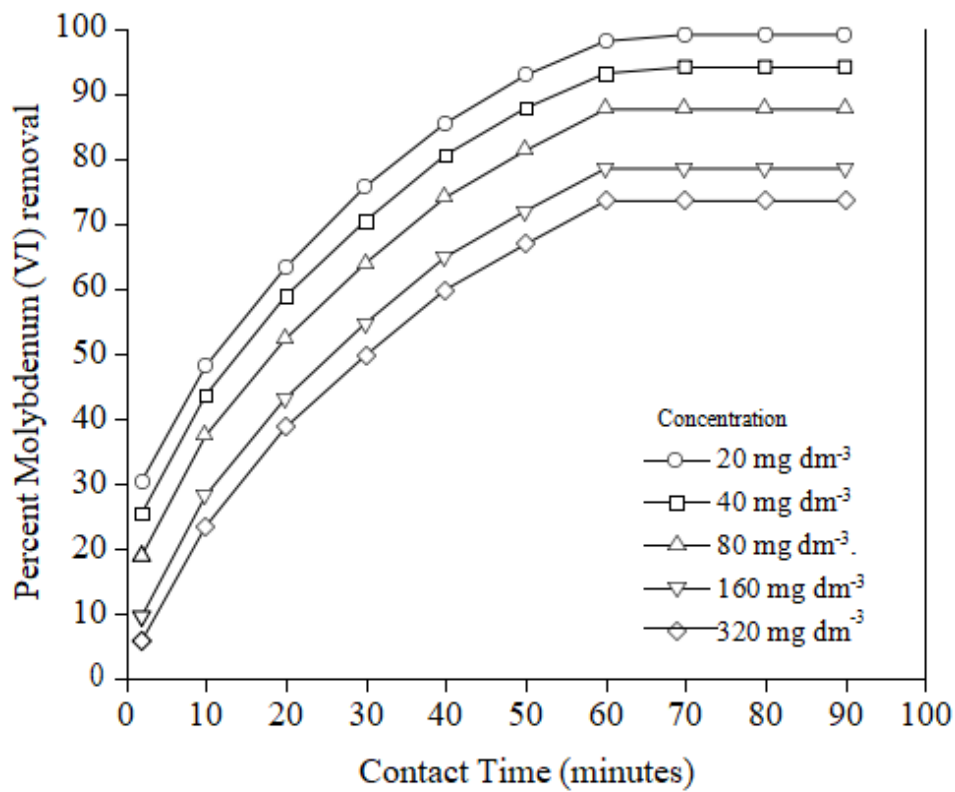
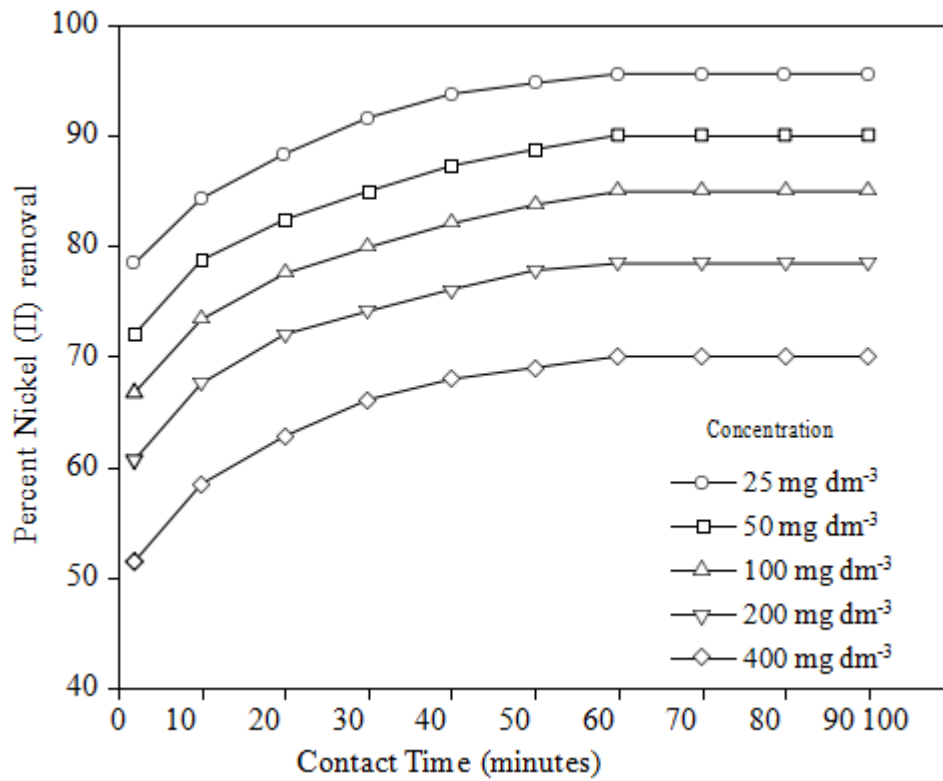
$$q_e = f(C_e, T) \quad 5.1$$

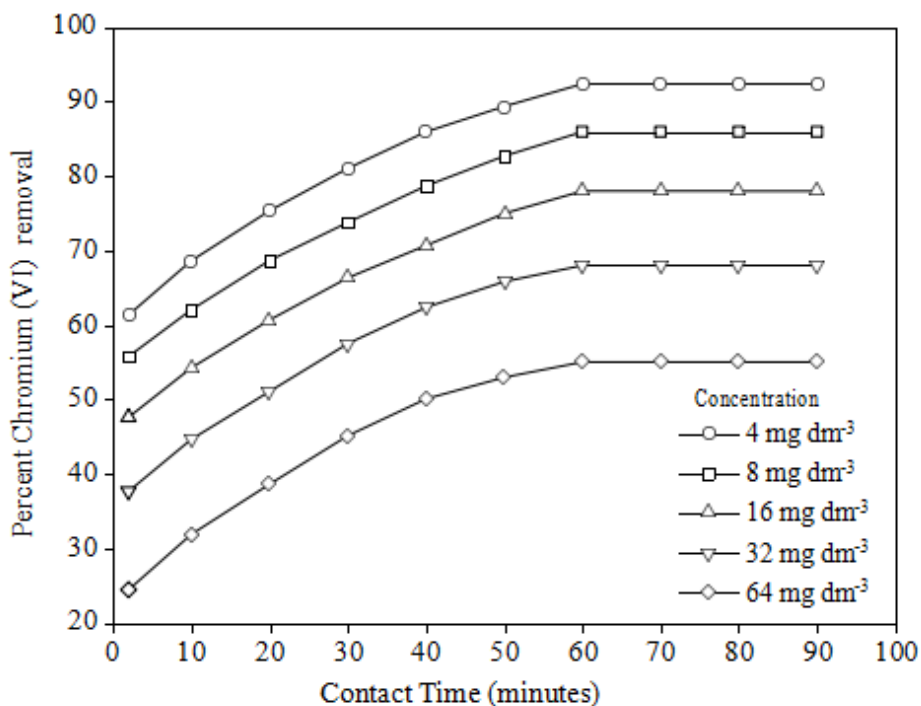
Where, C_e (mg dm^{-3}) is the equilibrium concentration of the adsorptive solution. At constant temperature this is called the adsorption isotherm.

$$q_e = fT(C_e) \quad 5.2$$

The present section deals with the effect of initial concentration, on removal efficiency of metal ion per unit weight of adsorbent and contact time to establish equilibrium. The study of removal of Chromium (VI), Molybdenum (VI) and Nickel (II) by the adsorbent Lantana Camara ash at different initial concentration of metal ions present in solution has been performed.

Effect of initial Chromium (VI), Molybdenum (VI) and Nickel (II) concentrations on the removal efficiency of adsorbents and time to reach equilibrium were studied over a wider range of Chromium (VI), Molybdenum (VI) and Nickel (II) concentrations. All other conditions (agitation speed, dose, temperature) were kept same and pH was maintained at the respective optimum value. The results at equilibrium condition are given in Tables 5.1 - 5.3 and Figures 5.1 - 5.3. It may be observed that Chromium (VI), Molybdenum (VI) and Nickel (II)





Conclusion

The following significant conclusions could be drawn on the basis of the present study:

- Physico-chemical analysis of the adsorbent Lantana Camara ash by X-ray diffraction and IR spectrum shows the presence of iron oxide and lead oxide which are tetragonal, iron lead oxide, silicon oxide, sodium carbonate which are hexagonal and calcium and manganese oxides which are orthorhombic, -OH, C-H, C=O, Si-O, Al-O, Fe-O, Ca-O, Na-O groups are present.
- Lantana Camara ash shows great potential for the adsorption of Mo (VI) from waste water. Its adsorption capacity for Mo (VI) is much- much higher than any other reported adsorbents. It can be used to remove Cr (IV) also from water if concentrations are low. Lantana Camara ash shows a good adsorption capacity for Ni (II).
- Optimum pH value for adsorption of Cr (VI) on Lantana Camara ash is 2.00 for Mo (VI) on Lantana Camara ash is 2.00 and for Ni (II) on Lantana Camara ash is 11.00 i.e., Ni (II) is adsorbed in alkaline medium by the adsorbents while Cr (VI) and Mo (VI) required acidic conditions for being adsorbed.
- The equilibrium time was found to be independent upon initial concentrations of Cr (VI), Mo (VI) and Ni(II).
- The adsorption follows 1st order rate kinetics and follows both Langmuir and Freundlich models for the concentration range studied.
- Removal of Cr (VI), Mo (VI) and Ni (II) were found to be rapid in initial stages followed by slow adsorption upto saturation limit. Percentage removal of the Cr (VI), Mo (VI) and Ni (II) were found to increase with decrease in Cr (VI), Mo (VI) and Ni (II) concentration and increase in adsorbent dose.

- The effect of temperature on adsorption of Cr (VI) and Mo (VI) on Lantana Camara ash indicates the endothermic nature of the adsorption process. While in case of adsorption of Ni (II) on Lantana Camara ash, it was exothermic in nature. Endothermic nature is supported from increase in Q^0 , b , K_F and n values with rise in temperature in case of Cr (VI) and Mo (VI) on Lantana Camara ash. Whereas exothermic nature is supported from decrease in Q^0 , b , K_F and n values with rise in temperature in case of Ni (II) on Lantana Camara ash.

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